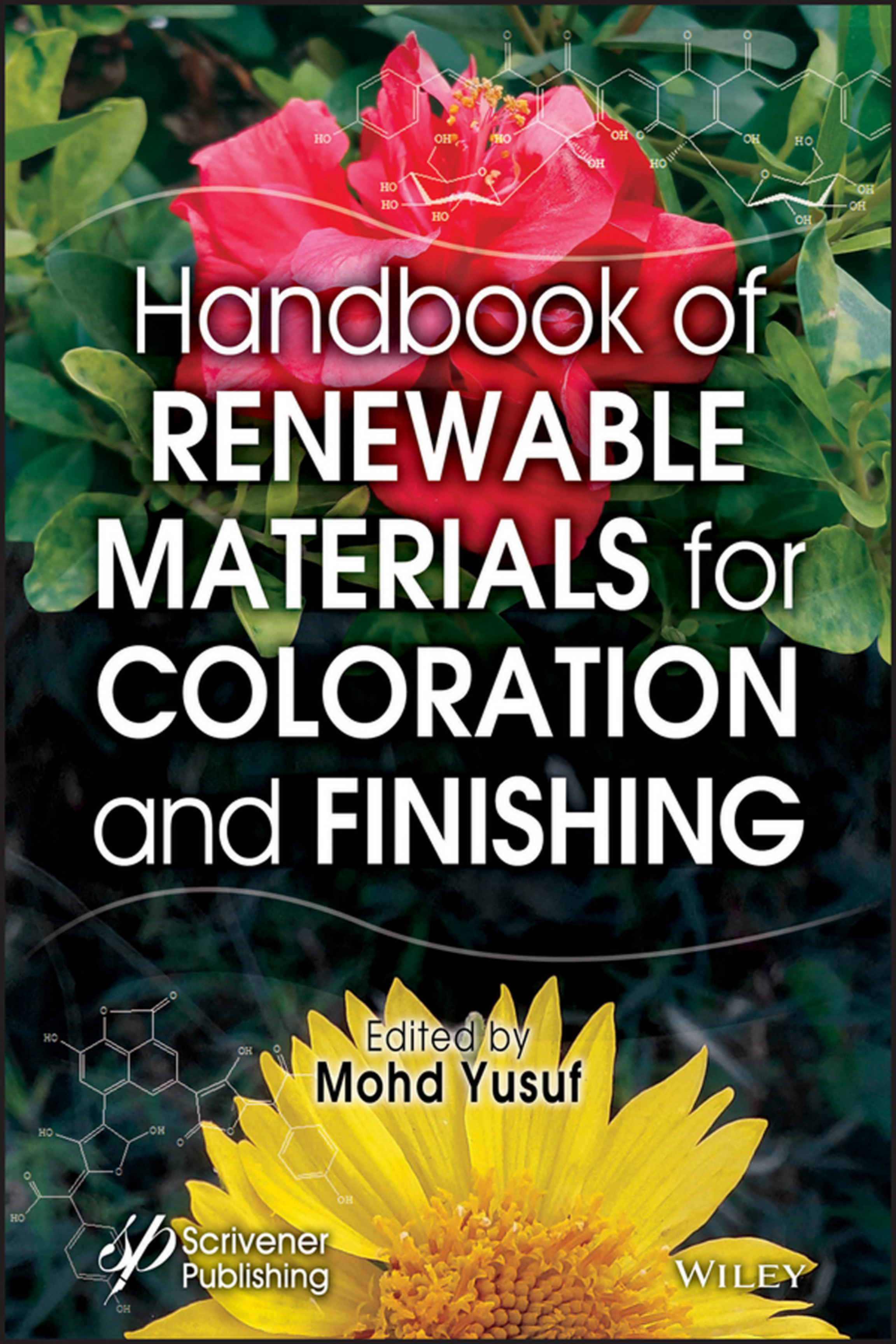

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Edited by

Mohd Yusuf

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Preface

A sustainable world requires the utilization of renewable materials or resources that can be produced in huge quantities for a wide range of applications. To adopt the use of active materials for textile coloration and finishing, they should reach the technical demands of the modern world such as eco-preservation, economic and ecological requirements. Therefore, there is a need to discuss and understand the challenges and solutions of textile coloration and functional finishing methodologies.

An attempt is to be made to give the handbook a multidisciplinary dimension through technological perspectives to perform further research regarding new opportunities and sustainable products. As a matter of fact, this book is oriented to give general to specific knowledge to the readers working in the field of textile engineering step by step. The purpose of the handbook is to provide reference material that includes basic principles and current developments in the field of natural coloration and finishing.

The handbook is divided into four segments; Substrates for Coloration and Finishing, Renewable Colorants and their Applications, Advanced Materials and Technologies for Coloration and Finishing and Sustainability.

Part I contains three chapters that overview the systematic discussion on the suitability, physical, chemical and processing aspects of substrates for coloration and finishing. Part II includes nine chapters and covers in-depth arguments on renewable colorants and their various applications including a chapter on bio-colorant's application as photosensitizers for dye sensitized solar cells. Part III contains five chapters in which modern advancements and processing methods/technologies for coloration and functional finishing are presented comprehensively. Part IV contains two chapters that provide sustainable aspects of coloration and finishing. Overall, the *Handbook of Renewable Materials for Coloration and Finishing* provides a vivid digest on the most important topics that will surely be beneficial to academicians, industry scientists and students. Additionally, the book will be a useful instrument to overview the fragmented situation and support a rapid and efficient entry into the emerging field of green and sustainable chemistry.

My sincere thanks go to the eminent authors for their priceless contributions. I welcome our readers valuable comments, which will help to improve future volumes.

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PART I

SUBSTRATES FOR COLORATION AND FINISHING

1

Introduction to Textile Fibers: An Overview

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Abstract

Basic molecular units or the monomeric units of macromolecules or polymers decide the characteristic features of them. Textile fiber is a material mainly made from natural or synthetic sources. The fibers are transformed to make various products such as yarns, knitted, woven or nonwoven fabrics, and carpets. A growing textile industry is always in search of new materials, whether these are the resources of textile fibers or the other functional materials. Textile fibers can be obtained naturally from animals and various parts of plants, while a lot of synthetic or semi-synthetic textile fibers are being produced in the laboratories that are developed at industrial scale later. This chapter highlights the various kinds of textile fibers, concisely.

Keywords: Textile, Fibers, Polymers, Materials

1.1 Introduction

Textile fibers have been utilized to make clothes for several thousand years. Wool, flax, cotton, and silk were commonly used textile fibers. Textile fibers are characterized by their several value added virtues such as flexibility, fineness, and large length in relation to the maximum transverse dimension. In general, evolution of human being is thought about behavioral and mind strength changes, but it is also accompanied with the understanding of clothing on the basis of availability of resources and protection against environmental changes. Now clothing has been considered as second basic

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need of mankind after food. Present scenario of the world demands not only the protection of human body but also the comfortness via clothing [1]. Textile fibers have been discovered or developed from natural resources in the starting and with scientific growth, the synthetic fibers. These have been utilized to develop textiles of various characteristics such as wool for thermoregulation, silk for shining colors, cotton for softness, and bamboo fiber textiles for antimicrobial characteristics [2, 3]. First manufactured fiber was produced commercially on 1885 and was produced from fibers of plants and animals. Since from the past, there are many types of textile fibers that have been used or developed in textile production such as cloth, rope, household etc. [2, 3, 4, 5]. This chapter is all about concise overview of the classification of textile fibers.

1.2 Classification

Textile fibers can be classified on different basis; depending on their chemical structures, resources, and their production methods.

On the basis of their origin, textile fibers are classified into three categories, which can be further classified in to several groups (Figure 1.1 and Figure 1.2).

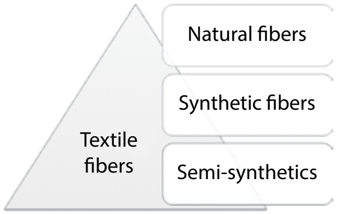


Figure 1.1 Classification of textile fibers on the basis of their origin.

Animal fibers	Plant fibers	Synthetic fibers
Wool	Cotton	Acrylic
Silk	Flex	Polyamide
Hairs etc.	Hemp	Polyester
	Jute	Rayon
	Kenaf	Modal
	Ramie etc.	Tencel
		Triacetate etc.

Figure 1.2 Broad categorization of textile fibers.

1.2.1 Natural Fibers

Textile fibers obtained from plants and animals fall into this category.

Wool and silk are the examples of natural fibers obtained from animals (sheep and silkworm). These fibers are protein based with respect to their chemical structure (Figure 1.3). Amino acids are the repeating units in their chemical structure. Wool fibers are well known for their characteristics such as heat insulation, fire resistance, and high dyeability. Another protein fiber silk also have some peculiar characteristics such as smoothness, light reflection and anti-crease [6, 7].

A range of natural fibers are produced from plant parts (Figure 1.4), such as cotton (seed hairs), flex and hemp (stem fibers), sisal (leaf fibers), husk fibers and coir (coconut). These fibers have their specific characteristics and exclusively utilized for them, such as cotton is used for the summer clothing for its comfort on human skin. Many of them are used for ropes, mattresses, geo-textiles other than clothing [8, 9, 10].

1.2.2 Synthetic Fibers

These fibers are synthesized in laboratories via chemical reactions of precursor molecules (Figure 1.5).

Polyesters (poly-ethylene terephthalate (PET), poly-butylene succinate (PBS), and poly lactic acid (PLA)) are the synthetic fibers that have ester linkage in between their monomeric units.

Nylon is a synthetic fiber like polyester derived from petrochemicals. It is a versatile fiber and used for various kinds of applications such as stockings and parachutes, carpets, packaging and even car parts. Nylons are a

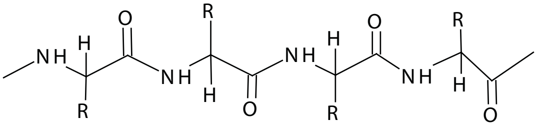


Figure 1.3 Chemical structure of protein fibers.

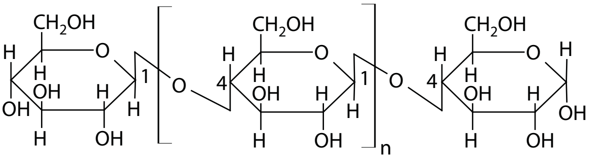
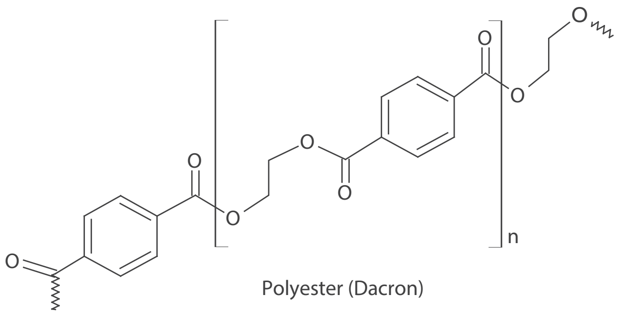
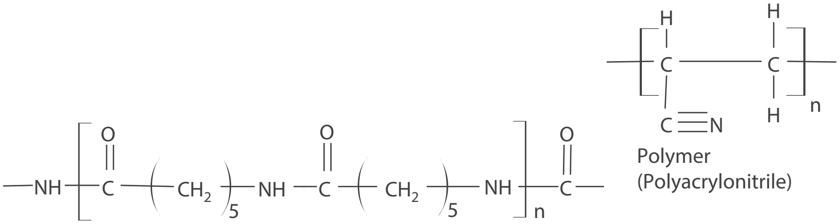


Figure 1.4 Chemical structure of cellulosic fibers.



Polyester (Dacron)



Polymer (Polyacrylonitrile)

Nylon

Figure 1.5 Chemical structure of synthetic fibers.

group of materials called polyamides. Nylon is also not much suited to natural dyes and some chemical dyes, so need high efforts for coloration.

Acrylic fibers are also a type of synthetic fibers made from a polymer polyacrylonitrile with an average molecular weight of ~100,000, about 1900 monomer units. Acrylic is lightweight, soft, and warm, with a wool-like feel [11, 12, 13].

1.2.3 Semi-Synthetic Fibers

Rayon is an artificial textile material composed of reconstituted or regenerated cellulose compounds. It has polymer chain structure from nature and is only modified and partially degraded by chemical processes, so called a semi-synthetic fiber (Figure 1.6). On the basis of properties variation, rayon also developed into fibers such as viscose rayon, high wet modulus (HWM) rayon and lyocell etc. [1, 3].

1.3 Conclusion

Population explosion and high awareness among people created more choices of clothing as well as their demands. To meet the needs of this

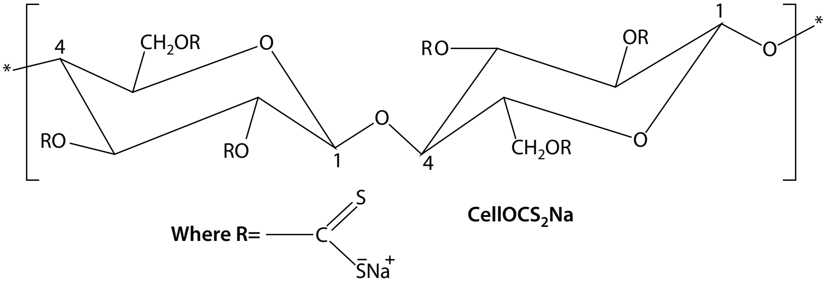


Figure 1.6 Chemical structure of semi-synthetic textile fibers.

generation, higher attention towards high productivity resources and qualitative research is required. Productivity of animal fibers such as wool and silk can be increased by improving farming practices. Inherent properties of wool and silk can also be improvised with the help of materials (nanomaterials and plasma etc.) and modern techniques. Textile fibers (cotton, jute, hemp etc.) obtained from plants are the good alternatives as these are considered as biocompatible and produced from never ending resources that are plants. Production of plant based textile fibers simultaneously can provide benefits toward environment and human health. Regenerated cellulosic fibers among synthetic fibers are also the good alternatives and can help to fulfill the current demands. These fibers have been known to have high quality characteristics and their production can also utilize the lower grade cellulose materials like paper waste, cotton, grass etc. Better understanding of the textile fiber's chemical and structural properties is the basic thing for the improvisation and functionalization of the textile materials.

References

1. Shabbir, M. and Mohammad, F., Natural textile fibers: Polymeric base materials for textile industry, in: *Natural Polymers: Derivatives, Blends and Composites,* S. Ikram and M. Shakeel (Eds.), 2, pp. 89–102, Nova Science Publishers, USA, 2017.
2. Tortman, E.R., *Dyeing and Chemical Technology of Textile Fibers*, 4th Ed., Charles Griffin and Co., USA, 1975.
3. Shabbir, M. and Mohammad, F., Sustainable production of regenerated cellulosic fibres, in: *Sustainable Fibres and Textiles*, S. Muthu (Ed.), pp. 171, Woodhead Publishing, USA, 2017.
4. Cook, J.G., *Handbook of Textile Fibers: Natural Fibers*, Vol I, Woodhead Publishing Limited, Sawton, Cambridge, UK, 1984.
5. Lewis, D.M., *Wool Dyeing*, Society of Dyers and Colorists, UK, 1992.

6. Bradbury, J.H., The structure and chemistry of keratin fibers, in: *Advances in Protein Chemistry*, C.B. Anfinsen Jr, J.T. Edsall, F.M. Richards (Eds.), 27, pp. 111–211, Academic Press, New York, 1973.
7. Hall, D.M., Adanur, S., Broughton Jr., R.M., Brady, P.H., Polymers and fibers, in: *Wellington Sears Handbook of Industrial Textiles*, 1st Edn, S. Adanur (Ed.), pp. 37–52, CRC Press, New Holland, USA, 1995.
8. Wakelyn, P.J., Bertoniere, N.R., French, A.D., Thibodeaux, O.P., Triplett, B.A., Rousselle, M.A., Goynes Jr, W.R., Edwards, J.V., Hunter, L., McAlisten, D.D., Gamble, G.R., (Eds.), *Cotton Fiber Chemistry and Technology*, CRC Press, Florida, USA, 2007.
9. Basu, G., Sinha, A.K. and Chattopadhyay, S.N., Properties of jute based ternary blended bulked yarns. *Man. Made. Text.* India., 48, 350, 2005.
10. Brühlmann, F., Leupin, M., Erismann, K.H., and Fiechter, A., Enzymatic degumming of ramie bast fibers. *J. Biotechnol.*, 76, 43–50, 2000.
11. Karthik, T. and Rathinamoorthy, R., Sustainable synthetic fibre production, in: *Sustainable Fibres and Textiles*, S. Muthu (Ed.), pp. 191–240, Woodhead Publishing, USA, 2017.
12. Kirk, R.E., Othmer, D.F., Mark, H.F., *Encyclopedia of Chemical Technology*, Wiley-Interscience, Chichester, 1965.
13. Dyer, J. and Daul, G.C., Rayon fibers, in: *Handbook of Fiber Chemistry*, 2nd Edn., M. Lewin, E.M. Pearce (Eds.), pp. 738–744, Marvel Decker Inc., New York, 1998.

2

Effect of Processing and Type of Mechanical Loading on Performance of Bio-Fibers and Bio-Composites

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Abstract

Bio-material is a buzz word these days among research fraternity to be used in every possible field of applications like automobile, sports, and textile industry. The textile industry is now focusing all of its fabric variants to be environment loving that is bio-based materials instead of synthetic materials and fabrics. These bio-based materials include plant based natural fibers (jute, hemp, flax, sisal, ramie etc.), animal fibers like silk, wool, kapok etc. These fibers can be reinforced with polymer to fabricate polymer based bio-composites that are used for variety of applications. To convert reinforcing fibers from raw state to finished form, these have to undergo various processes which severely affect their properties. This chapter will cover a detailed discussion on processing and its effect on the performance of bio-fibers and bio-composites. Also, a discussion on mechanical and wear performance of bio-composites when these natural fibers are reinforced with polymer will be included in this chapter.

Keywords: Textile fabric, bio-composites, natural fiber, mechanical, characterization

2.1 Introduction

Awareness towards ecological balance has forced application of natural fiber (jute, cotton, wool, hemp, flax etc.) based polymer composites. These

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bio-composites have immense interest of material researchers because of its impressive properties like low density, non-toxic, non-abrasive, good wear, and mechanical strength. Low cost and eco-friendly nature of natural fibers are the two major characteristics that have the potential consumption of these fibers to fabricate the bio-composites [1]. Natural fibers and its composites are being globally used in different industries such as textile, automobile, aerospace, medical, and civil industry. Bio-composites have been used to fabricate various small components of automobile vehicles like door panels, head liner, dashboards and in building constructions like doors, windows, and roofs. In real time applications, various environmental conditions such as humidity, moisture, variation in temperature etc. are imposed to these bio-composites. These environmental conditions degrade the composites physically as well as mechanical strength of both natural fibers and polymer matrix [2].

To overcome these problems, proper processing and treatment of bio-fibers/matrix becomes imperative before fabrication of bio-composites to enhance its performance and durability. Mostly natural fibers are hydrophilic in nature and contain cellulose, hemi-cellulose, lignin, and pectin in its chemical composition. Impurities like lignin, pectin, wax, and other oily compounds present at the surface of the fibers create hindrance to make strong interfacial adhesion between bio-fiber and polymer matrix. To minimize these unwanted contents, surface treatment of bio-fibers (silylation, acetylation, benzoylation, maleated coupling agents, isocyanate treatment etc.) is an unavoidable step to have good interfacial adhesion between fiber and polymer which increases the overall strength of the developed composites and protect the bio-composites during harm environmental conditions [3]. Treatment of polymer such as grafting of synthetic polymer increases the interfacial adhesion between fiber/matrix interfaces. Figure 2.1 shows the application of bio-fibers in different sectors. Figure 2.2 represents the various surface treatment methods of bio-fibers.

The present chapter covers a detailed discussion on processing and surface modification of bio-fibers. How these processing methods affect the mechanical and tribological performance of bio-composites has been incorporated in this chapter.

2.2 Extraction of Bio-Fibers

Bio-fibers are extracted from the natural sources like plants, animals, and minerals. Plant fibers consist of seed fibers (cotton, calotropis, and kapok), leaf fibers (abaca, date palm, pineapple, banana, and agave), bast

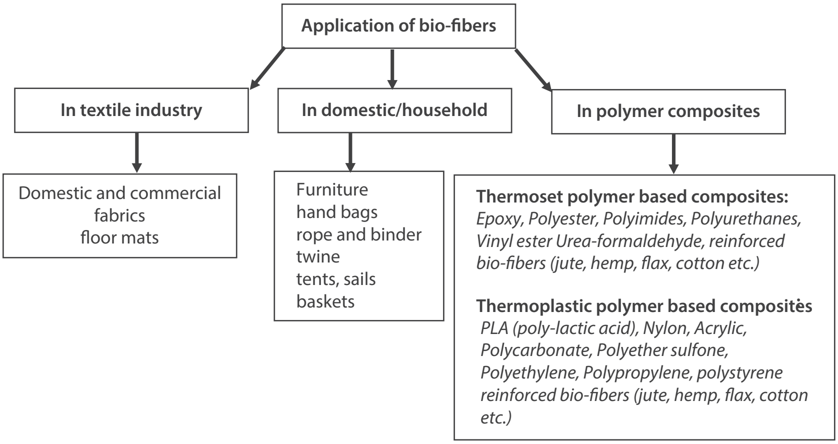

Figure 2.1 Various applications of bio-fibers and its fabric.

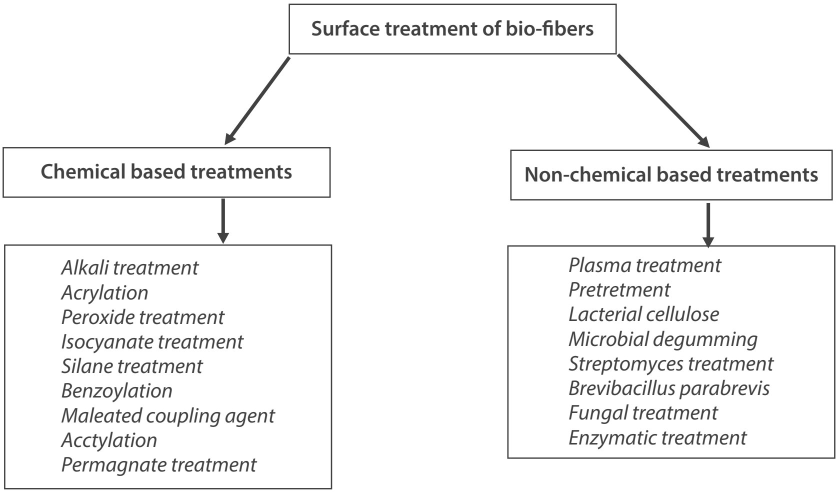

Figure 2.2 Treatment of bio-fibers/fabric.

fibers (flax, jute, kenaf, industrial hemp, ramie, rattan, and vine fibers), fruit fibers (coir) and stalk fibers (wheat, rice, barley, bamboo, and straw). Animal fibers consist of animal hair (sheep's wool, goat hair, horse hair etc.), silk fiber, and avian fiber and mineral fiber consists of asbestos. All raw form of bio-fibers are extracted from its origin source and undergo various processing stages which are shown in Figure 2.3, to convert into finished bio-fibers [4].

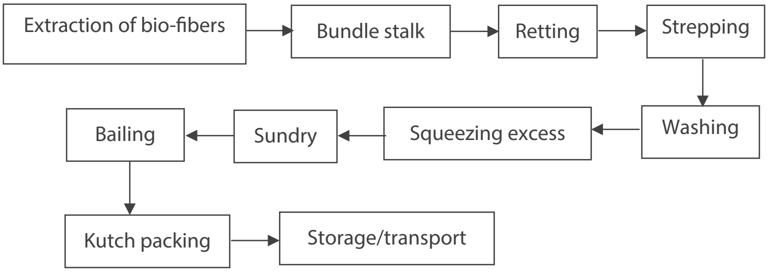

Figure 2.3 Extraction and processing stages of bio based fibers.

Stalking of fiber bundles is the first step in fiber extraction. Fiber bundle stalks are extracted from the origin source and these stalks are converted into bundles by adding all the fiber stalks. After stalking of fiber bundle, retting of fiber bundles is done. In retting process, the fibers are separated from the stem of the plant by removing the pectin and cellular tissues present on the outer surface of the bundle stalks. In the process of water retting, bundle stalks are submerged in the water for a specific time. The water penetrates into the inner cells of the bundle stalk thus bursting the cellular tissues and pectin of the outer most layer of fiber stalk. In stripping process, each bundle stalk is taken and the strips of fiber are separated from each other. The strips of fiber are easily visible after the process of retting. After the stripping process, the fiber strips are washed with clean water. This cleaning process of fibers is known as washing. The excess water content of the fiber strips is removed by squeezing. There is still some water content left in the fiber strips even after the squeezing process. That water content is removed by putting the fiber strips directly under the sun-light for specific time of interval. This process is known as sun-drying. For the trading purpose, these fiber strips are bundled in the form of kutcha bales. The weight of each kutcha bale is kept constant as defined by the local market. This process is known as bailing. After bailing process, the packaging is done [5–6]. These bundles can be stored or transported directly to the market. Some of the common bio-fabrics in the form of mat are shown in Figure 2.4.

2.3 Mechanical Loading

Evaluation of mechanical properties (tensile, flexural, compressive, impact, and hardness) of bio-composites is very necessary to find out the overall structural strength of the developed bio-composite. Some important

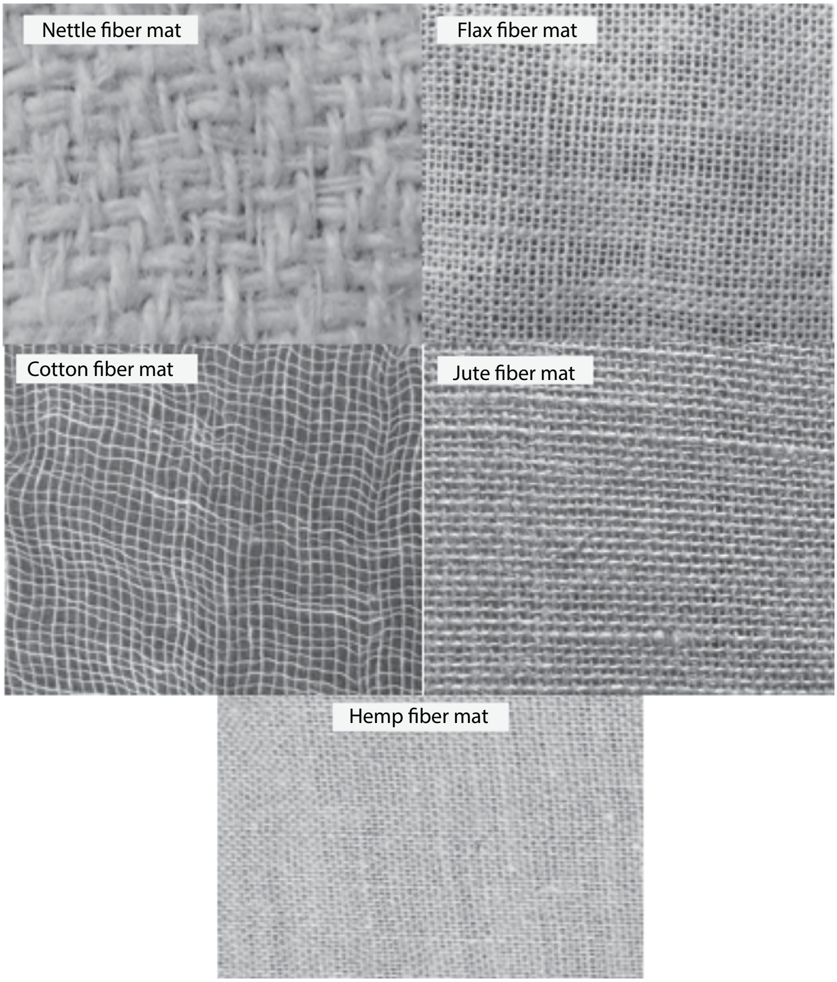

Figure 2.4 Variants of bio based textile fabric.

factors like bio-fiber types, polymer matrix, and processing method largely influence the mechanical properties of bio-composites. Proper wettability of bio-fiber with polymer matrix improves the interfacial adhesion between fiber/matrix interfaces, which increases the overall mechanical properties of the developed bio-composites. Evaluation of mechanical properties helps a material scientist to put these bio-composites in appropriate application in different sectors like aerospace, building and construction, electrical appliances, automotive and household products [7–8]. Mechanical properties such as tensile, flexural, and impact strength of bio-composites

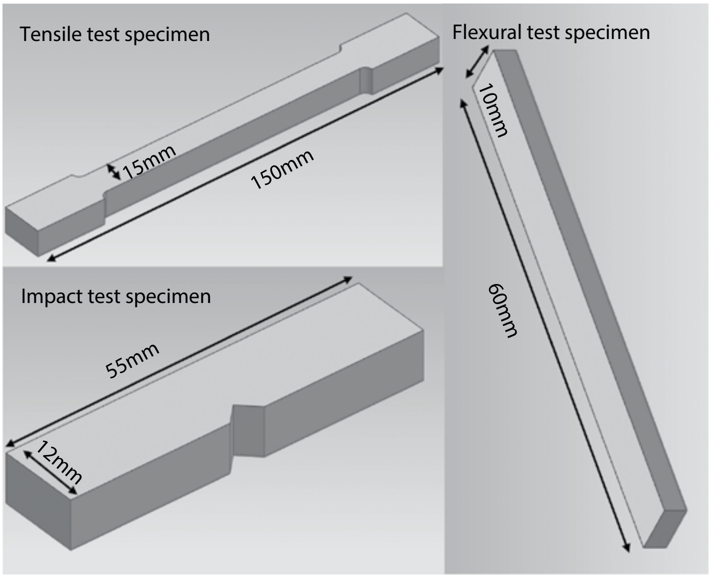

Figure 2.5 Specification of test specimen for polymer composites in mechanical testing.

are discussed in this chapter. Figure 2.5 shows the standard specimen used in tensile, flexural, and impact test.

2.4 Tensile Test

Tensile test is the basic test to know the tensile strength of any material under tensile loading. Tensile test is conducted on the universal testing machine (UTM) having various predefined load cell capacity. It measures the strain, which is change in length per unit length of the specimen. This strain is due to the external force applied in axial direction of the specimen. The specimen is in the form of rectangular bar. Various authors developed bio-composites and conducted tensile test in their research work to evaluate the tensile strength of the bio-composites. Chaudhary *et al.* [9] developed jute, hemp, and flax reinforced epoxy and their hybrid composites using hand lay-up technique. Authors preformed the mechanical characterization of the developed composite materials and concluded that the incorporation of bio-fibers with polymer matrix improved the tensile strength of the developed composites as compared to tensile strength of neat epoxy. Authors also found that hybridization of different bio-fibers enhanced the tensile strength of the developed composite material. Sawpan *et al.* [10]

developed alkali treated hemp/polylactide bio-composite and investigated the mechanical properties of the developed composites. Author concluded that 30 wt% of hemp fiber reinforced polylactide composite achieved the highest tensile strength value.

2.5 Flexural Test

Flexural strength of a material can be checked on the basis of the shear stress that it can bear before failure. A bending load is applied on the specimen by using a special fixture on the UTM. The fixture and the loading point on the specimen make it a three point loading system. The test sample rests on two supports with some overhanging length. The load is applied on the mid-point of the specimen. The flexural test gives the extension against the flexural load. Various authors developed bio-composites and conducted flexural test in their research work to evaluate the flexural strength of the bio-composites. Lee *et al.* [11] manufactured silane treated kenaf/PLA bio-composite and conducted flexural test on the developed composites. Authors concluded that flexural strength of treated kenaf/PLA composite was significantly high as compared to untreated bio-composites. Bajpai *et al.* [12] developed grewia optiva, sisal and nettle fiber reinforced polylactic acid and grewia optiva, sisal and nettle fiber reinforced polypropylene composites using hot pressing through film stacking technique. Authors performed complete mechanical characterization of the developed composites and concluded that incorporation of natural fibers, flexural strength of the developed composite increased as compared to neat polylactic acid and neat polypropylene. Also, results of flexural strength showed that sisal/PLA composite achieved highest flexural strength of 249.8MPa as compared to all other developed composites.

2.6 Impact Test

The energy absorbance capacity of the material is a representation of the ability of a material to withstand against the sudden load. In the impact test, the impact tester consists of a hammer of known length and weight that is locked at a position. As the hammer is released from a standard height, it strikes to the specimen and the impact energy transferred to the material is calculated by comparing the difference in the height of the hammer after and before striking the specimen [13]. A notched specimen is generally used to conduct the impact test. Various authors developed bio-composites and conducted impact test in their research work to evaluate the impact strength of the bio-composites. Zong and Wei [14] developed sisal/urea-formaldehyde composite using compression molding. Authors investigated the effect of fiber loading on the impact strength of the developed bio-composites. Authors concluded that when the wt% of fiber loading increases from 30 to 50 wt%, then composite showed increment in impact strength from 5.78kJ/m^2 to 9.72 kJ/m^2, but further increment in fiber loading (60%), decreased the value of impact strength of the developed composite.

2.7 Tribological Performance

Tribology deals with the relative motion and its effect, when two surfaces interact with each other. Friction between the surfaces, type of wear (sliding, adhesive, and erosive wear) and the lubrication used are the factors which affect the tribological performance of the mating surfaces. Evaluation of tribological performance (wear and friction) of bio-composites is also important because there are many situations when bio-composites are under tribological loading condition in various industrial and commercial applications [15–16]. Tribological analysis of bio-composites has been reported by various authors in their research work. Zong and Wei [14] investigated the wear resistance property of sisal/urea-formaldehyde composite against stainless steel counterface in dry contact condition. Authors concluded that 30 wt% of sisal/ urea-formaldehyde composite achieved the highest wear resistance properties. Bajpai *et al.* [17] developed grewia optiva, sisal and nettle reinforced polypropylene composites using compression molding through film stacking technique. Experiments were conducted using pin-on disc tribometer under dry sliding condition at different sliding speeds (1–3 m/s), applied loads (10–30 N) and sliding distances (1000–3000 m). Authors concluded that incorporation of different natural fiber mats to polypropylene had enhanced the wear resistance of neat polymer.

2.8 Conclusion

Bio-based fibers and its fabrics are being experimented in every possible field of application whether it is textile industry, construction or automobile sector due to awareness towards safety of environment and ecosystem. Nowadays, polymer composites have a big utilization of bio-fibers to produce bio-fiber based composite materials. Proper processing of these bio-fibers is a key step before fabrication of high strength bio-composites. Performance of bio-composites is judged on the basis of mechanical, thermal, and tribological analysis which decides the application spectrum of the developed bio-composite. The present chapter has thrown light on different aspects of bio-fibers and their fabrics, its extraction methodology and treatment of bio-fibers. Mechanical and tribological properties of bio-composites fabricated using bio-fibers and its fabric have also been discussed in the present chapter.

References

1. Chaudhary, V., Bajpai, P.K., and Maheshwari, S., Mechanical characterization of bio-composites: A review. *Int. J. Appl. Eng. Res.*, 10 (78), 50–53, 2015.
2. Bajpai, P.K., Singh, I., and Madaan, J., Development and characterization of PLA-based green composites: A review. *J. Thermoplast. Compos. Mater.*, 27(1), 52–81, 2014.
3. Kabir, M.M., Wang, H., Lau, K.T., and Cardona, F., Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. *Compos. Part B: Eng.*, 43(7), 2883–2892, 2012.
4. Cherian, B.M., Leão, A.L., de Souza, S.F., Costa, L.M.M., de Olyveira, G.M., Kottaisamy, M., Nagarajan, E.R., and Thomas, S., Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications. *Carbohydr. Polym.*, 86(4), 1790–1798, 2011.
5. Xiao, L., Mai, Y., He, F., Yu, L., Zhang, L., Tang, H., and Yang, G., Bio-based green composites with high performance from poly (lactic acid) and surface-modified microcrystalline cellulose. *J. Mater. Chem.*, 22(31), 15732–15739, 2012.
6. Saba, N., Tahir, P.M., and Jawaid, M., A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. *Polym.*, 6(8), 2247–2273, 2014.
7. Claramunt, J., Fernández-Carrasco, L.J., Ventura, H., and Ardanuy, M., Natural fiber nonwoven reinforced cement composites as sustainable materials for building envelopes. *Construc. Build. Mater.*, 115, 230–239, 2016.
8. Boopalan, M., Niranjanaa, M., and Umapathy, M.J., Study on the mechanical properties and thermal properties of jute and banana fiber reinforced epoxy hybrid composites. *Compos. Part B: Eng.*, 51, 54–57, 2013.
9. Chaudhary, V., Bajpai, P.K., and Maheshwari, S. Studies on Mechanical and Morphological Characterization of Developed Jute/Hemp/Flax Reinforced Hybrid Composites for Structural Applications. *J. Nat. Fibers*, 15(1), 80–97, 2018.
10. Sawpan, M.A., Pickering, K.L., and Fernyhough, A., Improvement of mechanical performance of industrial hemp fibre reinforced polylactide bio-composites. *Compos. Part A: Appl. Sci. Manuf.*, 42(3), 310–319, 2011.

11. Lee, B.H., Kim, H.S., Lee, S., Kim, H.J., and Dorgan, J.R., Bio-composites of kenaf fibers in polylactide: Role of improved interfacial adhesion in the carding process. *Compos. Sci. Technol.*, 69(15), 2573–2579, 2009.
12. Bajpai, P.K., Singh, I., and Madaan, J., Comparative studies of mechanical and morphological properties of polylactic acid and polypropylene based natural fiber composites. *J. Reinf. Plas. Compos.*, 31(24), 1712–1724, 2012.
13. Adekunle, K., Cho, S.W., Patzelt, C., Blomfeldt, T., and Skrifvars, M., Impact and flexural properties of flax fabrics and Lyocell fiber-reinforced bio-based thermoset. *Reinf. Plas. Compos.*, 30(8), 685–697, 2011.
14. Zhong, J.B., Lv, J., and Wei, C., Mechanical properties of sisal fibre reinforced urea formaldehyde resin composites. *Exp. Polym. Lett.*, 1(10), 681–687, 2007.
15. Xin, X., Xu, C.G., and Qing, L.F., Friction properties of sisal fibre reinforced resin brake composites. *Wear*, 262(5), 736–741, 2007.
16. Chegdani, F., Mezghani, S., El Mansori, M., and Mkaddem, A., Fiber type effect on tribological behavior when cutting natural fiber reinforced plastics. *Wear*, 332, 772–779, 2015.
17. Bajpai, P.K., Singh, I., and Madaan, J., Frictional and adhesive wear performance of natural fibre reinforced polypropylene composites. Proc. Inst. Mech. Eng. Part J: *J. Eng. Tribol.*, 227(4), 385–392, 2013.

3

Mechanical and Chemical Structure of Natural Protein Fibers: Wool and Silk

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Abstract

Generally, proteins are the most prolific and functional biological substances. Animal derived fibers hair/fur, feathers (wool), and silk are natural fibers that consist largely of particular proteins arranged in continuous amino acid chains, like keratin, fibroin etc. This diversity comes from the different side-chain groups in the constituent amino acid residues. The fibers possess moderate strength, resiliency, elasticity, excellent moisture absorbency, and transport characteristics. Most commonly used natural protein fibers are obtained from domestic sheep and silk worms. In the present chapter, chief attention is given to the morphology, structure, and significant applicable properties of wool and silk protein fibers.

Keywords: Protein fibers, morphology, wool, silk, amino acids

3.1 Introduction

Textile fibers have been used to make cloth for several thousand years. Wool, silk, flax, cotton etc. textile fibers have been commonly used. Textile fibers are characterized by the flexibility, fineness, and large length in relation to the maximum transverse dimension. First man-made manufactured fiber was produced commercially on 1885 by Chardonnet, who developed an artificial silk using cellulose nitrate dry-spun using alcohol-ether. On the basis of origin, fibers can be classified broadly into three categories; (a) Natural fibers: Fibers which grow or develop and come from natural resources like plant and animals, (b) Manufactured/Man-made

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Mohd Yusuf (ed.) Handbook of Renewable Materials for Coloration and Finishing, (19–40)

fibers: Fibers produced by industrial processes, whether from natural polymers transformed upon the action of chemical reagents or through polymers obtained by chemical synthesis and, (c) Mineral Fibers: Asbestos is the only naturally occurring mineral fiber that was used extensively for making industrial products but currently is restricted on account of its suspected carcinogenic effectiveness.

Natural fibers from plants and animals play an important role in our lives, not only in ethical clothing and other textiles, but also in another unexpected area such as the automotive industry. The protein fibers from protein polymers are originated from natural animal sources such as keratin (hair/fur) that are obtained from fleece of sheep (wool) or secreted by insects (silk) and formed through condensation of amino acids to make repeating units of polyamide. The presence of both amino and carboxylic groups in the protein molecule renders the ionic nature. The sequence and type of amino acids as well as their bonding in the protein chains partly contribute to the whole properties of the resulting fibers [1].

3.2 Wool

Wool is an important natural fiber used in textile industries, which is obtained from different animals; Sheep wool has more significance of them due to its commercial utility [2–4]. Sheep are the principal source of natural animal fiber and there are more than 200 breeds of sheep worldwide. The largest number of breeds in one country is in Britain, with around 65. Natural wool fiber is biodegradable. It is unclear when wool was first used as textile material; Archeological findings suggest that the earliest type of product made from animal's fiber particularly wool, might be wool felt.

Wool types are classified according to the diameter and length of the fiber. The most important breed for producing premium type of fine wool is Merino, which has been originated in Spain during the Middle Ages; this breed was so highly valued that export was forbidden until the eighteenth century. After eighteenth century it was introduced in other countries, the most notable of these are Australia and New Zealand. Sheep farms have been developed to produce highly prized wool with exceptional fineness, length, color, lustre, and crimp.

3.2.1 Physical Properties

Colour: Most of the wool from modern sheep is white or near white in color. Some breeds of sheep produce a quantity of brown or black wool, the proportion of brown or black wool being the highest in the breeds, provide the coarsest wool.

Lustre: The lustre of wool varies, although sheep wool does not have a great deal of lustre. Lustre varies among the different breeds of sheep, the different sections of fleece and conditions under which the animals have been raised.

Density: The density of wool is relatively low.

Strength: Wool has the lowest tensile strength amongst natural fibers.

Elasticity: Wool fibers are highly elastic and after stretching, it will return to their original shape again. In wool fiber, millions of protein molecules are lying alongside one another, held together at intervals by chemical cross links. When fiber is stretched, the chains are unfolded; when stretching force is removed, they return to their folded state again.

Dimensional Stability: Wool has poor dimensional stability. The tendency of wool to shrink and felting of wool can cause fabric and garment to decrease in size.

Effect of Moisture: Wool absorbs moisture to a greater extent than any other fiber. This property plays an important role in making wool a desirable material to wear next to the skin because it has considerable capacity to absorb perspiration.

Effect of Heat: Wool becomes weak and loses its softness when heated at boiling temperature for long period of time.

Effect of Age: Wool shows little deterioration when stored carefully.

Effect of Sunlight: The keratin of wool decomposes under the action of sunlight. Wool subjected to strong sunlight is particularly sensitive to alkalis, including soapy water.

3.2.2 Chemical Properties

Effect of Acids: Acid does not harm wool except in very strong condition. It decomposes completely by hot concentrated sulphuric acid.

Effect of Alkalis: Wool fibers are quickly damaged by strong alkali solutions and relatively weak alkalis have deleterious effect on wool. A strong alkali such as sodium or potassium hydroxide hydrolyses keratin into the alkali salts of amino acid, slowly in the cold but very rapidly at higher temperatures.

Effect of Organic Solvents: Wool has no resistance to dry cleaning and other common organic solvents.

Insects: One of the major problems in case of wool is its susceptibility to be damaged by insects.

Micro-organisms: Wool has a poor resistance to mildew and bacteria.

Chemical Reactivity: Wool contains three main types of reactive groups: peptide bonds, the side chain of amino acid residues, and disulphide linkage.

3.2.3 Morphology

Figure 3.1 illustrates the schematic diagram of fine wool fiber that contains two types of cells: (a) the cells of external cuticle, and (b) the internal cortex that constitute the major part of the mass of clean wool fiber.

Coarse keratin fibers may contain a third type of cell; medulla. This is a central core of cells, arranged either continuously or intermittently along the fiber axis and wedged between the cortical cells, often in a ladder-like manner; air filled spaces lie between the medulla cells. The function of the medulla on the live animal appears to be conferring maximum thermal insulation, coupled with economy of weight. The presence of a medulla increases the light-scattering properties of fibers, particularly for blue light. Cuticle cells are separated from the underlying cortex, and individual cortical cells are separated from each other by the cell membrane complex.

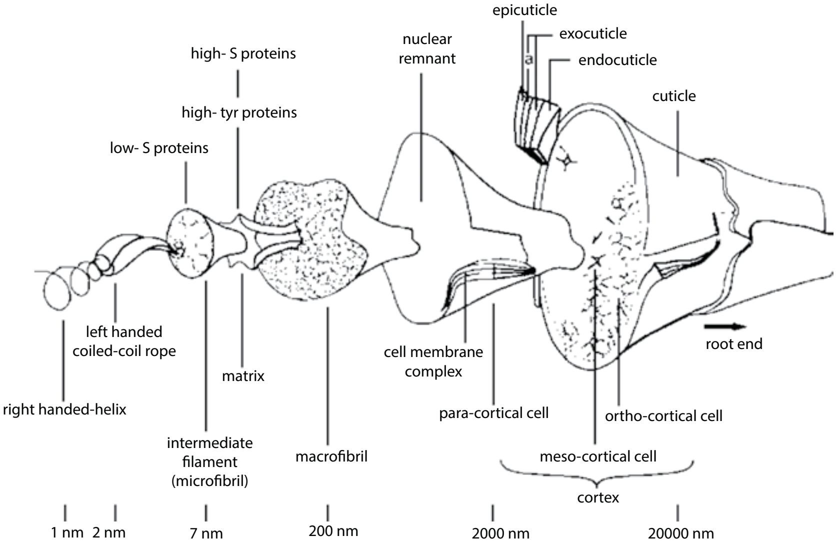


Figure 3.1 Schematic diagram of the morphological components of single fine wool fiber.

Each individual cuticle and cortical cell is surrounded by a thin, chemically resistant proteinaceous membrane which constitute approximately 1.5% of the total mass of the fiber.

An important function of cuticle cells is to anchor wool fibers in the skin of sheep. The exposed edge of each cuticle cell points from the fiber root towards the tip. This gives rise to a larger surface frictional value when a fiber is drawn in the against-scale direction than in the with-scale direction. The frictional difference helps to expel dirt and other contaminants from the fleece, but it is also responsible for wool's property of felting when agitated in water. This characteristic, which is not shared by any other textile fiber, enables wool fabrics with very dense structures to be produced, such as blankets, felts, coats, and overcoats materials. Felting is regarded as an undesirable characteristic in knitted garments when they are machine-washed. Processes are available to remove the frictional difference and make wool shrink-resistant. The fiber surface is also largely responsible for natural softness of wool and its property as one of the smoothest textile fibers [5].

From natural wool, grease has been removed by scouring with a detergent. Wool fibers are relatively difficult to wet compared with other textile materials. This natural water repellency characteristic of wool makes wool fabrics 'shower-proof' and water resistant.

The cuticle is formed of thin scales of hard and horny consistency and overlap protrude for about one third of its length, the ends being directed towards the tip of the fiber. The outermost of these scales are tough membrane known as epi-cuticle. Beneath this, exo-cuticle is situated and the innermost layer is described as the endo-cuticle. The epi- and the exo-cuticles contain a high proportion of sulphur with many cysteine cross-linkages, giving them high measures of resistance to biological and chemical attacks. The endo-cuticle on the other hand is somewhat less resistant. There are intracellular membranes which act as a cement holding the cuticle to the adjacent tissues.

The cortex contributes about 90% of the wool fiber. The cortex consists of long spindle shaped cells, thick in the center and tapering towards points at each end. These cortical cells are 100–200 μ long and 2–5 μ wide. The tensile strength, elastic properties, and the natural color of wool are determined mainly by the nature of cortical cells. Further, the medulla of wool fiber is sometimes a hollow canal, and in coarser fibers may consist of a hollow tubular network. Coarse and medium wools are characterized by the presence of a greater proportion of modulated fibers. In majority of the Merino fibers, the medulla is either absent or so fine as to be almost invisible.

3.2.4 Chemical Structure

Wool fibers contain mainly keratinous proteins of high relative molecular mass (RMM). The building blocks of proteins are about twenty amino acids, which have a typical chemical formula (Figure 3.2). The side chains of various amino acids present in wool vary in size and chemical nature (Table 3.1).

The presence of acidic carboxylic (–COOH) and basic amino (–NH_2) groups make its nature to be amphoteric. When amino group of one molecule is condensed with the carboxylic acid group of second molecule, a dipeptide is formed. Condensation with a further amino acid gives a tripeptide, and the process continues to form a polypeptide. With twenty different R groups, the polypeptide can be linked to a string of colored beads, each different coloured bead representing an amino acid "residue" with a different R group. The nature and the position of R groups give the protein its unique properties. In wool, individual polypeptide chains are joined together to form proteins by a variety of covalent (chemical bonds) called crosslinks, and non-covalent physical interactions (Figure 3.3).

The most important crosslinks are the sulphur containing disulphide bonds, which are formed during the growth of fiber by a process called "keratinisation." These make keratin fibers insoluble in water and more stable to chemical and physical attack than other types of proteins. Disulphide bonds are involved in the chemical reactions that occur in the 'setting' of fabrics during finishing. In this process, disulphide crosslinks are rearranged to give wool fabrics smooth-drying properties so that ironing is not required after laundering. Another type of crosslink is the isopeptide bond, formed between amino acids containing acidic or basic groups. In addition to the chemical crosslinks, some other types of interactions also help to stabilize the fiber under both wet and dry conditions. These arise from interactions between the side groups of the amino acids that constitute wool proteins. Thus, hydrophobic interactions occur between hydrocarbon side groups; and ionic interactions occur between groups that can exchange protons. These ionic interactions or 'salt linkages' between acidic

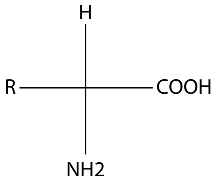
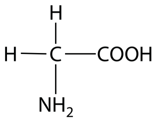
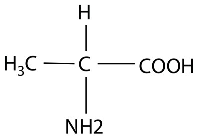
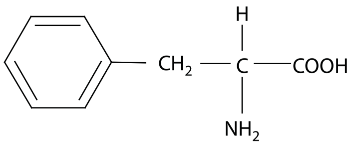
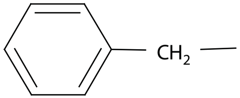
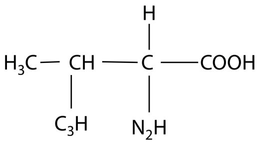
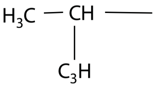


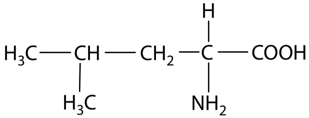
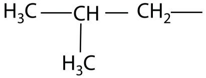
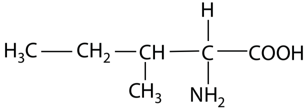
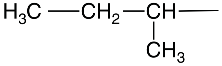
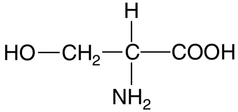
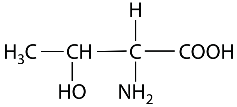
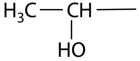
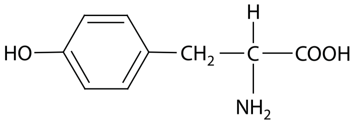
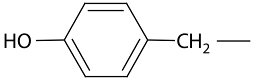
Figure 3.2 The typical structure of amino acids present in wool (R = side chain).

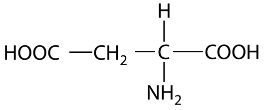
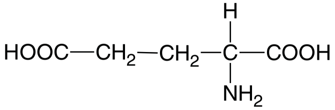
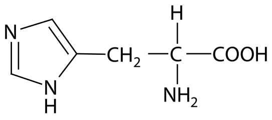
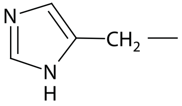
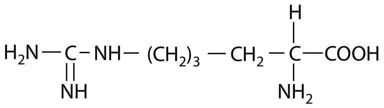
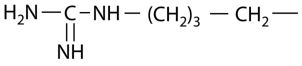
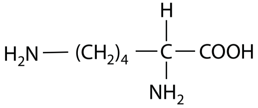
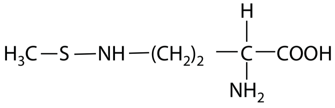
Table 3.1 Several amino acids present in wool.

S. no.	Amino acid	Chemical structure	Side chain (R)
1.	Glycine	 $\mathrm{H{-}\overset{H}{\underset{NH_2}{C}}{-}COOH}$	–H
2.	Alanine	 $\mathrm{H_3C{-}\overset{H}{\underset{NH2}{C}}{-}COOH}$	$-CH_3$
3.	Phenylalanine		
4.	Valine	 $\mathrm{H_3C{-}\underset{C_3H}{CH}{-}\overset{H}{\underset{N_2H}{C}}{-}COOH}$	 $\mathrm{H_3C{-}\underset{C_3H}{CH}{-}}$

(*Continued*)

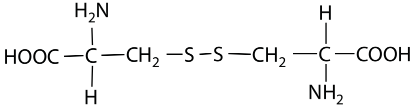
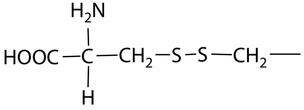
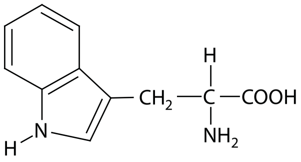
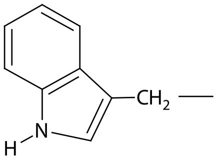
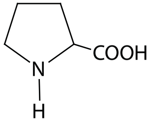
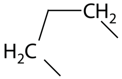
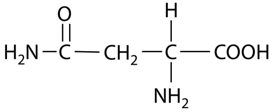
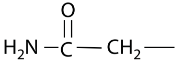
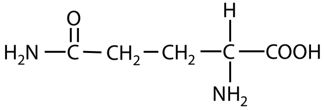
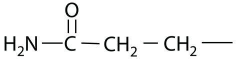
Table 3.1 Cont.

S. no.	Amino acid	Chemical structure	Side chain (R)
5.	Leucine	 $H_3C{-}\underset{\substack{\mid\\H_3C}}{CH}{-}CH_2{-}\overset{\substack{H\\\mid}}{\underset{\substack{\mid\\NH_2}}{C}}{-}COOH$	 $H_3C{-}\underset{\substack{\mid\\H_3C}}{CH}{-}CH_2{-}$
6.	Isoleucine	 $H_3C{-}CH_2{-}\underset{\substack{\mid\\CH_3}}{CH}{-}\overset{\substack{H\\\mid}}{\underset{\substack{\mid\\NH_2}}{C}}{-}COOH$	 $H_3C{-}CH_2{-}\underset{\substack{\mid\\CH_3}}{CH}{-}$
7.	Serine	 $HO{-}CH_2{-}\overset{\substack{H\\\mid}}{\underset{\substack{\mid\\NH_2}}{C}}{-}COOH$	$HO{-}CH_2{-}$
8.	Threonine	 $H_3C{-}\underset{\substack{\mid\\HO}}{CH}{-}\overset{\substack{H\\\mid}}{\underset{\substack{\mid\\NH_2}}{C}}{-}COOH$	 $H_3C{-}\underset{\substack{\mid\\HO}}{CH}{-}$
9.	Tyrosine		

10.	Aspartic Acid	 $\mathrm{HOOC-CH_2-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{-COOH}$	$\mathrm{HOOC-CH_2-}$
11.	Glutamic Acid	 $\mathrm{HOOC-CH_2-CH_2-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{-COOH}$	$\mathrm{HOOC-CH_2-CH_2-}$
12.	Histidine		
13.	Arginine	 $\mathrm{H_2N-}\underset{\mathrm{NH}}{\underset{\Vert}{\mathrm{C}}}\mathrm{-NH-(CH_2)_3-CH_2-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{-COOH}$	 $\mathrm{H_2N-}\underset{\mathrm{NH}}{\underset{\Vert}{\mathrm{C}}}\mathrm{-NH-(CH_2)_3-CH_2-}$
14.	Lysine	 $\mathrm{H_2N-(CH_2)_4-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{-COOH}$	$\mathrm{H_2N-(CH_2)_4-}$
15.	Methionine	 $\mathrm{H_3C-S-NH-(CH_2)_2-}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{-COOH}$	$\mathrm{H_3C-S-NH-(CH_2)_2-}$

(*Continued*)

Table 3.1 Cont.

S. no.	**Amino acid**	**Chemical structure**	**Side chain (R)**
16.	Cysteine	 $HOOC-\overset{H_2N}{\underset{H}{C}}-CH_2-S-S-CH_2-\overset{H}{\underset{NH_2}{C}}-COOH$	 $HOOC-\overset{H_2N}{\underset{H}{C}}-CH_2-S-S-CH_2-$
17.	Tryptophan		
18.	Proline		
19.	Asparagine	 $H_2N-\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{H}{\underset{NH_2}{C}}-COOH$	 $H_2N-\overset{O}{\overset{\parallel}{C}}-CH_2-$
20.	Glutamine	 $H_2N-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-\overset{H}{\underset{NH_2}{C}}-COOH$	 $H_2N-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-$

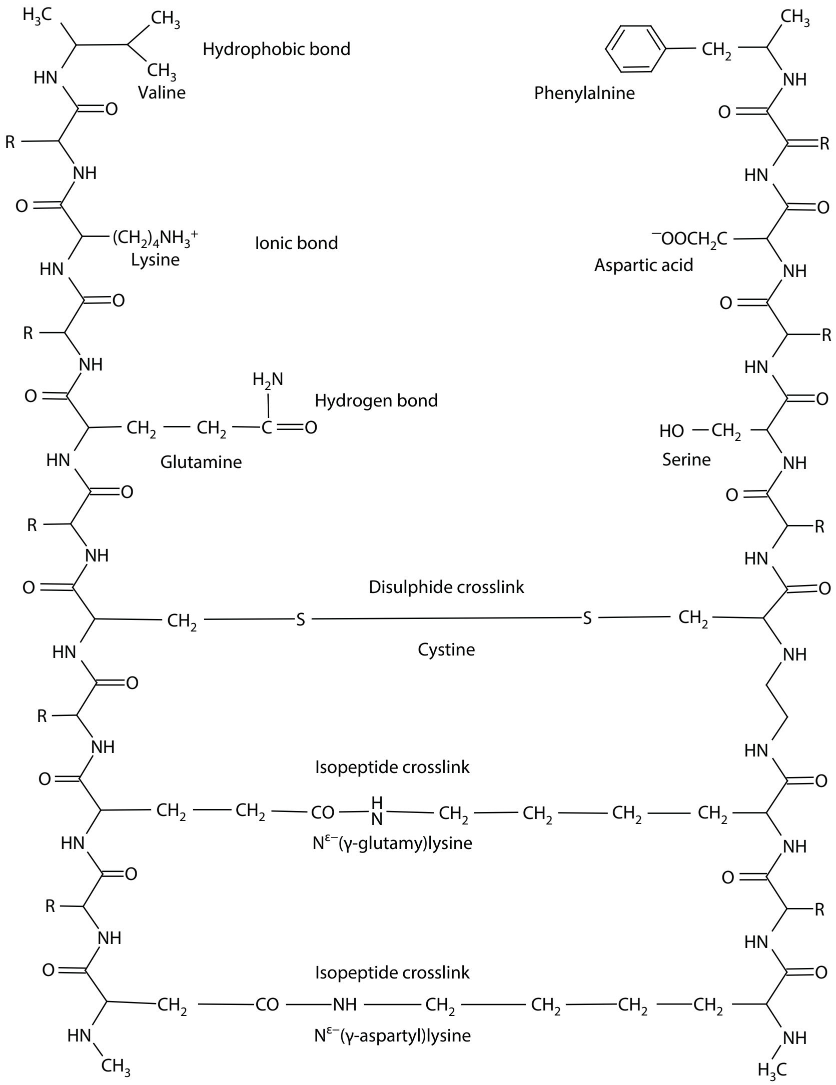


Figure 3.3 Chemical bonding in wool.

(carboxyl) and basic (amino) side chains are the most important of non-covalent interactions.

The carboxyl and amino groups in wool are also important because they give wool its amphoteric or pH buffering properties. This is wool's ability to absorb and desorbs both acids and alkalis. The ionic groups also control the dyeing behavior of the fiber, as a result of their interactions with negatively charged dye molecules. Figure 3.4 shows the schematically complex formation of wool functional groups, mordant, and dye molecule. Metallic mordants have different linking interactions with wool and thereby may darken, brighten or alter the overall color of the dyed wool samples [6, 7].

In the view of several published investigations [5–10], mordants have a propensity to combine with dye and fibre that possibly contribute imparting stable color, attributed to a chemical bridging/bonding between dye and fiber molecules. Mordanting has little effect on colorimetric properties as subsidiary changes were observed in colorimetric values (L*, a*, b*) for mordanted samples in comparison to untreated samples. In a consequent recent study, Gawish *et al.*, demonstrated that in case of cotton, wool, silk, and nylon fabrics dyed with curcumin with/without ferrous sulphate as mordant, wool fabric acquires excellent transmission blocking, and dyed

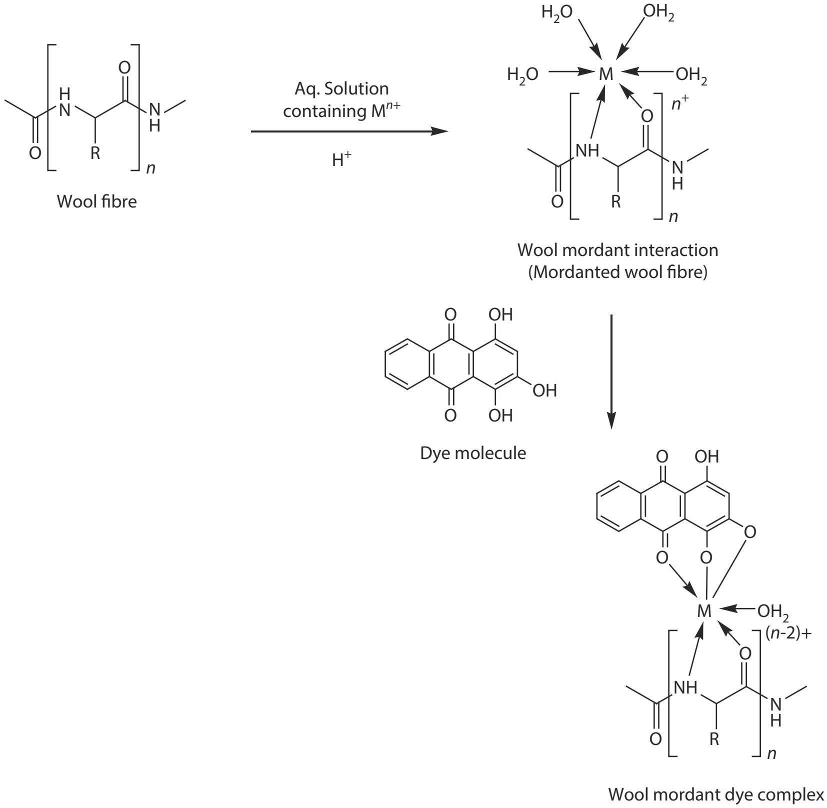


Figure 3.4 Schematically complex formation of wool functional groups, mordant, and dye molecule

silk fabrics give very good UPF (Ultraviolet Protection Factor) results but the dyed nylon and cotton fabrics have bad transmission blocking [11].

3.3 Silk

Silk is one of the popular fabrics for apparel usage because of its unique properties such as luxurious and comfortability [12, 13]. Silk is a natural protein fiber and best-known type of silk is obtained from the cocoons of the larvae of the mulberry silkworm *Bombyxmori* reared in captivity (sericulture). The silk worms are treated to a luxurious life to produce their cocoons. Each silkworm cocoon is made up of a single fiber of 600 to 900 m long. Five to eight strands of the filament that are unwound from a silk worm cocoon are used to create silk thread. The silk thread is then used to create silk fabric. Silk production is especially common in the Hymenoptera (bees, wasps, and ants) and is sometimes used in nest construction. Other types of arthropod produce silk, most notably various arachnids such as spiders. The shimmering appearance of silk is due to the triangular prism-like structure of the silk fiber, which allows silk cloth to refract incoming light at different angles, thus producing different colors.

3.3.1 Physical Properties

Silk has the several physical properties [14, 15] which can be described as under:

Tenacity: The silk filament is strong. This strength is due to its linear, beta configuration polymers and very crystalline polymer system. These two factors permit many more hydrogen bonds to be formed in a much more regular manner. Silk loses strength on wetting. This is due to water molecules hydrolyzing a significant number of hydrogen bonds and in the process weakening the silk polymer.

Specific gravity: Degummed silk is less dense than cotton, flax, rayon or wool. It has a specific gravity of 1.25. Silk fibres are often weighted by allowing filaments to absorb heavy metallic salts; this increases the density of the material and increases its draping property.

Elasticity: Silk is considered to be more plastic than elastic because its very crystalline polymer system does not permit the amount of polymer movement which could occur in a more amorphous system. Hence, if the silk material is stretched excessively, the silk polymers that are already in a stretched state (They have a beta configuration) will slide past each other. The process of stretching ruptures a significant number of hydrogen bonds.

Elongation nature: Silk fiber has an elongation at the break of 20–25% under normal condition. At 100% R.H. the extension at break is 33%.

Hygroscopic nature: As silk has a very crystalline polymer system, it is less absorbent than wool but it is more absorbent than cotton. The greater crystallinity of silk's polymer system allows fewer water molecules to enter than do the amorphous polymer system of wool. It absorbs water well (M.R.11%), but it dries fairly and quickly.

Thermal sensitivity: Silk is more sensitive to heat than wool. This is considered to be partly due to the lack of any covalent cross links in the polymer system of silk, compared with the disulphide bonds which occur in the polymer system of wool. The existing peptide bonds, salt linkages, and hydrogen bonds of the silk polymer system tend to break down once the temperature exceeds 1000 C.

Electrical nature: Silk is a poor conductor of electricity and tends to form static charge when it is handled. This causes difficulties during processing, particularly in dry atmosphere.

Stiffness: The handle of the silk is described as a medium and its very crystalline polymer system imparts a certain amount of stiffness to the filaments. This is often misinterpreted, in that the handle is regarded as a soft, because of the smooth, even, and regular surface of silk filaments.

Flexibility: Silk fiber is flexible enough and if silk fiber is used to make garments, then the fabric drapes well and this is why it can be tailored well too.

Abrasion resistance: Silk fabric possesses good abrasion resistance as well as resistance to pilling.

Effect of sunlight: Silk is more sensitive to light than any other natural fiber. Prolonged exposure to sunlight can cause partially spotted color change. Yellowing of silk fiber is generally occurred due to photo degradation by the action of ultraviolet radiation of sunlight. The mechanism of degradation is due to the breaking of hydrogen bonds followed by the oxidation and the eventual hydrolytic fission of the polypeptide chains.

3.3.2 Chemical Properties

Action of water: The absorption of water molecules takes place in the amorphous regions of the fiber, where the water molecules compete with the free active side groups in the polymer system to form cross links with the fibroin chains. As a result, loosening of the total infrastructure takes place accompanied by a decrease in the force required to rupture the fiber and increase extensibility. Treatment of silk in boiling water for a short period of time does not cause any detrimental effect on the properties of silk fiber. But on prolonged boiling, silk fiber tends to loss its strength to some degree, which thought to occur because of hydrolysis action of water. Silk fiber withstands, however, the effect of boiling better than wool.

Effect of acids: Silk is degraded more readily by acids than wool. Concentrated sulphuric and hydrochloric acids, especially when hot, cause hydrolysis of peptide linkages and readily dissolve silk. Nitric acid turns the color of silk into yellow. Dilute organic acids show little effect on silk fiber at room temperature, but when concentrated, the dissolution of fibroin may take place. On treating of silk with formic acid of concentrated about 90% for a few minutes, a swelling and contraction of silk fiber occur. Like wool, silk is also amphoteric substance, which possesses the ability to appear as a function of the pH value either as an acid or as a base.

Effect of alkalis: Alkaline solutions cause the silk filament to swell. This is due to partial separation of the silk polymers by the molecules of alkali. Salt linkages, hydrogen bonds, and Van der Waals' forces hold the polymer system of silk together. Since these inter-polymer forces of attraction are all hydrolyzed by the alkali, dissolution of the silk filament occurs readily in the alkaline solution. Initially, this dissolution means only a separation of the silk polymers from each other. However, prolonged exposure would result in peptide bond hydrolysis, resulting in a polymer degradation and complete destruction of the silk polymer. Whatever, silk can be treated with a 16–18% solution of sodium hydroxide at low temperature to produce crepe effects in mixed fabric containing cotton. Caustic soda, when it is hot and strong, dissolves the silk fiber.

Action of oxidizing agent: Silk fiber is highly sensitive to oxidizing agents. The attack of oxidizing agents may take place in three possible points of the protein; (a) at the peptide bonds of adjacent amino groups, (b) at the N-terminal residues, and (c) at the side chains. Though fibroin is not severely affected by hydrogen peroxide solution, nevertheless may suffer from the reduction of nitrogen and tyrosine content of silk indicate that hydrogen peroxide may cause breakage of peptide bonds at the tyrosine residues resulting in the weight loss of the fiber. The action of chlorine solution on the silk fibroin is more harmful than does the solution of hypochlorite. These solutions, even at their lower concentration, cause damage to fibroin.

Action of reducing agents: The action of reducing agents on silk fiber is still a little bit obscure. It is, however, reported that the reducing agents that are commonly found in use in textile processing such as hydrosulfite, sulfurous acids and their salts do not exercise any destructive action on the silk fiber.

Effect of sunlight and weather: The dearth of covalent cross-link in the polymer system of silk makes it affected by sunlight. The ultraviolet rays of the sun cause peptide bonds to break which causes polymer degradation on the surface of fibers. These degradation process cause the silk fiber to not only absorb more light but to scatter the incident light to a great extent. The result is yellowing or dulling of silk.

3.3.3 Morphology

The morphological structure of silk (from *Bombyxmori* and spider dragline) is very simple, having core-shell structure (Figure 3.5). Silk is produced in benign and aqueous conditions in silk glands throughout the instar stages. At the end of the fifth instar, *Bombyxmori* silkworms spin a large amount of silk from its pair of silk glands (Figure 3.6A) into a continuous thread of raw silk to construct a silk cocoon. The raw silk consists of two parallel fibroin fibers held together with a layer of sericin on their surfaces (Figure 3.6B) [16, 17].

Fibroin fibers can be fabricated conventionally into braided, knitted, and non-woven matrices. With its versatile processability, various morphologies can be regenerated from dissolved fibroin fibers, including but are not limited to hydrogels, sponges, films, mats, microparticles and microneedles (Figure 3.7) [18].

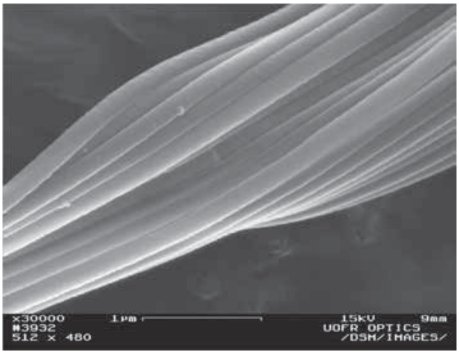
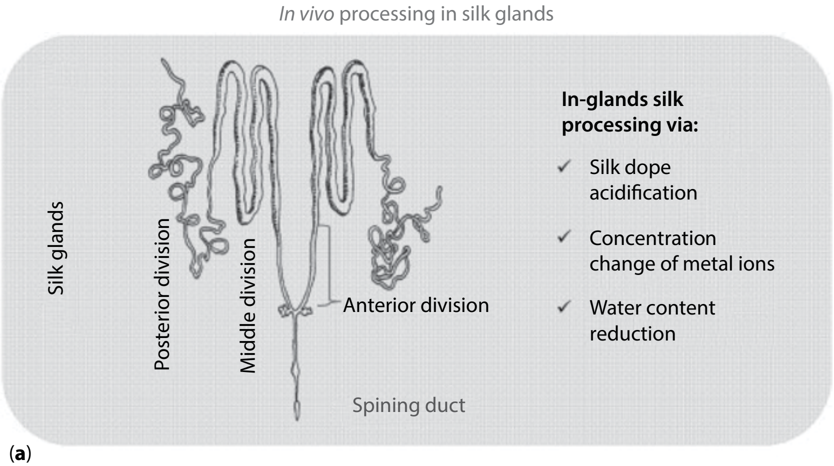


Figure 3.5 Scanning electron micrograph of silk fiber.



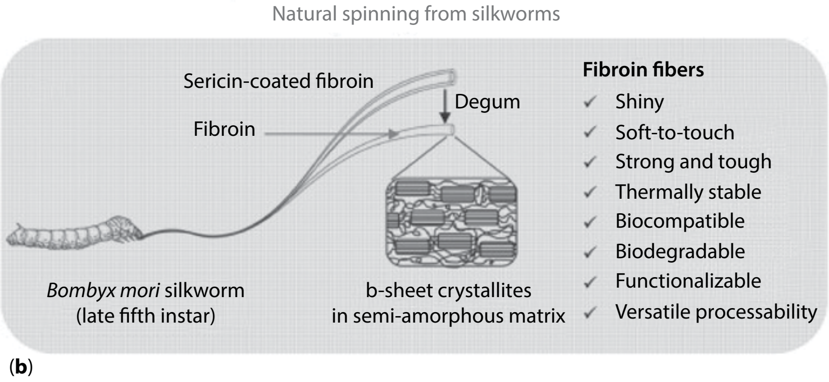


Figure 3.6 (a) *In vivo* processing in silk glands, and (b) Natural spinning by silkworms to produce fibroin fibers with unique features. Reprinted with permission from Elsevier Ltd Copyright 2015.

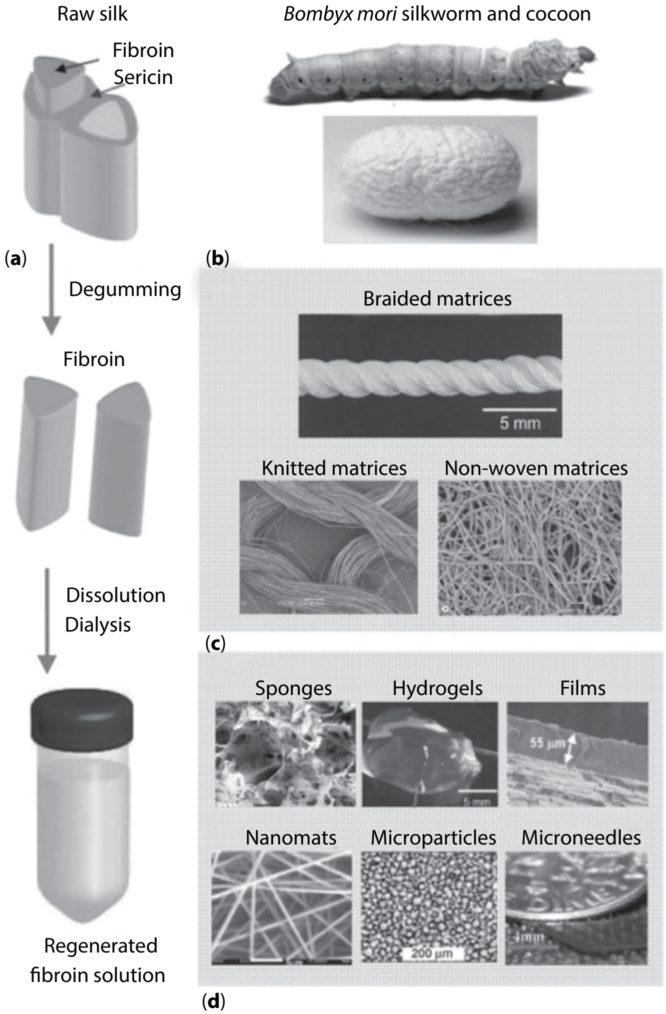
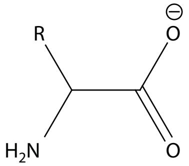


Figure 3.7 Various morphologies of silk and silkworm (*Bombyxmori*). (a) The raw silk consists of two fibroin fibers held together with a layer of sericin on their surfaces. After degumming to remove sericin, the fibroin fibers are dissolved in lithium bromide solution followed by dialyzing against ultrapure water or polyethylene glycol to obtain regenerated fibroin solution, (b) Mature silkworm and produced cocoon, (c) Silk braided, knitted, and non-woven matrices constructed from the fibroin fibers, and (d) Silk sponges, hydrogels, films, nanofibrous mats, microparticles, and microneedles constructed from the regenerated fibroin solution. Reprinted with permission from Elsevier Ltd Copyright 2015.

3.3.4 Chemical Structure

Silk structure is similar like wool but with a much simpler. It is an extruded fiber which is structurally uniform across its diameter. The amino acids



R = H, glycine; R = CH_3, alanine; R = CH_2OH, serine

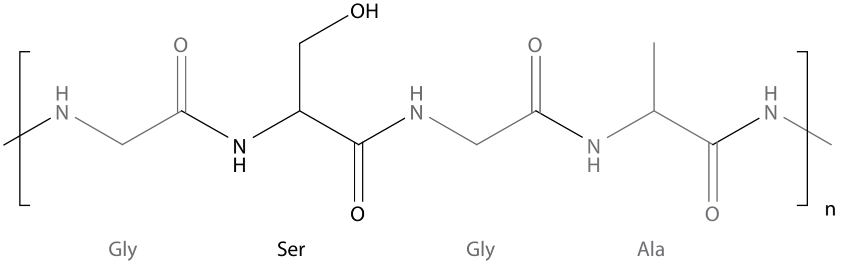


Figure 3.8 Chemical structure of silk.

have smaller pendant groups than those found in wool, allowing a pleated-sheet structure rather than helical to occur. Silk contains about 78% protein and is much stiffer than wool in spite of both being proteins made from amino acids chains. Fibroin is largely made up of the amino acids Gly-Ser-Gly-Ala-Gly-Ala and forms β-pleated sheets. Hydrogen bonds form between chains, and side chains form above and below the plane of the hydrogen bond network. *B. mori* silk fibroin contains a high proportion of three α-amino acids, glycine (Gly, 45%, R=H), alanine (Ala, 29%, R=CH_3), and serine (Ser, 12%, R=CH_2OH) (Figure 3.8), in the approximate molar ratio of 3:2:1, respectively. Tyrosine, valine, aspartic acid, glutamic acid, etc. make up the remaining 13% [19].

The analysis of archeological textiles (wool and silk) using reversed-phase HPLC (High Performance Liquid Chromatography) with diode-array UV–VIS (Ultraviolet-Visible) spectrophotometric detection revealed that several natural dyes were used to dye them. The examined objects originate from the 4th to the 12th century in Egypt and belong to the collection of Early Christian Art at the National Museum in Warsaw, one of the largest museums in Poland. In medieval times, silk fabrics were the most famous, sophisticated, and luxurious fabric. The silk dyers in Italy and France were only to be found where the silk worm flourished. The Classical antiquity held white to be the noblest color, but already towards the close of the second century closefitting, long-sleeved woolen garments became fashionable among the wealthy sons of Rome; these, like the short linen trousers, were colored. This fashion was not of Oriental, but rather of Germanic origin. In the earliest period of their history, the Germanic and Gallic tribes painted their bodies, as was, and is the custom among many hunting tribes. At the time of the Romans, this practice, originally bound up with totem beliefs, had been transferred to the clothing, which was generally striped or checked. These people had learnt very early to dye their stuffs in the wool; it is therefore not surprising that their natural love of color led them to admire and imitate the gorgeous dress of the late Roman period. Since Diocletian, the Roman emperors had enforced a rigid etiquette in the use of colors, especially with regard to the purple mantle of Chinese silk, which became sacrosanct. The Gothic princes of the Dark Ages, and after them the Merovingians, adopted this privilege, but the shifting social order of these unstable empires made it easy for others, especially for the warriors, to infringe on this privilege [20, 21].

3.4 Conclusion

For centuries, fabrics containing silk and wool fibers have been utilized. Addition of color to the fabrics depends upon the mechanical and chemical structures of the fibers used. The molecular structure of hair fiber is complex; single hair fiber is a multi celled array wrapped with a surface layer of small scale reminiscent like fish scales. The fiber is constructed of proteins, having 10 to 20 different kinds of amino acid monomers in its chain. The pendant chemical groups on the amino acids force the protein into α-helical arrangement similar to a spring. Cysteine crosslinks between adjacent protein molecules keep the helices tied together. Furthermore, the silk structure is similar like wool but with a much simpler. It is an extruded fiber which is chemically and structurally uniform across its diameter. The amino acids have smaller pendant groups than those found in wool, allowing a pleated-sheet structure rather than helical to occur. It is concluded that this chapter will provide the more exact knowledge of wool and silk characteristics which is needed to inaugurate new research opportunities. Of course, genetic engineering that utilized in current era opened new dimensions in textile fiber researches. Imaginative work is needed for successful routes for textiles with biomimetic functionalities.

References

1. John, M.J. and Thomas, S. (eds.), *Natural Polymers: Composites, Vol. 1*, RSC Publishing, Cambridge, UK, 2012.

2. Tortman, E.R., *Dyeing and Chemical Technology of Textile Fibers*, *4th Edn*, Charles Griffin and Co., USA, 1975.
3. Cook, J.G., *Handbook of Textile fibers: Natural Fibers, Vol 1*, Woodhead Publishing Limited, Sawton, Cambridge, UK, 1984.
4. Lewis, D.M., *Wool Dyeing*, Society of Dyers and Colorists, UK, 1992.
5. Haji, A., Qavamnia, S.S., Bizhaem, F.K., Oxygen plasma as a pretreatment for environmentally friendly low temperature dyeing of wool natural fiber. *J. Biodiversity Environ. Sci.*, 5, 602–607, 2014.
6. Uslu, H. and Bamu, H.S., Effect of Solvent and pH on the Extraction of Carbolic Acid from Aqueous Solution by TOMAC. *J. Chem. Eng. Data*, 61, 1676–1680, 2016.
7. Khan, S.A., Ahmad, A., Khan, M.I., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., Antimicrobial Activity of wool yarn dyed with *Rheum emodi* (Indian Rhubarb). *Dyes Pigm.*, 95(2), 206–204, 2012.
8. Yusuf, M., Ahmad, A., Shahid, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsonia inermis*). *J. Clean. Prod.*, 27, 42–50, 2012.
9. Yusuf, M., Shahid, M., Khan, S.A., Yusuf, M., Khan, M.A. and Mohammad, F., Investigations of the colourimetric and fastness properties of wool dyed with colorants extracted from Indian madder using reflectance spectroscopy. *Optik-Int. J. Light Electron Optics,* 127(15), 6087–6093, 2016.
10. Yusuf, M., Shahid, M., Khan, S.A., Khan, M.I., Shahid-ul-Islam, Mohammad, F., Khan, M.A., Eco-dyeing of wool using aqueous extract of the roots of Indian madder (*Rubiacordifolia*) as natural dye. *J. Nat. Fibers*, 10, 14–28, 2013.
11. Gawish, S.M., Mashaly, H.M., Helmy, H.M., Ramadan, A.M., Farouk, R., Effect of Mordant on UV Protection and Antimicrobial Activity of Cotton, Wool, Silk and Nylon Fabrics Dyed with Some Natural Dyes. *J. Nanomed. Nanotechnol.*, 8(421), 1–9, 2017.
12. Hall, D.M., Adanur, S., Broughton, R.M., Brady, P.H., Polymers and Fibers, in: *Wellington Sears Handbook of Industrial Textiles, 1st Edn.,* S. Adanur (Ed.), pp. 33–56, Wellington Sears Co., Lancaster, Pennsylvania, USA, 1995,
13. Robson, R.M., Silk: Composition, structure, and properties, in: *Handbook of Fiber Chemistry, 2nd Edn.*, M. Lewin and E.M. Pearce (Eds.), Marcel Dekker, New York, 1988, 415–464.
14. https://textileapex.blogspot.in/2015/01/physical-chemical-properties-silk.html (Accessed on 14.09.2017)
15. http://textilelearner.blogspot.in/2013/06/physical-and-chemical-properties-of.html (Accessed on 14.09.2017)
16. Foo, C.W.P., Bini, E., Hensman, J., Knight, D.P., Lewis, R.V., Kaplan, D.L., Role of pH and charge on silk protein assembly in insects and spiders. *Appl. Phys. A: Mater. Sci. Process*, 82, 223–233, 2006.
17. Willcox, P.J., Gido, S.P., Muller, W., Kaplan, D.L., Evidence of a Cholesteric Liquid Crystalline Phase in Natural Silk Spinning Processes. *Macromol.*, 29, 5106–5110, 1996.

18. Altman, G.H., Horan, R.L., Lu., H.H., Moreau, J., Martin, I., Richmond, J.C., Kaplan, D.L., Silk matrix for tissue engineered anterior cruciate ligaments. *Biomater.*, 23, 4131–4141, 2002.
19. Fraser, R.B.D., MacRae, T.P., Conformation of Fibrous Proteins and Related Synthetic Polypeptides, pp. 293–343. Academic Press, New York, 1973.
20. http://www.elizabethancostume.net/cibas/ciba1.html (Accessed on 14.09.2017)

21 Ahmed, H.E., Zidan, Y., Elnagar, K., Ageing behavior of silk dyed fabric with safflower dye, in *26th Meeting on Dye in Historical Textiles and Archaeology*, Vienna, Austria, 7–10 November, 2007.

PART II

RENEWABLE COLORANTS AND THEIR APPLICATIONS: A REVOLUTIONARY APPROACH

4

Animal Based Natural Dyes: A Short Review

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Abstract

Natural dyes have been practiced since the mankind's history for different purposes i.e., dyeing, painting, printing, food, as well as for decorative purposes. But in the nineteenth century their routine has been clogged by the invention of synthetic dyes, due to their high fastness properties and cost-effective nature. But recent readings tell the noxious effects of synthetic dyes that drive the people around the world to make their use less and to focus on the colors from natural resources, which are granted with numerous beneficial properties over synthetic dyes. These sources may be animal based, plant based, mineral based or micro-organisms based. This chapter has comprised the short information regarding the animal based natural colorant and their extraction through the conventional and modern methods, which help to gain the properties analogous to their counterpart. It is expected that this chapter will give the valuable information to their readers and researchers who are resurging new sources of natural colorant particularly animal based in different applied field.

Keywords: Cochineal, kermes, lac, modren extraction methods, natural dyes, sea snail

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Mohd Yusuf (ed.) Handbook of Renewable Materials for Coloration and Finishing, (43–74)

4.1 Introduction of Natural Dyes

Man is always fascinated with the beauty of nature that has been bestowed with beautiful and charming color and without color man cannot imagine his life and feel aimless to work. It is a sense of pleasure that gives aesthetic value to human. Numerous historical records have proved his interest by application of color in different ways such as decoration of walls, caves, body paints, textiles, painting, and cosmetics [1]. They obtain these colors from natural sources such as plants, animals or insects, micro-organisms, and minerals without any specific methods. Tyrian purple was the first color introduced by Phoenicians that was obtained from genus Murex and Purpura [2]. Egyptians used to dye their textile with madder. Similarly, yellow colorant obtained from saffron was only used to dye robes for Chinese emperors, while people of China dyed their cloth with gardenia having same color "yellow" as saffron has. However, the downfall of natural dyes was started with the accident discovery of synthetic dye "mauvine" by W.H. Perkin in 1856. It was found that this dye have many advantages over natural dyes such as good fastness properties, brightest color, cost and time effective properties [3, 4]. However, after the mid of twentieth century their carcinogenic effects have been realized during their production and their wastes not only effect ecosystem but also cause serious health hazards. Another problem is the enhanced global warming regarding the use of synthetic dyes whereas these are highly stable to light, heat, and oxidizers due to highly analyzed structures. For this reason, different countries USA, Germany, and EU have strictly banned the production of such dyes and imposed restriction on their use in many daily life things. Such extreme drawbacks have compelled whole community to revisit the natural dyes. The revival is due to their eco-friendly, non-carcinogenic, non-toxic with several beneficial functional properties such as ultraviolet (UV) protective, anti-inflammation, anti-microbial, anti-oxidant properties [5, 6, 7]. These dyes are easily bio-degradable and their wastes cannot cause any sort of problem to environment as their wastes acts as health cure material [8]. Natural dyes also give wide spectrum of color because these dyes are obtained from different parts of the plants (such as bark, leaves, stem, root, fruit, flower etc.) and by the method of mordanting that gives different shades. Due to such reasons, these dyes have been involved in wide range of application in the fields of textiles, dye sensitized solar cells, paints, inks, food, cosmetics, pH, Indicators etc. [9]. The current study will give you a brief overview of sustainability of natural colorants, particularly the color obtained from animals and their applications.

4.2 Sustainability of Natural Dyes

Sustainability is very important term that has been used with respect to any production or new invention in scientific field showing green concerns. As sustainability is concerned with the material that will apply to global mart, so it should be cost effective, eco-friendly, easily available, and soothing to community and must fulfill the demand of present consumer without affecting the needs of coming generation. Textile industry is one of the big industries and it is found that in textile sectors the synthetic dyes which are consumed and wasted in large amounts are carcinogenic and have toxic effects to the environments [9, 10]. So as to reduce the effluent bulk, there is a dire need to resuscitate natural dyes for maintaining the sustainability of environment with eco-friendly, cost effective nature for any country. Various factors of natural dyes have influence on the sustainability of nature.

- Natural dyes can raise the economy of any country through their import and export at international level. Many countries are the great exporters of natural colorants such as Pakistan, Iran, Sudan, Egypt, Mexico, India, UK, USA etc.
- Similarly, the source of natural colorants is very cheap, as they can be obtained from primary source (leaves, bark of henna, neem, eucalyptus etc.) and secondary source i.e., waste material of vegetable, fruit, beverages waste and others e.g., onion peel, pomegranate peel, tea waste etc. [11] It is not only cost effective but also gives the opportunity of job for the farmers [12, 13].
- Natural dyes have enormous beneficial functional properties such as anti-microbial, antioxidant, antiviral, anti-hemolytic, and several others. With such properties the fabric which is to be dyed become protective agent from several sever diseases [14, 15].
- Natural dyes are easily bio-degradable and can also help to reduce the toxic effluents for the environment by adsorbing them to maintain the sustainable value of entire world [16]
- These dyes also increase the carbon fixation in the form of biomass by growing more and more plants for dye production. A dye plant contains almost 5% of dye where the remaining part can be used as fertilizer, which is useful for agriculture.
- Natural dyes are from renewable sources which have no disposal issues e.g., myrobalan, tesu, annatto etc. [17].

These factors reveal that introduction of natural dyes instead of synthetic dye in different field, especially in textile, would help to maintain the sustainability of nature regarding their economy, health aspects, social values etc.

4.3 Classification of Natural Dyes

Natural dye has been classified on different basis (given in Figure 4.1) are:

1. Source (Animals, Plants, Micro-organisms and Minerals)
2. Structure (Anthraquinone, Indigoid, Carotenoidsand Chlorophyll etc.)
3. Color (Red, Green, Yellow, Blue, Orange, Purple and Black etc.)
4. Application (Vat dye, Acid dye, Reactive dye, Disperse dye etc.)

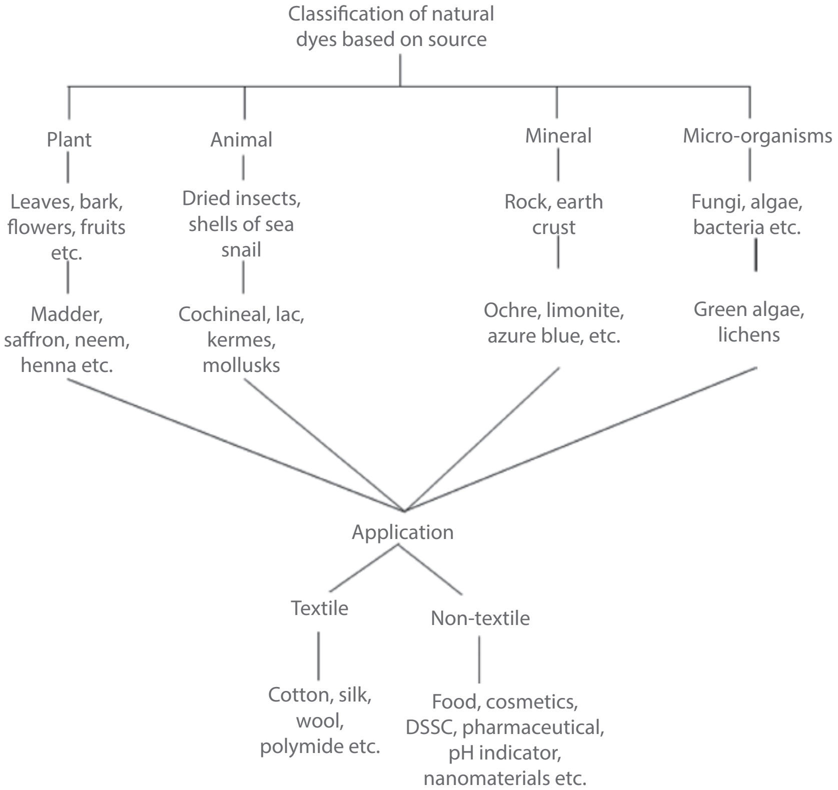

Figure 4.1 Flow sheet diagram of Natural dye's classification and their application.

4.4 Animal Based Natural Dyes

There are different sources of natural dyes but the role of animal as natural colorant is unique.

4.4.1 Cochineal

Cochineal is one of the ancient dyes that has been used by Aztecs and then after by Spaniards which replaced Kermes dye. As both dyes have similar structure but cochineal contains twelve fold more the concentration of Carminic acid and thus named as *Grana cochininilla* by Spaniards [18]. This dye is obtained from the dried bodies of female insects of *Coccus cacti* i.e., *Dactylopiuscoccus* that lives on cacti of prickly pear cactus (*Nopaleacoccinellifera*) (Figure 4.2 a & b). It is also known as Nopal, opuntia or Indian fig that is mainly found in Mexico in Central America and Brazil in South America [19]. However, nowadays the main sources of such dye are Peru and Canary Islands. The skin of female insects has brownish red

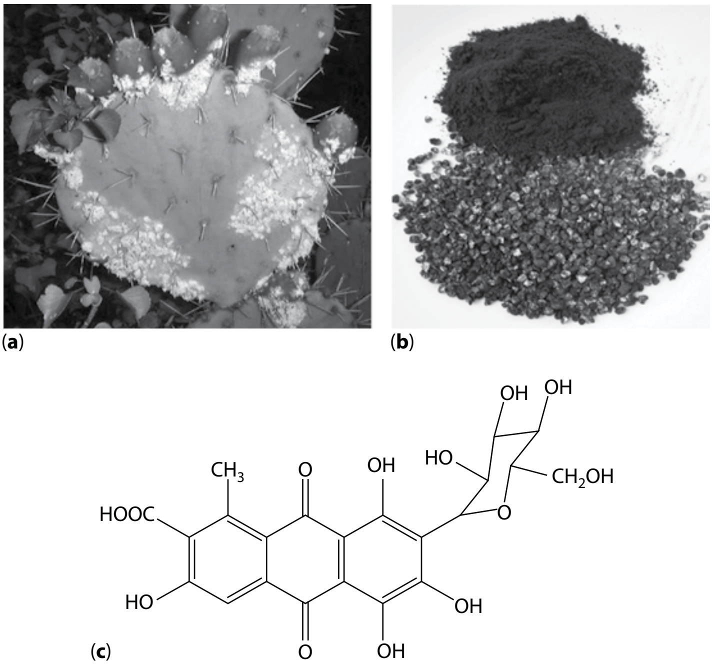

Figure 4.2 (a) Cochineal insect on prickly pear cacti (b) Cochineal dye powder (c) Carminic acid (C.I. Natural Red 4).

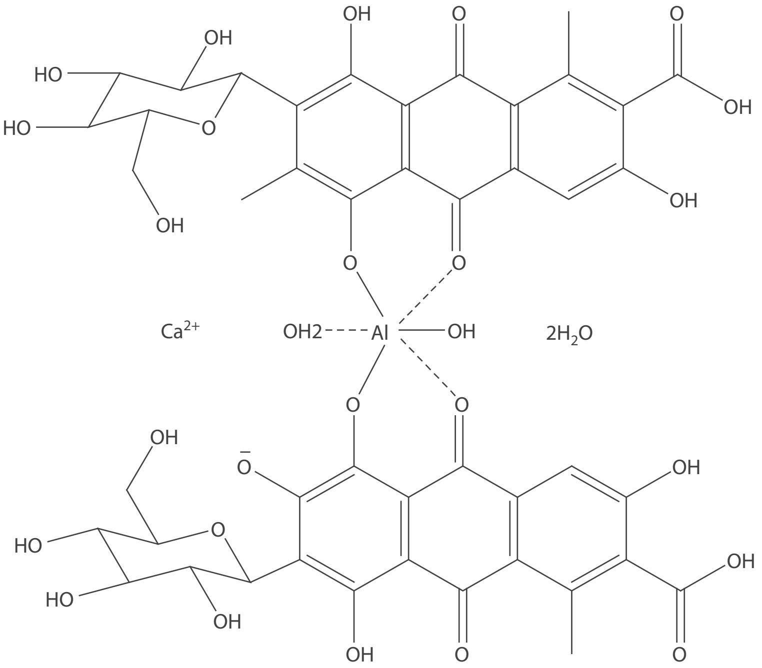

Figure 4.3 Calcium-aluminium lake of Carminic acid.

color and resides on cactus where it feeds on sap and lays thousands of eggs that contain the dye in the form of white fluid. The fluid contains 9–10% of Carminic acid as a colorant present along with glycerylmyristae (a fat) and coccerin (cochineal wax) (structure given below). Carminic acid (C.I. Natural Red 4) has various applications in food stuffs, drugs and in dyeing of natural fiber due to its good fastness characteristics [20]. Carminic acid is more stable to light and oxidants and more resistant to degradation with time. With different mordant used, it gives various shades of pink, crimson red, scarlet red, and blue onto fabric.

Carmine, carmine lake and Florentine lake which is not true colorant but produces as dissolution of Carminic acid with China clay as an additive but with alum it produces precipitation. Simply it is calcium-aluminium chelate (Figure 4.3) so it is sometimes known as "semi-synthetic dye". Carmine has been used in food, cosmetics, drug, water colors etc. The main comparison among carminic acid and carmine is given in Table 4.1.

However, before sixteenth century this dye was also obtained from Armenian cochineal (*Porphyrophorahamelii*) and Polish cochineal

Table 4.1 Comparison Between Carminic Acid and Carmine.

Carminic acid	**Carmine**
Molecular formula is $C_{22}H_{20}O_{13}$	Molecular formula is $C_{44}H_{43}AlCaO_{32}$
Easily soluble in water	It is insoluble pigment
Directly extracted from dried female body	It is calcium-aluminium lake of Carminic acid
True color	Semi-synthetic dye
Expensive to use	Cost effective
Low color intensity	High color intensity
Give orange at low pH and bluish red at high pH	Give yellow-red and blue color

Figure 4.4 Polish Cochineal.

(*Phorphyrophorapolonica*) that lived on the roots of the weed e.g., Perennial knawel (*Scleranthusperennis*).

4.4.1.1 Polish Cochineal

Polish cochineal (*Phorphyrophorapolonica*) shown in Figure 4.4 are commonly found throughout in Palerctic, Eaurasia and Central Europe. It is also known as Polish carmine scales or Saint John's blood. However, its application was stopped in the end of twentieth century because its name comes in the list of endangered species [21]. Lech and Jarosz, identified historical Polish cochineal dyed fabric using high performance liquid chromatography and also differentiated Polish cochineal with American

Figure 4.5 Armenian Cochineal.

cochineal. They found that although both imparted red color on substrate but presence and quantity of colorant component in both dyes were different as Kermesic and flavokermesic acid present in Polish cochineal in greater amount than in American cochineal [22].

4.4.1.2 Armenian Cochineal

It is so called Armenian due to its origin in Armenia plain and River valley (Figure 4.5). It is commonly known as Ararat cochineal or Ararat scale [23]. It is one of the ancient sources of red colorant since 714 B.C. and has been used by Middle East and Europe to dye silk and wool fabric [24, 25]. Other species that give the same dye are *Dactylopiusindicus Green, D. tomentosur, Anthracoccusuvae-ursi*etc.

4.4.2 Kermes

Kermes is a small worm and familiar as "kermes grains" due to its shape similarity with vegetable seeds. Kermes insect and Kermes dye powder is shown in Figure 4.6 (a & b). It has been used since the early times in England, South France, Spain, Turkey, and Scotland for dyeing textiles [26]. The red dye is present in the dried bodies of female scale insects of the genus Kermes. Examples include *vermilio* that lives on kermes oak (*Quercuscoccifera)* and *Kermes ilicis* that lives on durmast oak (*Quercus ilex)* which is native to Mediterranian and Asia. It also lives on leaves and stems of oak and feeds on its sap and after laying eggs, the mother died and eggs are killed by using vinegar fumes, where on boiling in water, the color is isolated. The colorant is soluble in hot water and gives yellowish-red color due to presence of Kermesic acid which is aglycon of Carminic acid (structure given in Figure 4.6 c). However, it also contains flavokermesic acid but of minor importance [27, 28].

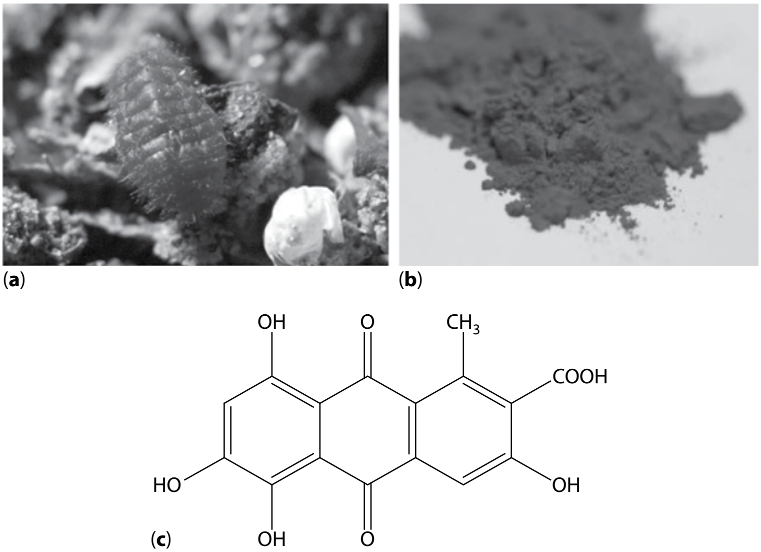

Figure 4.6 (a) Kermes insect (b) Kermes dye powder (c) Kermesic acid (C.I. Natural Red 3).

With different mordant applications, it forms different shades, such as with tin it gives scarlet red and with alum gives scarlet with bluer casting. It is considered as the cheaper dye than Tyrian purple.

4.4.3 Lac Insect

Another red dye, which is known as lac dye, is one of the most ancient of all insect dyes and has been used since prehistoric times [29]. The word lac is derived from Indian word “Lakh” which describes that it produces a small quantity of dye from hundreds of thousands of insects. This dye is obtained from resinous secretion of *Coccuslaccae* (i.e., *Lacciferlacca* and *kerrialacca*) shown in Figure 4.7 (a & b), which belongs to *Tachardiidae* family and found on the remains of branches and twigs of certain rain trees such as *Samaneasaman*, *Pithecolobiumsaman* etc. in India, Thailand, Cambodia, the Moluccas and Sumarta. The secretion contains sticky mass that produces lac dye on extraction with water. However, it is fairly soluble in methanol, acetone, and acetic acid. It consists of five coloring components i.e., Laccaic acid A, B, C, D, and E (C.I. Natural Red 25) that closely resemble with each other in structure and yield red color (Figure 4.8 a–f). It also gives scarlet red on mordanting with tin. All structures contain di-carboxylic acid except Laccaic acid D that contain only one carboxyl compound [30]. Due to carboxyl compound having acidic nature, it is used to dye wool and silk fabric. Other insoluble and minor important components are also present such as terpenic acid, aleuritic acid, Erythrolaccin, and several fatty acids [31]. It is also used as coloring agent in material industry, drugs, foods, dye

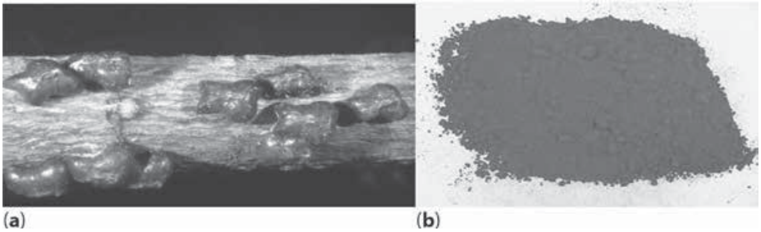

Figure 4.7 (a) Lac insects (b) Dye powder.

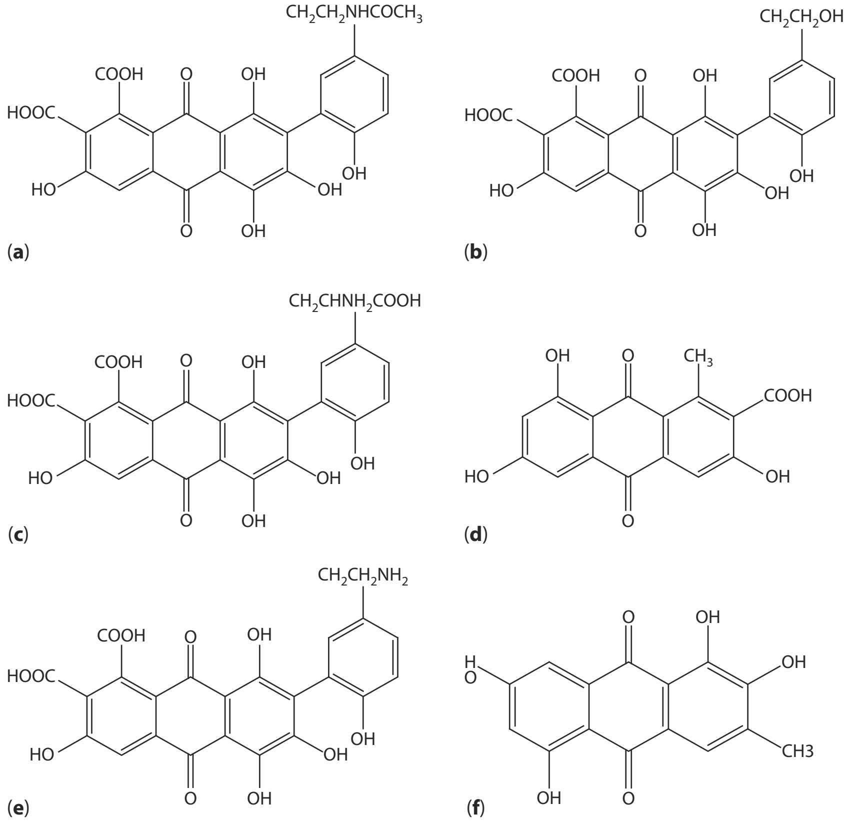

Figure 4.8 C.I. Natural Red 25 (a) Laccaic acid A (b) Laccaic acid B (c) Laccaic acid C (d) Laccaic acid D (e) Laccaic acid E (f) Erythrolaccin.

sensitized solar cells. Different studies also revealed that, lac dye possesses functional properties as well as antioxidant properties. Zhang *et al.* [32] used three different types of free radicals i.e., DPPH, ABTS and O_2 and investigated its antioxidant activity, where due to having good properties, it is fairly applicable in food industry as natural colorant.

4.4.4 Sea Snails

Sea snail contains purple dye (Tyrian purple) as well as blue dye (Tekhtelet) which is obtained from marine mollusks. It consists of two genera i.e., Murex which belongs to *Muricidae* and Purpura which belongs to *Thaididae* family. Many thousand years ago, the people of Aegean discovered this previous dye and it was found that to get 1g of dye 10,000 of predatory sea snails were needed [33]. There are three well known species that are used to get purple color such as:

1. *Bolinusbrandaris*
2. *Hexaplextrunculus*
3. *Stramonitahaemastoma*

4.4.4.1 Bolinusbrandaris

*Bolinusbrandaris*isalso called as *Murex brandaris* or *Haustellum brandaris* and is commonly known as spiny dye-murex or purple dye murex (Figure 4.9). Being edible and medium size mollusk, it has been recorded since 3.6–2.6 million years ago. Its shell has length of about 60–90 mm, which is golden brown in color. It is mainly found in Mediterranean Sea, Indian Ocean, and South China Sea [34].

Figure 4.9 Bolinusbrandaris.

4.4.4.2 Hexaplex Trunculus

Hexaplex trunculus is commonly known as *Murex trunculus*, *Phyllonotus trunculus* or banded dye- murex (Figure 4.10). It has been found that this specie was found since 3.6–0.012 million years ago mainly present in Mediterranean Sea and Atlantic coasts. It consists of conical shell which has length ranging from 4 to 10 cm [35].

4.4.4.3 Stramonita Haemastoma

It is known as mouthed rock shell or Florida dog winkle having size ranging from 22 mm to 120 mm (Figure 4.11). It is mainly found in areas of tropical, Eastern Atlantic, Mediterranean Sea [36].

The dye obtained from such species has been categorized into two types depending on its color:

1. Tekhelet
2. Tyrian purple

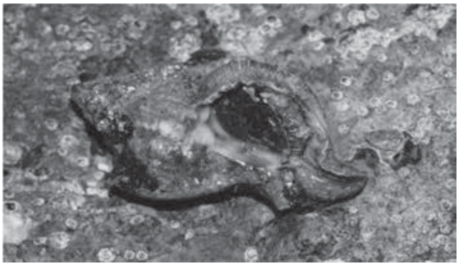

Figure 4.10 Hexaplex trunculus.

Figure 4.11 Stramonita haemastoma.

4.4.4.3.1 Tekhelet

Tekhelet dye also known as hyacinthine purple is bluish purple in color and has been obtained from hillazon. It was applied by Jews to dye their shawls but their use was diminished after seventh and eighth century [37].

4.4.4.3.2 Tyrian Purple

Tyrian purple also known as argaman has been obtained from the secretion of colorless liquid produced in hypobronchial glands adjacent to respiratory cavity of the species of mollusks i.e., Spiny dye murex (*Bolinus brandaris*), Banded dye murex (*Hexaplex trunculus*) and Red mouthed rock shell (*Stramonita haemastoma*) [38]. The secretion is not a true dye but considered as pro-dye or dye precursor. Through hydrolysis by enzyme 'purpurase', on photo-oxidation to air, the color changes from yellow to green to blue and then finally turns into stable purple colorant (Figure 4.12 a).

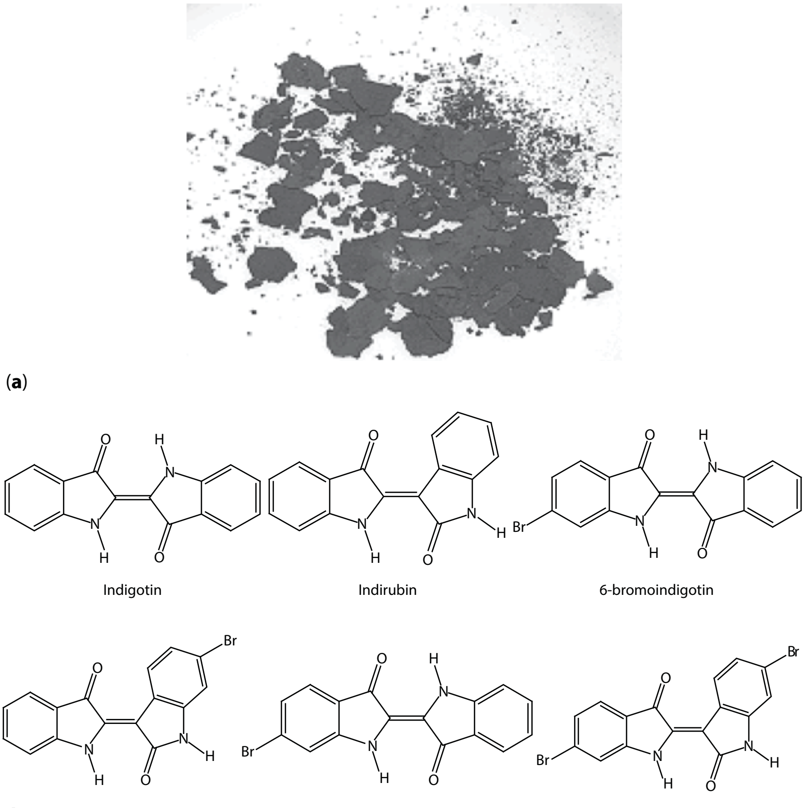

Figure 4.12 (a) Tyrian purple dye powder (b)????.

These species contain indigotin, Indirubin, 6-bromoindigo, 6-bromoindirubin, 6, 6-dibromoindigotin and 6,6-dibromoindirubin (Figure 4.12 b–f) [39]. Friedander was the first person who isolated 6,6–dibromoindigo structure from chromagen (tyrindoxylsulphate and tyriverdin) present in hypobronchial glands that gave fast reddish-purple dye. It is also known as Tyrian purple that reveals its place of origin [40]. The mechanism of action to produce 6,6'-dibromoindigo is given in Figure 4.13. Other species that are responsible for purple dye are *Nucelllapidus, Purpurapatula* and *Purpurapansa.*

Dolabella auricularia

Dolabella auricularia is found as sea hare that belongs to *Aplisiidae* family (Figure 4.14a). It is another species of sea sludge i.e., mollusks and produces natural purple ink. It is 46 cm in length and mainly found in Indian region, Western and North-West Pacific oceans. The chemical constituents that secrete by sea hare are Aplysiobviolin, Dolabellin, Auriside A, Dolastatin 10 (shown in Figure 4.14 b–e) [41].

4.5 Extraction Methodology

Extraction is a process that is used to isolate the desired material and efficiently transferred in to the solvent. In natural dyeing process, the extraction is one of the basic steps on which the yield of colorant is dependent. Up till now, researchers are using different methods to extract the colorant present in natural sources. These methods include conventional (i.e., soxhlet method, boiling method, and solvent method) and modern method i.e., supercritical fluid extraction method (SFE), pressurized liquid extraction (PLE) etc. [42]. Modern methods also include radiation technology based extraction such as microwave radiation, gamma radiation, plasma radiation, UV radiation, and Ultrasonic radiation. These methods are now being used for extraction, dyeing and as well as for pretreatment of fabric [43]. Modern methods are considered to be superior to the conventional methods due to their high efficiency, high color yield, and goo mass transfer kinetics, less consumption of energy, water, time, and cost. These methods are discussed below in detail:

SFE method is the simple, water free, and clean process that uses SFE having properties which are similar to water. The method involves the dissolution of the dye material with SFE materials which is then applied to fabric. SFE has the ability to penetrate the fabric easily and causes swelling in fabric which absorbs dye molecule readily. The remaining dye and

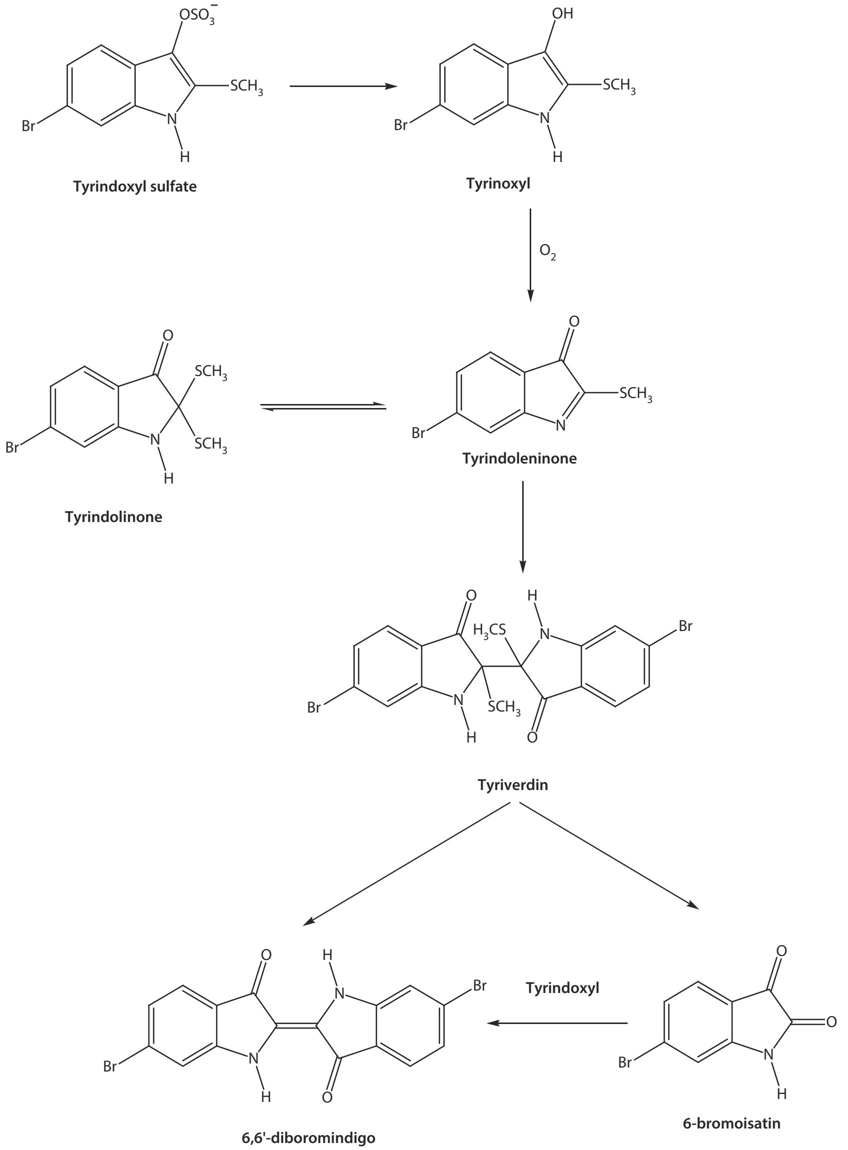

Figure 4.13 Mechanism of action to produce 6,6’-dibromoindigo.

supercritical fluid is recovered after dyeing process to reuse again thus save water, energy, and dye material which in turn helps to increase color strength. Borges *et al.* [44] extracted Carminic acid from cochineal insect using supercritical fluid method and PLE method and compared the result

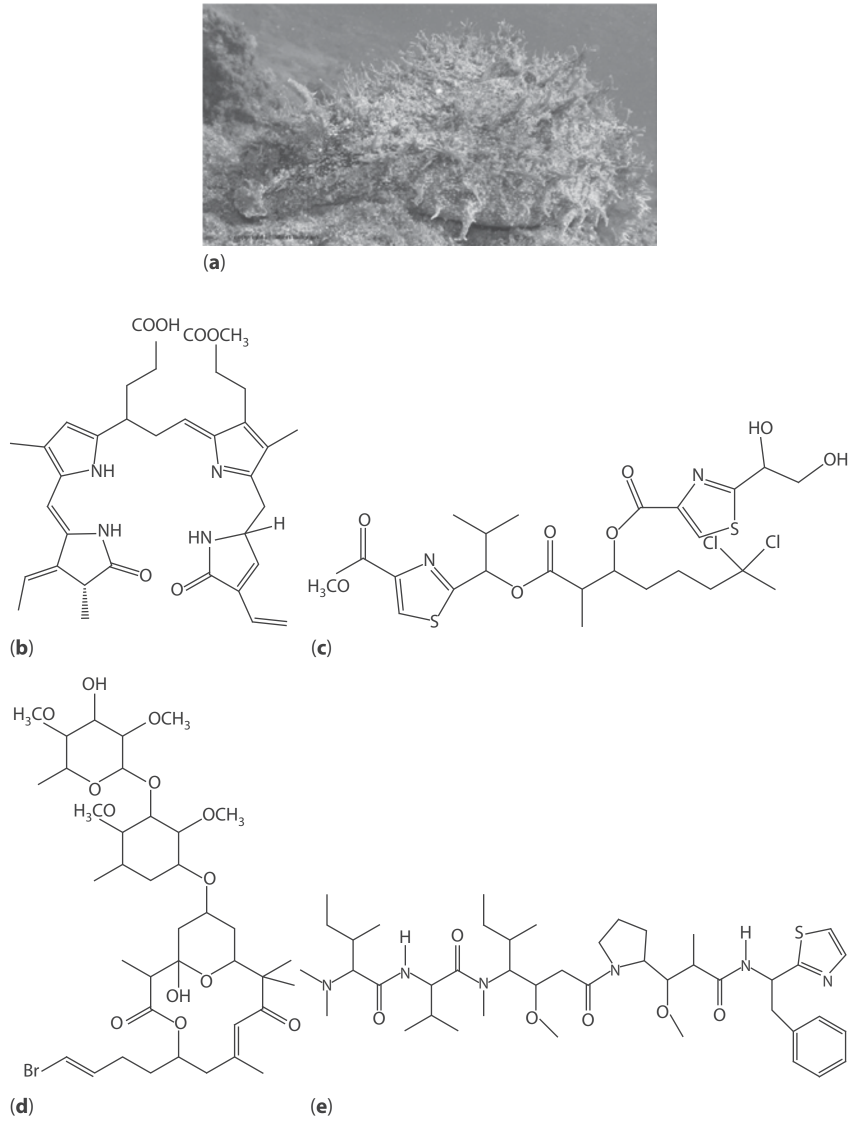

Figure 4.14 (a) Dolabella auricularia (b) Aplysioviolin (c) Dolabellin (d) Auriside A (e) Dolastatin 10.

obtained from conventional method. They found that modern methods have provided more yield as compared to the traditional one. Similarly, Rudd and Benkendorff [45] extracted bio-active component (brominated indole) which is precursor of Tyrian purple dye from *Dicathaisorbita* using SFE method.

UV radiation which is electromagnetic radiation having wavelength ranges from 200–400nm. It has high energy that is enough to modify the surface of fiber by forming free radicals and improve dye ability. UV radiation produces more functional groups on surface of the fabric that adds value in coloration at low temperature [46]. Thus, it is a source of saving energy, time, cost, and improve dye ability and color strength [47]. This type of radiation has been successfully applied in wool and cotton dyeing.

Plasma is the mixture of ions, electrons, free radicals that are produced at high temperature and pressure. It is safe, clean, and water free source that has high activation energy with potential to remove the hydrophobic layer over the surface of fabric and adding different functional group to surface i.e., carboxylate to the cellulosic fiber and Sulphonated group to the proteneous fabric [48]. Upon treatment, the hydrophilic functional groups make the dye molecule more capable to attach on fabric by making firm bonding and increase the dye ability at fabric surface. Plasma radiation not only helps to increase the dye uptake ability of fabric but also reduces the need of mordant used and improves the antimicrobial activity of dyed fabric. Ahmed *et al.* [49] used air plasma in combination with US treatment to modify the surface of polyester blended cotton fabric and dyed with cochineal dye. Both radiations enhanced the color fastness properties, wettability, and printability of dyed fabric. Boonla and Saikrasun [50] modified the surface of silk fabric with oxygen and argon plasma and dyed with lac dye. They found that after treatment with plasma radiation, absorption capacity of dye molecule on fabric has been dramatically increased.

Gamma radiation has high frequency (above 10^{19} Hz) and energy (<100 keV). Gamma radiation increases the dye uptake, color strength, and reduces the dyeing concentration by turning the fabric surface. Thus it is found as a source of greener technology for extraction and dyeing. Cosentino *et al.* [51] extracted colorant from cochineal, annatto, and turmeric and examined the effect of gamma radiation on their color stability that has been used as food additive. They found that gamma radiation not affected the color intensity of cochineal dye.

Ultrasound radiation has frequency, which is greater than human audible range. This technique produces small bubbles in the liquid through cavitation which increase the activation energy of dye molecule and makes it possible to penetrate the fabric via forming firm bonding [52]. Thus it increases the rate of dyeing by lowering the temperature and save energy. Kamel *et al.* dyed wool fabric with lac dye using ultrasonic radiation and found that radiation has increased the absorption of dye on fabric [53]. Similarly, Kamel *et al.* [54] also found the same result on dyeing cationised cotton fabric with lac dye using ultrasonic radiation. Kamel *et al.* [55, 56] cationised cotton fabric with Solfix E and Quat 188 and dyed with cochineal dye. The dye was extracted using conventional and ultrasonic radiation. Their studies showed that the US treatment has improved the color characteristics.

Microwave energy is also a form of electromagnetic radiation that has important role in extraction and dyeing process of natural colorant. It has numerous advantages over conventional heating, as conventional heating is the surface heating while microwave radiation is volume heating that penetrates the whole material and provides energy constantly. It ruptures the cell wall by rapid heating and increases the transfer of dyeing material to the solvent [57].

Since all these techniques are the greatest source of energy and heat which are used to produce the desired maximum color strength and shade to maintain the sustainability.

4.6 Application of Animal Based Dyes

Animal based dyes has been used to color in various fields such as textile dyeing of fabric and non-textile material i.e., pharmaceutical, food, dye sensitized solar cells, electronic products, cosmetics etc.

4.6.1 Textile

Textile industry is one of the big industries in the global community and the use of synthetic dyes in textile sector is much greater than any other sector [58]. However, it has been known for last decades that the use of synthetic dyes in textile can cause allergic reactions, toxicity, and carcinogenic to human [59]. For these reasons, the researchers, traders, and industrialists urge to use eco-friendly labeled products that not only protect them from some carcinogenic reactions but also give them health benefits too. The animal based natural colorants are also making their worth in different fields particularly in textiles. Lac, Cochineal, and Kermes are mostly used for coloration of fabrics [60]. Various researchers are using insects based colorants to color the natural and synthetic textiles. Chairat *et al.* [61, 62] dyed silk fabric with lac dye and observed their absorption kinetics and rate of dye material on fabric. Liu *et al.* [63] examined the functional properties of chitosan fabric dyed with lac dye and found remarkable results in terms of antioxidant and de-odorizing properties. Similar results have been obtained from studies of Li and Tang [64] where chitosan fiber was first crosslinked with azridine to increase the absorption of dye material and then dyed with lac dye, which increased the antioxidant activity of lac dyed chitosan fabric.

Zhang *et al.* [65] dyed wool fabric with lac dye in acidic condition in the presence of mordant and found color depth and good fastness properties. Yaqub *et al.* [66] also extracted laccaic acid from lac insect and applied on silk fabric in the presence of mordant and found excellent coloring characteristics. Mongkholrattanasit *et al.* [67] dyed silk fabric with lac dye using padding technique in the presence of different mordant and found increase in the fastness properties to acceptable level. Teli *et al.* [68] dyed organic cotton fabric with lac dye using metal mordant (alum) and bio-mordant (harda) and evaluated their fastness properties.

Janhom *et al.* [69] investigated the effect of NaCl and Polyethyleneimine (PEI) on absorption and desorption of lac dye on cotton fabric. They found that presence of NaCl and PEI increased the absorption of lac dye on fabric. Janhom *et al.* [70] also pretreated cotton with PEI and bovine serum albumin that ultimately increased the absorption of lac dye molecule onto cationized fabric.

Shams Nateri *et al.* [71] dyed polyamide fabric with cochineal dye in the presence of iron sulphate and alum mordant using different mordanting method and evaluated their fastness properties to light, washing, and heat. Valipour *et al.* [72] pre mordanted wool fabric with different mordant and dyed with cochineal dye at different pH. They not only found good shades but also rated good color fastness characteristics. Velmurugan *et al.* [73] dyed cotton fabric with cochineal and *Monascuspurpureas* (a fungus specie) and compared their color stability on dyed fabric. Their comparative studies showed that Cochineal gave darker shades than that of fungal specie upon mordanting. Merparvar *et al.* [74] treated wool fabric with chitosan-polypropylene imine dendrimer hybrid to replace toxic metal mordants and dyed the wool fabric with cochineal fabric. They found that bio-mordant has greatly enhanced the dyeing properties of wool fabric due to increase in the free amino group which is dye sorbing site that helped to increase the absorption of dye molecule. Gawish *et al.* [75] indicated that simultaneous dyeing of wool, silk with weld and cochineal dye. They investigated an increase in the functional properties dyed natural fabrics. Ammayappan and Shakyawar [76] dyed wool carpet with cochineal dye in the presence of different metal mordant which demonstrated that mordant has increased the color fastness characteristics to great extent. Nazari *et al.* [77] treated wool with enzyme protease to increase its absorption efficiency and dyed with madder and cochineal dye powder. They found that enzyme pre-treatment has remarkable effect on dyeing properties of wool fabric and increased the Color strength (K/S) and fastness properties of dyed fabric. An alternative method has been adopted by Han *et al.* [78] where cochineal colorant is extracted using protease enzyme and used this extracted colorant to dye non-treated wool fabric. The result indicated that protease helps to reduce the temperature of extraction process, water consumption, and time to great extent and gave higher yield that also gave high color strength on dyed fabric. Sea snail has been used to dye natural fibers i.e., silk, cotton and, wool, which gave remarkable purple hue [79]. Hence over all the role of animal based natural colorants in textiles has been welcomed wide spread.

4.6.2 Dye Sensitized Solar Cells

Solar cells are very efficiently converting the light energy directly from the sun into the electrical energy. For such reason, many heavy metals such as Rh-complex have been used to transfer electron to the conduction band of TiO_2 [80]. Although these metals are fast enough to get desired result, however, there are some drawback using metal complex owing to their cost, toxicity toward human and environment [81]. Later on this moiety was replaced by using synthetic organic dyes that work similar but more efficiently than the former. The urge to use natural eco-friendly products have compelled researchers to move toward the green products in electronics [82]. Natural dyes contain anthocyanin, anthraquinone, carotenoids, chlorophyll, flavonoids and such other group that has been used in dye sensitized solar cells [83]. Many researchers have used natural colorant obtained from insects, micro-organisms, and plant for dye-sensitized solar cells and found remarkable results [84].

Sang-aroon *et al.* [85] obtained natural dye from cochineal and lac dye and found remarkable result in fabrication of solar cells. They found that lac dye due to presence of OH and COOH group can be bi-coordinated and double bi-coordinated with TiO_2 resulted in efficient transfer of electron from dye to TiO_2 band (Figure 4.15 a & b).

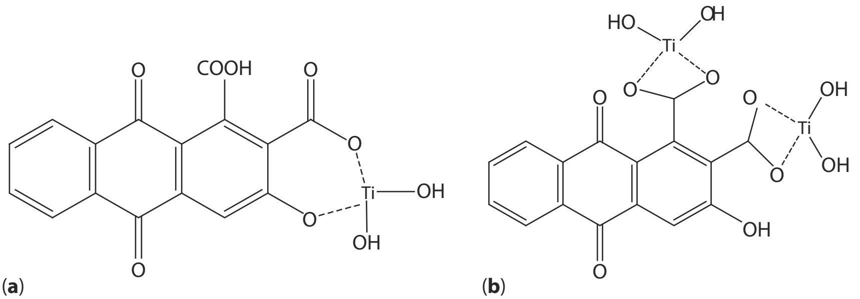

Figure 4.15 (a) Bi-coordination of Lac dye with TiO_2 (b) Double bi-coordination of Lac dye with TiO_2.

Similarly, Park *et al.* [86] obtained Carminic acid from cochineal insects and used the dye for conversion of solar energy into electrical energy. They found that due to presence of OH group and COOH group in Carminic acid it forms strong chelation with TiO_2 that helped to increase the conversion of light energy into electrical energy. Glowacki *et al.* [87] and Robb *et al.*[88] used tyrian purple from marine mollusks and applied them for the synthesis of organic electronic products (Figure 4.16).

4.6.3 Food

Food industries not only provide the material that is beneficial for health but also concern with the consumer interest to use. Coloring food product gives a great pleasure and joy to foodies but also enhances the appetite. However, synthetic food colors increase the toxicity of the food product especially the usage of sodium nitrite that makes difficult and toxic to consume. Thus there is a great need to apply natural food color instead of artificial flavor to minimize the environmental toxicity. Many reports have revealed that the application of natural color obtained from plants, animal sources as food additive has been welcomed [89]. Singh *et al.,* [90] used lac dye as food colorant in meat product that not only gives brilliant red color but also increased antimicrobial and antifungal activity to some extent. Due to non-toxic effects of lac dye, it can be used in different food product such as fruit beverages, vegetable juice, fruit-flavored, jam and chocolate product also. Carmine which is calcium aluminium lake of Carminic acid is insoluble in water but it can be used in meat, making sausage, bakery products, topping, dairy products, sweet etc. [91, 92]. It has also been used for the preparation of canned fruit such as cherries, jams, pulp etc. [93]. Hence natural colorants from animal source have also a wide application in food industries.

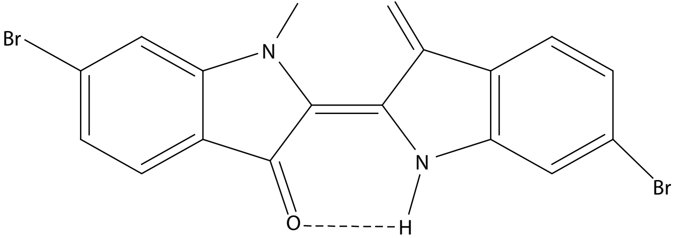

Figure 4.16 Hydrogen bonding in tyrian purple.

4.6.4 Pharmaceuticals

With the passage of time, numerous drugs are being introduced all over the world to minimize the mortality caused by severe and chronic diseases such as cancer, cardiovascular diseases, asthma, kidney failure etc. Natural dyes which are obtained from animal sources also have an important role in pharmaceutical industry and drug preparation [94]. In pharmaceutical industry, carmine has been used to color the tablet, capsules, cough syrup, and ointments [95]. These colorants also have found their use in making medicine for the treatment of coronary artery diseases, cancer chemo-preventive activity, lipid metabolism, Alzheimer's disease etc. [96, 97]. Lac dye can be used to treat cancer cells in human body and the studies of Shamim *et al.* [98] found the same result in which mixture of laccaic acid A, B, C, D, and E has been subjected to human malignant cell and found that lac dye was efficient to stop the proliferation of leukemia cells thus act as anticancer agent. Dosio *et al.* [99] extracted bio-active component from *Dollabelaauricularia* that has potential to treat cancer. Similarly, Senter and Sievers, extracted dolastatin 10 from *Dollabelaauricularia* and found that has been used as antimitotic drug [100]. Bagratuni *et al.* and Zhao *et al.* [101, 102] found that 6-bromoindirubin-3'oxime (BIO) obtained from marine mollusks is a potent kinase inhibitor and can be used as anticancer, for the treatment of intracerebral hemorrhage and also as neuroprotective. Thus, animal based colorants have a great potential in pharmaceutical industry due to their good functional properties.

4.6.5 Nano-Technological Image

Nanoparticles are those moieties that have very small particle size ranging from 1–100 nm. They have gained the intention due to their various beneficial properties such as strong optical absorption in visible region, having optical, chemical, electronic, and photo-chemical properties. These particles also contain antimicrobial, antitoxic, and therapeutic value which make their effective use in medical field. There are many ways to synthesize nanoparticles of noble metal (i.e., AgNPs, AuNPs, ZnONPs, PtNPs etc.) by using several reducing agents such as hydrazine, starch, formaldehyde and borohydride, liquid ammonia etc. [103]. However, the recent studies urged to synthesize such nanoparticles using green synthesis route that have good reducing and capping characteristics [104]. Goudarzi *et al.* [105] used cochineal and pomegranate extract for the synthesis of silver nanoparticles and found well dispersed and narrow size distribution of nanoparticles. In the same way, Goudarzi *et al.* [106] also found remarkable photo-catalytic efficiency of silver-alumina Nano-composite which is synthesized by using cochineal powder. Kumar *et al.* [107] obtained coloring component (Carminic acid) from cochineal and used it for the green fabrication of silver nanoparticles. Mousavi-Kamazani *et al.* [108] prepared copper sulphide nanostructure using carminic acid-Cu complex and found it very effective in increasing the efficiency of dye-sensitized solar cells. Pattanayak *et al.*[109] obtained laccaic acid from lac and applied it for the synthesis of gold nanoparticles. These nanoparticles have showed antimicrobial and antitoxic activity that make them able for their potential application in therapeutic field. In nanotechnology, the natural colorants of animal origin apart from other sources are making their place due to their sustainable and eco-friendly nature.

4.7 Future Prospects

It is well known that natural colorants from natural sources are more eco-friendly than their synthetic counterpart. Due to global demand for eco-labeled products, the need for replacing synthetic dyes with natural dyes has been increased [110]. Many researchers have found and proved their value at laboratory level as well as industrial scale. However, some drawbacks regarding natural colorant have made them impossible to introduce such colorant at commercial level. These drawbacks include poor fastness properties, low color yield, need bulky amount of such sources to obtain brighter color and to fulfill the demand of whole world like preparative dyes [111]. These problems should be resolved to make sure their usage at commercial level. Careful investigation about natural dyes, to find their all possible sources, improvement in extraction as well as application methodology should be evaluated. To overcome such problem, scientists are in need of finding and exploring other species of insects to employ in various fields using modern extraction methods [112]. The amount of natural dye sources can also be increased by introducing bio-technology i.e., gene manipulating technique, bio-technological tool etc. Similarly, the extraction process should be done with advance technology that not only minimize the colorant requirement but also reduce the time, energy and chemical consumption with an improved color yield and fastness properties [113]. The use of non-toxic chemical mordant or eco-friendly bio-mordant that can form chelation, helps in adding more value in coloration and their functional characteristics [114]. All of these points should be considered by scientists, researchers or those who have a great interest in animal based natural dyes and to make the system more sustainable at global mart.

4.8 Conclusion

The resurge of natural dyes using various sources, particularly of animal based, has been welcomed by many traders, where the researchers are trying to find various means for maximum extraction of colorant to make their possible use in fashion, textiles, electronics, food as well as in ayurvedic system. But to adopt these methodologies on large scale is a big challenge because to get a large amount of dye, thousands of animals are needed. However, on account of sustainability as well as cost, time, and energy effectiveness, various modern methods are being applied to implement these colors in various walks of life. To revive the traditional culture and to harmonize the lives with natural colors, especially the bright red colors from animal sources such as lac, kermes, cochineal, there is still a place to adopt big strategies to get good results with utilization of minimum sources.

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References

1. Gurses, A., Acikyildiz, M., Gunes, K., Gurses, M.S., Historical development of colorants. *Dyes Pigm.,* 1, 2016.
2. Whitworth, I., Koren, Z.C., Orchil and Tyrian purple: Two centuries of bedfords from leeds. *Ambix.,* 63, 244, 2016.
3. Lomax, J.F., Lomax, S.Q., Moore, T.J., Synthesis of historical azo pigment: The challenge and opportunity of the nearly forgotten. *MRS Advances.,* 1, 2017.

4. Li, D., Sun, G., Coloration of textiles with self-dispersible carbon black nanoparticles. *Dyes Pigm.,* 72, 144, 2007.
5. Baldin, J.C., Michelin, E.C., Polizer, Y.J., Rodrigues, I., de Godoy, S.H.S., Fregonesi, R.P., Fernandes, A.M., Microencapsulated jabuticaba (Myrciariacauliflora) extract added to fresh sausage as natural dye with antioxidant and antimicrobial activity. *Meat Sci.,* 118, 15, 2016.
6. Ren, Y., Gong, J., Fu, R., Li, Z., Li, Q., Zhang, J., Cheng, X., Dyeing and antibacterial properties of cotton dyed with prodigiosins nanomicelles produced by microbial fermentation. *Dyes Pigm.*, *138*, 147, 2017.
7. Shahid, M., Ahmad, A., Yusuf, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Dyeing, fastness and antimicrobial properties of woolen yarns dyed with gallnut (*QuercusinfectoriaOliv.*) extract. *Dyes Pigm.,* 95, 53, 2012.
8. Gawish, S.M., Mashaly, H.M., Helmy, H.M., Ramadan, A.M., Farouk, R., Effect of mordant on UV protection and antimicrobial activity of cotton, wool, silk and nylon fabrics dyed with some natural dyes. *J. Nanomed. Nanotechnol.*, 8, 2, 2017.
9. Eli, D., Ahmad, M., Maxwell, I., Ezra, D., Francis, A., Sarki, S., Dye sensitized solar cells using natural dyes extracted from Roselle (Hibiscus Sabdariffa) flowers and Pawpaw (Carica Papaya) leaves as sensitizers. *J. Energ. Nat. Res.*, 5, 11, 2016.
10. Yusuf, M., Shabbir, M., Mohammad, F., Natural colorants: historical, processing and sustainable prospects. *Nat. prod. bioprospect.*, 7, 123, 2017.
11. Singh, P., Borthakur, A., Singh, R., Awasthi, S., Pal, D.B., Srivastava, P., Tiwari, D., Mishra, P. K., Utilization of temple floral waste for extraction of valuable products: A close loop approach towards environmental sustainability and waste management. *Pollut.*, 3, 39, 2017.
12. Chung, K.T., Azo dyes and human health: A review. *J. Environ. Sci. Health, Part C.*, 34, 233, 2016.
13. Yusuf, M., Shahid, M., Khan, M.I., Khan, S.A., Khan, M.A., Mohammad, F., Dyeing studies with henna and madder: a research on effect of tin (II) chloride mordant. *J. Saudi. Chem. Soc.*, 19, 64, 2015.
14. Fuad, M., Amri, F., Renewable energy source using natural dye molecular for dye-sensitized solar cells extracted from dragon fruit and pomegranate/ *FaridAmriMdFuad* (Doctoral dissertation, Universiti Teknologi MARA). 2016
15. Khan, S.A., Ahmad, A., Khan, M.I., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., Antimicrobial activity of wool yarn dyed with *Rheum emodi* L. (Indian Rhubarb). *Dyes Pigm.,* 95, 206, 2012.
16. Colak, M., Determination of antifungal and antibacterial activities of natural dye of pomegranate skin (punicagranatum l.) Implemented on wooden materials. *Wood Res.*, 61, 709, 2016.
17. Felaza, E., Priadi, C.R. (2016, January). Implementation of Cleaner Production in a Natural Dye Batik Industry SME: A way to Enhance Biodegradability of Batik Wastewater, in *MATEC Web of Conferences* (Vol. 62). EDP Sciences.

18. Khan, M.Z.H., Al-Mamun, M.R., Al-Amin, M., Moniruzzaman, M., Hasan, M.R,. Dye-sensitized solar cell using used semiconductor glass and natural dye: towards alternative energy challenge. *Int. J. Renew. Energ. Res.*, 5, 38, 2016.
19. Serrano, A., Sousa, M.M., Hallett, J., Lopes, J.A., Oliveira, M.C., Analysis of natural red dyes (cochineal) in textiles of historical importance using HPLC and multivariate data analysis. *Anal. Bioanal. Chem.*, *401*, 735, 2011.
20. Serrano, A., Sousa, M., Hallett, J., Simmonds, M.S., Nesbitt, M., Lopes, J.A., Identification of Dactylopius cochineal species with high-performance liquid chromatography and multivariate data analysis. *Anal.*, 138, 6081, 2013.
21. Maynez-Rojas, M.A., Casanova-González, E., Ruvalcaba-Sil, J.L., Identification of natural red and purple dyes on textiles by Fiber-optics Reflectance Spectroscopy. *Spectrochim. Acta. Mol. Biomol. Spectrosc.*, 178, 239, 2017.
22. Lech, K., Jarosz, M., Identification of Polish cochineal (Porphyrophorapolonica L.) in historical textiles by high-performance liquid chromatography coupled with spectrophotometric and tandem mass spectrometric detection. *Anal. Bioanal. Chem.*, 408, 3349, 2016.
23. Deveoglu, O., Torgan, E., Karadag, R., Characterization of colouring matters by HPLC-DAD and colour measurements, preparation of lake pigments with Ararat kermes (Porphyrophorahameli Brand). *Jordan J. Chem.*, 5, 307, 2010.
24. Baraldi, P., Keheyan, Y., Characterization of pigments of some armenian illuminated manuscripts by ramanmicroscopy. *Electron J. Natl. Sci.*, 27, 8, 2016.
25. Mantzouris, D., Karapanagiotis, I., Karydis, C., Identification of cochineal and other dyes in byzantine textiles of the 14th century from mount athos. *Mediterranean Archaeology and Archaeometry*, 16, 159, 2016.
26. Al-Ghadeer, H.A., Acute ocular complications from self-administered topical Kermes. *Middle East Afr. J. Ophthalmol.*, 17, 382, 2010.
27. Domenech-Carbo, A., Domenech-Carbo, M.T., Calisti, M., Maiolo, V., Identification of naphthoquinonic and anthraquinonic dyes via sequential potential steps applied to the voltammetry of microparticles methodology. *J. Sol. State Electrochem.*, 14, 465, 2010.
28. Karadag, R., Yurdun, T., Dolen, E., Identification of natural red dyes in 15–17th centuries ottoman silk textiles (kaftans, brocades, velvets and skullcaps) by HPLC with diode array detection. *Asian J. Chem.*, 22, 7043, 2010.
29. Lluveras-Tenorio, A., Parlanti, F., Degano, I., Lorenzetti, G., Demosthenous, D., Colombini, M.P., Rasmussen, K.L., Spectroscopic and mass spectrometric approach to define the Cyprus Orthodox icon tradition-The first known occurrence of Indian lac in Greece/Europe. *Microchem. J.*, 131, 112, 2017.
30. Sharma, K.K., Lac insects and host plants. *Int. J. Indust. Entomol.,* 157, 2017.
31. Ramani, R., Pal, G., Lac marketing and crop economics. *Beneficial Insect Farming-Benefits and Livelihood Generation*, 133, 2016.
32. Zhang, E., Fang, G.G., Zheng, H., Guo, Y.H., Li, K., Study on the antioxidant of lac dye. *Appl. Mech. Mater.*, 140, 451, 2012.

33. CookSey, C., Tyrian purple: the first four thousand years. *Sciprog.*, 96, 171, 2013.
34. Mantzouris, D., Karapanagiotis, I., Identification of indirubin and monobromoindirubins in Murex brandaris. *Dyes Pigm.*, 104, 194, 2014.
35. Oliver, A.V., An ancient fishery of banded dye-murex (Hexaplextrunculus): Zooarchaeological evidence from the Roman city of Pollentia (Mallorca, Western Mediterranean). *J. Archaeol. Sci.*, 54, 1, 2015.
36. Giacoletti, A., Rinaldi, A., Mercurio, M., Mirto, S., Sara, G., Local consumers are the first line to control biological invasions: A case of study with the whelk Stramonitahaemastoma (Gastropoda: Muricidae). *Hygie.*, 772, 117, 2016.
37. Green, Y., Kahn, P., The mystery, meaning and disappearance of the Tekhelet. *Jewish Bible Quarterly*, 39, 108, 2011.
38. Sukenik, N., Iluz, D., Amar, Z., Varvak, A., Bar, S., New evidence of the Purple-Dye Industry at Tel Shiqmona, Israel. *Archaeometr.*, 1, 2017.
39. Vasileiadou, A., Karapanagiotis, I., Zotou, A., Determination of Tyrian purple by high performance liquid chromatography with diode array detection. *J. Chromatogr. A*, 1448, 67, 2016.
40. Valles-Regino, R., Mouatt, P., Rudd, D., Yee, L.H., Benkendorff, K., Extraction and quantification of bioactive TyrianPurple precursors: A comparative and validation study from the hypobranchial gland of a Muricid Dicathaisorbita. *Mol.*, 21, 1672, 2016.
41. Yamada, K., Ojika, M., Kigoshi, H., Suenaga, K., Cytotoxic substances from two species of Japanese sea hares: Chemistry and bioactivity. *Proc. Jpn. Acad. Ser. B.*, 86, 176, 2010.
42. Mirjalili, M., Nazarpoor, K., Karimi, L., Eco-friendly dyeing of wool using natural dye from weld as co-partner with synthetic dye. *J. Clean. Prod.*, 19, 1045, 2011.
43. Sinha, K., Saha, P.D., Datta, S., Response surface optimization and artificial neural network modeling of microwave assisted natural dye extraction from pomegranate rind. *Indus. Crop. prod.*, 37, 408, 2012.
44. Borges, M.E., Tejera, R.L., Díaz, L., Esparza, P., Ibanez, E., Natural dyes extraction from cochineal (Dactylopiuscoccus). New extraction methods. *Food chem.*, 132, 1855, 2012.
45. Rudd, D., Benkendorff, K., Supercritical CO2 extraction of bioactive Tyrian purple precursors from the hypobranchial gland of a marine gastropod. *J. Supercrit. Fluids.*, 94, 1, 2014.
46. Cristea, D., Vilarem, G., Improving light fastness of natural dyes on cotton yarn. *Dyes Pigm.*, 70, 238, 2006.
47. Rehman, F., Adeel, S., Hanif, R., Muneer, M., Zia, K.M., Zuber, M., Khosa, M.K., Modulation of marigold based lutein dye and its dyeing behaviour using UV Radiation. *J. Nat. Fibers.*, 14, 63, 2017.
48. Dave, H., Ledwani, L., Nema, S.K., Surface modification by atmospheric pressure air plasma treatment to improve dyeing with natural dyes: An

environment friendly approach for leather processing. *Plasma Chem. Plasma P.*, 36, 599, 2016.

49. Ahmed, H.M., Ahmed, K.A., Mashaly, H.M., El-Halwagy, A.A., Treatment of cotton fabric with dielectric barrier discharge (DBD) plasma and printing with cochineal natural dye. *Ind. J. Sci. Technol.*, 10, 1, 2017.
50. Boonla, K., Saikrasun, S., Influence of silk surface modification via plasma treatments on adsorption kinetics of lac dyeing on silk. *Text Res. J.*, 83, 288, 2013.
51. Cosentino, H.M., Takinami, P.Y., del Mastro, N.L., Comparison of the ionizing radiation effects on cochineal, annatto and turmeric natural dyes. *Radiat. Phy. Chem.,* 124, 208, 2016.
52. Baaka, N., Haddar, W., Ben Ticha, M., Amorim, M.T.P., M'Henni, M.F., Sustainability issues of ultrasonic wool dyeing with grape pomacecolourant. *Nat. Prod. Res.*, 1, 2017.
53. Kamel, M.M., El-Shishtawy, R.M., Yussef, B.M., Mashaly, H., Ultrasonic assisted dyeing: III. Dyeing of wool with lac as a natural dye. *Dyes Pigm.*, 65, 103, 2005.
54. Kamel, M.M., El-Shishtawy, R.M., Youssef, B.M., Mashaly, H., Ultrasonic assisted dyeing. IV. Dyeing of cationised cotton with lac natural dye. *Dyes Pigm.*, 73, 279.
55. Kamel, M.M., El Zawahry, M.M., Ahmed, N.S.E., Abdelghaffar, F., Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 1: Cationization of cotton using Solfix E. *Ultrason. Sonochem.*, 16, 243, 2009.
56. Kamel, M.M., El Zawahry, M.M., Ahmed, N.S.E., Abdelghaffar, F., Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 2: Cationization of cotton using Quat 188. *Indus. Crop Prod.*, 34, 1410, 2011.
57. Adeel, S., Azeem, M., Kamal, S., Rehman, F., Ghaffar, A., Habib, N.,Shabir, A.U., Microwave assisted investigation of golden duranta (durantarepnes l.) leaves as a natural colorant for surface oxidised cellulosic dye. *Oxidcommun.*, 39, 3507, 2016.
58. Arora, J., Agarwal, P., Gupta, G., Rainbow of natural dyes on textiles using plants extracts: Sustainable and eco-friendly processes. *Green Sustain. Chem.*, 7, 35, 2017.
59. Ford, L., Henderson, R.L., Rayner, C.M., Blackburn, R.S., Mild extraction methods using aqueous glucose solution for the analysis of natural dyes in textile artefacts dyed with Dyer's madder (Rubiatinctorum L.). *J. Chromatogr. A.*, 1487, 36, 2017.
60. Swamy, V.N., Gowda, K.N., Sudhakar, R., Dyeing of silk using Madhucalongifolia as natural dye source. *Ind. J. Text Fibre Res.*, 40, 419, 2016.
61. Chairat, M., Rattanaphani, S., Bremner, J.B., Rattanaphanti, V., Adsorption kinetic study of lac dyeing on cotton. *Dyes Pigm.*, 70, 1, 2006.
62. Chairat, M., Rattanaphani, S., Bremner, J. B., Rattanaphani, V., Adsorption kinetic study of lac dyeing on cotton. *Dyes Pigm.*, 76, 435, 2008.

63. Liu, L., Zhang, J., Tang, R.C., Adsorption and functional properties of natural lac dye on chitosan fiber. *React. Funct. Polym.*, 73, 1559, 2013.
64. Li, X. Q., Tang, R.C., Crosslinked and dyed chitosan fiber presenting enhanced acid resistance and bioactivities. *Polym.*, 8, 119, 2016.
65. Zhang, J., Chen, Y.J., Xu, M.X., Dyeing properties of gardenia yellow, lac dye and sodium copper chlorophyll for wool. *Adv. Mater. Res.*, 1048, 85, 2014
66. Yaqub, A., Bhatti, R.A., Arif, M.F., Sheikh, I.A., Haq, H.U., Isolation and its purification of laccaic acid dye from stick lac and study of its (Colour Fastness) properties and reflactance on silk fabric dyed with heavy metal mordants. *Tech. J.*, 19, 6, 2014.
67. Mongkholrattanasit, R., Saiwan, C., Rungruangkitkrai, N., Punrattanasin, N., Sriharuksa, K., Klaichoi, C., Nakpathom, M., Ecological dyeing of silk fabric with lac dye by using padding techniques. *J. The Text. Inst.*, 106, 1106, 2015.
68. Teli, M.D., Valiaa, S.P., Kolambkara, D., Triyadib, R., Kambleb, M. Dyeing of organic cotton fabric with lac dye using different mordants. *J. Text. Associat.,*337, 2014.
69. Janhom, S., Griffiths, P., Watanesk, R., Watanesk, S., Enhancement of lac dye adsorption on cotton fibres by poly (ethyleneimine). *Dyes Pigm.,* 63, 231, 2004.
70. Jonhom, S., Watanesk, R., Watanesk, S., Griffiths, P., Arguero, O.A., Naksata, W., Comparativity study of lac dye adsorption on cotton fibre surface modified by synthetic and anatural polymers. *Dyes Pigm.,* 71, 188, 2006.
71. Shams Nateri, A., Shams Nateri, A., Dehnavi, E., Dehnavi, E., Hajipour, A., Hajipour, A., Ekrami, E., Dyeing of polyamide fibre with cochineal natural dye. *Pigm. Resin. Technol.*, 45, 252, 2016.
72. Valipour, P., Ekrami, E., Shams-Neteri, A., Colorimetric properties of wool dyed with cochineal: Effect of dye bath pH. *Prog. Color Colorants Coat.,* 7, 129, 2014.
73. Velmurugan, P., Algumuthu, T., Lakshmanaperumalsamy, P., Park, J., Oh, B., The use of cochineal and *monascuspurpureus* as dyes for cotton fabric. *Soc. Dyers Color, Color Technol.*, 129, 246, 2013.
74. Mehrparvar, L., Safapour, S., Sadeghi-Kiakhani, M., Gharanjig, K.,. Chitosan polypropylene imine dendrimer hybrid: A new ecological biomordant for cochineal dyeing of wool. *Environ. Chem. Lett.,*14, 533, 2016.
75. Gawish, S.M., Farouk, R., Ramadan, A.M., Mashaly, H.M., Helmy, H.M., Ecofriendly multifunctional properties of cochineal and weld for simultaneous dyeing and finishing of proteinic fabric. Int. *J. Eng. Technol.*, 8, 2246, 2016.
76. Ammayappan, L., Shakyawar, D.B B., Dyeing of carpet woolen yarn using natural dye from cochineal. *J. Nat. Fiber.,* 13, 42, 2016.
77. Nazari, A., Montazer, M., Afzali, F., Sheibani, A., Optimization of proteases pretreatment on natural dyeing of wool using response surface methodology. *Clean Technol. Environ. Policy.,* 16, 1081, 2014.

78. Han, X., Liu, S.Q., Zhang, D.W., Liu, W.W., Cui, Y.Z. Research on dyeing property of wool fabric based on cochineal carmine extracted by protease. *Wool Text J.,* 5, 016, 2012.
79. Doherty, B., Nowik, W., Miliani, C., Clementi, C., Tyrian purple in archaeological textiles: DMF extraction and recrystallization for the Raman identification of precursors and derivatives. *J. Raman Spectrosc.*, 48, 744, 2017.
80. Al-Alwani, M.A., Mohamad, A.B., Kadhum, A.A.H., Ludin, N.A., Safie, N.E., Razali, M.Z., Sopian, K,. Natural dye extracted from Pandannus amaryllifolius leaves as sensitizer in fabrication of dye-sensitized solar cells. *Int. J. Electrochem. Sci*, 12, 747, 2017.
81. Gong, J., Sumathy, K., Qiao, Q., Zhou, Z., Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renew. Sustain. Energ. Rev.*, 68, 234, 2017.
82. Lim, A., Ekanayake, P., Lim, L.B. L., Bandara, J.S., Co-dominant effect of selected natural dye sensitizers in DSSC performance. *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, 167, 26, 2016.
83. Teoli, F., Lucioli, S., Nota, P., Frattarelli, A., Matteocci, F., Di Carlo, A., Forni, C., Role of pH and pigment concentration for natural dye-sensitized solar cells treated with anthocyanin extracts of common fruits. *J. Photochem. Photobiol A: Chem*, 316, 24, 2016.
84. Yoon, S.J., Lim, I., Kim, J.H., Adhikari, S., Lee, W.Y., Lee, J.K., Han, S.H., Deprotonated curcumin as a simple and quick available natural dye for dye sensitized solar cells. *Energ. Source A Recovery, Util, Environ. Effects.*, 38, 183, 2016.
85. Sang-aroon, W., Laopha, S., Chaiamornnugool, P., Tontapha, S., Saekow, S.,Amornkitbamrung, V., DFT and TDDFT study on the electronic structure and photoelectrochemical properties of dyes derived from cochineal and lac insects as photosensitizer for dye-sensitized solar cells. *J. mol. model*, 19, 1407, 2013.
86. Park, K.H., Kim, T.Y., Han, S., Ko, H.S., Lee, S.H., Song, Y.M., Lee, J.W., Light harvesting over a wide range of wavelength using natural dyes of gardenia and cochineal for dye-sensitized solar cells. *Spectrochim. Acta. A Mol. Biomol. Spectrosc.*, 128, 868, 2014.
87. Głowacki, E.D., Voss, G., Leonat, L., Irimia-Vladu, M., Bauer, S., Sariciftci, N.S., Indigo and Tyrian purple–from ancient natural dyes to modern organic semiconductors. *Isr. J. Chem.*, 52, 540, 2012.
88. Robb, M.J., Ku, S.Y., Brunetti, F.G., Hawker, C.J., A renaissance of color: New structures and building blocks for organic electronics. *J. Polym. Sci. A Polym. Chem.,* 51, 1263, 2013.
89. Mala, K.S., Rao, P.P., Prabhavathy, M.B., Satyanarayana, A., Studies on application of annatto (Bixaorellena L.) dye formulations in dairy products. *J. Food Sci. Technol.*, 52, 912, 2015.
90. Singh, R.P., Baboo, B., Prasad, K.M., Evaluation of coloring efficacy of lac dye in comminuted meat product. *J Food Sci Technol.*, 48, 378.

91. Garcıa-Falcón, M.S., Simal-Gandara, J., Determination of food dyes in soft drinks containing natural pigments by liquid chromatography with minimal clean-up. *Food Control*, 16, 293, 2005.
92. De-Vargas, E.F., Jablonski, A., Flores, S.H., Rios, A.D.O., Obtention of natural dyes from industrial blackberry pulp residues (Rubussp). *J. Food Process Preserv*., 41, 12777, 2016.
93. Ordoudi, S.A., Staikidou, C., Kyriakoudi, A., Tsimidou, M.Z., A stepwise approach for the detection of carminic acid in saffron with regard to religious food certification. *Food Chem*., 1, 2017.
94. Devi, S., Rathinamala, J., Jayashree, S., Study on antibacterial activity of natural dye from the bark of Araucaria Columnaris and its application in textile cotton fabrics. *J. Microbiol. Biotechnol. Res*., 4, 32, 2017.
95. Bonfiglio, R.P., Antibacterial oral rinse formulation comprising bioflavonoid polyphenol for preventing coronary artery disease. *Chem. Abstr*., 147, 124648, 2007.
96. Kanekar, H., Khale, A., Coloring agents: current regulatory perspective for coloring agents intended for pharmaceutical and cosmetic use. *Int. J. Pharm. Phytopharm. Res*., 3, 365, 2017.
97. Paulsen, N.E., Johnson, R., Coffee, M., Process for manufacturing chewable dosage forms for drug delivery and products thereof. *Chem. Abstr*., 147, 39161, 2007.
98. Shamim, G., Ranian, S.K., Pandey, D.M., Sharma, K.K., Ramani, R., Lac dye as a potential anti-neoplastic agent. *J. Cancer Res. Ther.,* 12, 1033, 2016.
99. Dosio, F., Brusa, P., Cattel, L., Immunotoxins and anticancer drug conjugate assemblies: the role of the linkage between components. *Toxins*, 3, 848, 2011.
100. Senter, P.D., Sievers, E.L., The discovery and development of brentuximabvedotin for use in relapsed Hodgkin lymphoma and systemic anaplastic large cell lymphoma. *Nat. biotechnol*, 30, 631, 2012.
101. Bagratuni, T., Gaboriad-Kolar, N., Zakopoulou, R., Myrianthopoulos, V., Kastritis, E., Terpos, E., Dimopoulos, M.A., Indirubins: A potential therapeutic target in multiple myeloma. *Cl. Lymph. Myelom. Leuk*., 17, 40, 2017.
102. Zhao, Y., Wei, Z.Z., Zhang, J.Y., Zhang, Y., Won, S., Sun, J., Wei, L., GSK-3β Inhibition induced neuroprotection, regeneration, and functional recovery after intracerebral hemorrhagic stroke. *Cell Transplant*, 26, 395, 2017.
103. Kumar, B., Angulo, Y., Smita, K., Cumbal, L., Debut, A., Capuli cherry-mediated green synthesis of silver nanoparticles under white solar and blue LED light. *Particuol*., 24, 123, 2016.
104. Chang, H., Wu, H.M., Chen, T.L., Huang, K.D., Jwo, C.S., Lo, Y.J., Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea. *J. Alloys Compd*., 495, 606, 2010.
105. Goudarzi, M., Mir, N., Mousavi-Kamazani, M., Bagheri, S., Salavati-Niasari, M., Biosynthesis and characterization of silver nanoparticles prepared from two novel natural precursors by facile thermal decomposition methods. *Sci. Rep*., 6, 1, 2016.

106. Goudarzi, M., Zarghami, Z., Salavati-Niasari, M. Novel and solvent-free cochineal-assisted synthesis of Ag–Al2O3 nanocomposites via solid-state thermal decomposition route: characterization and photocatalytic activity assessment. *J. Mater. Sci. Mater. Electron.*, 27, 9789, 2016.
107. Kumar, B., Smita, K., Angulo, Y., Cumbal, L., Green synthesis of silver nanoparticles using natural dyes of cochineal. *J. Cluster Sci.*, 27, 703, 2016.
108. Mousavi-Kamazani, M., Zarghami, Z., Salavati-Niasari, M., Facile. Novel chemical synthesis, characterization, and formation mechanism of copper sulfide (Cu2S, Cu2S/CuS, CuS) nanostructures for increasing the efficiency of solar cells. *J. Phy. Chem. C.*, *120*, 2096, 2016.
109. Pattanayak, S., Chakraborty, S., Mollick, M.M.R., Roy, I., Basu, S., Rana, D., Chakraborty, M., *In situ* fluorescence of lac dye stabilized gold nanoparticles; DNA binding assay and toxicity study. *New J. Chem.*, 40, 7121, 2016.
110. Adeel, S., S. Rafi, M. Azeem, M. Salman, N. Iqbal, M. Zuber 2018. *Resurgence of natural dyes: Ideas and technologies for textile dyeing*. Studium Press LLC Press USA. 2018.
111. Adeel, S., F. Rehman, S. Rafi, M. Kamran, M. Zuber, I. A. Bhatti, N. Akhtar. *Current innovations in synthetic dyes and dyeing*. Studium Press LLC Press USA. 2018.
112. Adeel, S., S. Rafi, M. Salman, F. Rehman, S. Abrar. 2017. *Potential resurgence of natural dyes in applied fields*. Wiley Scrivener Publishing LLC USA. pp 1–26. 2107.
113. Adeel, S., S. Kiran, T. Ayesha, F. Rehman, T. Gulzar, S. Rafi, M. Zuber. 2017. *Radiation pre-treatment: A potential novel technology to improve fastness properties of plant derived natural dyes*. Wiley-Scrivener Publishing LLC USA, pp 65–87. 2018.
114. Adeel, S., M. Zuber, F. Rehman, K. M. Zia. 2018. Microwave-assisted extraction and dyeing of chemical and bio-mordanted cotton fabric using harmal seeds as a source of natural dye. *Environ. Sci. Pollut. Res.* 25: 11100. 2018.

5

Natural Dyes and Pigments: Extraction and Applications

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Abstract
Recently, there has been an increasing interest in the use of natural dyes in textile applications. This is a result of the meticulous environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes. Indeed natural dyes exhibit better biodegradability and are generally more compatible with the environment. Natural dyes are derived from natural resources; these are broadly classified as plant, animal, mineral, and microbialdyes. Natural dyes can be used for dyeing almost all types of natural fibers. Recent research shows that they can also be used to dye some synthetic fibers. Apart from their application in textiles, natural dyes are also used in the coloration of food, medicines, handicraft articles, and in leather processing, and many of the dye yielding plants are used as medicines in various traditional medicinal therapies. This book chapter attempts to review the classification of natural dyes and various sustainability issues involved in their production and application.

Keywords: Natural dyes, classification, extraction, application

5.1 Introduction

The use of plants, seashells, and coccid insects to create color is common to all civilizations [1]. With the advent of widely available and cheaper synthetic dyes in 1856, the use of natural dyes with poor to moderate wash and

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light fastness declined drastically and was replaced by more moderate to excellent color fastness properties of synthetic materials. Yet, it is primordial to note that the revival of natural dyes was mainly due to the hazardous and cancerogenic nature of synthetic dyes.

Textile industries, all over the globe, produce and use approximately 1.3 million tons of dyes, pigments, and dye precursors that cost around $23 billion. Textile production is mainly based on synthetic dyeing materials. Thus, textile industries generate toxic and hazardous chemical wastes which cause a threat to human health and environment. For these reasons, the use of natural dyes is attracting more and more interests from dyeing industries again. Natural dyes are generally extracted from vegetable substances or fungal species or animals. Since the antiquity, natural dyes have been used to help human beings in his life, for instance, 2000 BC Chinese and Sumerians in Iraq had already utilized indigo in painting and dyeing clothes. Today, an undeniable fact is that there are increasing demands for natural dyes in textile industries all over the world. Natural dyes have also been used for drawing in caves and historical sites, indicating their importance in design and decoration.

Natural dyes can be used for dyeing almost all types of natural fibers. Recent research shows that they can also be used to dye some synthetic fibers [2]. Apart from their application in textiles, natural dyes are also used in the coloration of food, medicines, handicraft articles, and in leather processing. Many of the dye yielding plants are used as medicines in various traditional medicinal therapies [2–4]. In spite of their inferior fastness, many of (THE) natural dyes are antibacterial, antifungal, antioxidant, antileishmanial, and (anticancer) [3, 5–7].Furthermore, they are more acceptable to environmentally conscious people around the world [8].

Natural colorants from plants with antimicrobial properties have been widely used as both herbal medicines and dyes for at least 4000 years. For example, black kohl or green malachite was used as cosmetics and also to cure or prevent eye diseases as well [4].

Recent renaissance in research and development on natural dye production and application is observed due to increasing popularity of more natural lifestyle based on naturally sustainable goods [9]. Natural flora/fauna is full of incomparable colors fascinating and attracting human being toward a vast range of possibilities [10]. A large number of plant and animal/insect sources have been identified for the extraction of color [4] and their diversified use in textile dyeing [1–5] and functional finishing [4, 6, 9], food coloration [4], cosmetics [11], dye-sensitized solar cells [12], histological staining [13], pH indicator [14] and several other application disciplines [15]. During the last few decades, increasing attention has been paid by researchers to various aspects of natural dyes. This chapter is intended to collect various informations about natural dyes classification, extraction, and applications.

5.2 Classification of Natural Dyes

Natural dyes can be classified in various ways. The earliest classification was according to the alphabetical order. Later it was shifted to chemical structure based, where grouping within each group structure class according to colourswas carried out. Later on, these were classified in various other ways, e.g., based on colours, chemical constitution, application, and origin [4, 16–18].

5.2.1 Classification Based on Color

Natural dyes are frequently categorised on the basis of the colour that they impart to the fiber substrate [17].

5.2.1.1 Red

The Colour Index lists 32 red natural dyes. Most of the red colourants are found in the barks or in roots of the plant or camouflaged in the bodies of the dull grey insects. Few prominent members are madder (*Rubiatinctorum*), manjistha (*Rubiacordifolia*), Brazil wood/sappanwood (*Caesalpineasappan*), Al or morinda (*Morindacitrifolia*), cochineal (*Coccuscacti*) and lac dye (*Coccuslacca*) [4, 19].

5.2.1.2 Blue

The Colour Index lists only four blue natural dyes, viz. natural indigo, sulphonated natural indigo, Kumbh (Manipur) and the flowers of Japanese 'Tsuykusa' used mainly for making awobana paper [20]. The only viable choice among the blue natural dyes is indigo.

5.2.1.3 Yellow

Yellow is the most common and abundant colour in the natural dye class. The Colour Index lists 28 yellow dyes. Some of the important are obtained from barberry (Berberisaristata), tesu flowers (Buteamonosperma) and kamala (Mallotusphilippensis) [16, 17].

The sources of natural yellow colour include turmeric, kamela, tesu, marigold, larkspur, harshingar, annatto, berberis, and dolu. The source of colour in turmeric is rhizomes of Curcuma longa. Kamela (orange–red powder occurring as a glandular pubescence on the pads of the tree Mallotusphillipinensis) comprises several colouring matters – e.g., chaconnes (rottlerin, isorottlerin) – the shade produced is fast to soap, alkalis, and acids but has moderate fastness to light.

5.2.1.4 Green

Plants that yield green dyes are rare. Both woad (Isatistinctoria) and indigo have been used since ancient times in combination with yellow dyes to produce green shades. Woollen cloth mordanted with alum and dyed yellow with dyer's green weed was over dyed with woad and, later with indigo, to produce the once-famous Kendal green. Soft olive greens are also obtained when textiles dyed yellow are treated with iron mordant.

5.2.1.5 Black and Brown

When it comes to natural brown, there is virtually no limit to the natural sources for that. Cutch is an ancient brown dye from the wood of acacia trees; particularly Acacia catechu is used for dyeing of cotton in brown hue. According to Colour Index, six dyes are there in black colour. Some common examples of black colour are roots of iris plant, lac, carbon, and caramel [4, 12].

5.2.1.6 Orange

Dyes that create reds and yellows can also yield oranges. The sources for a natural orange dye are barberry, annatto, sweet pepper blood roots etc. [21, 22].

5.2.2 Classification Based on Chemical Constitution

Natural organic dyes cover a wide range of chemical classes, viz. anthraquinone, indigoid, naphthoquinone, carotenoid, flavone, di-hydropyransanthocyanidin, and flavonol.

5.2.2.1 Anthraquinone Dyes

Few most important red dyes are based on the anthraquinone structure and are obtained both from plants as well as animals or insects. These are characterised by good fastness to light and on formation of metal salt complexes develop good wash fastness too. Examples of anthraquinone dyes are madder (extracted from the root and known as the alizarin), lac dye (animal dye), kermes (insect dye and the colouring matter is kermesic acid), cochineal (obtained from an insect and main colouring component is carminic acid).

5.2.2.2 Indigoid Dyes

Two very important natural dyes possess indigoid structure, namely indigo and tyrian purple. Indigo is perhaps the oldest natural dye used by man. The dye was used pre-historically in India, where it probably originated. The word is derived from 'Indican'. It occurs as the glucoside indicant in the plant Indigoferatinctoria and is known in India since about 4000 years as a-Naphthoquinone dyes [23]. The most prominent member in this class is lawsone or henna. It is obtained from *Lawsoniainermis*, cultivated mainly in India and Egypt [4]. Another similar dye is juglone obtained from the shells of unripe walnuts.

5.2.2.3 Carotenoid Dyes

The class name is derived from the orange pigment found in the carrots. In these, the colour is due to the presence of long conjugated double bond. Some common examples of the carotenoid structure based dyes are annatto, saffron etc.

5.2.2.4 Flavonoid Dyes

Flavonoids, which yield yellow color, can be classified under flavones, isoflavones, aurones, and chalcones. Flavones are colourless organic compounds. Most of the natural yellows are derivatives of hydroxyl and methoxy substituted flavones and isoflavones. Common example is weld (containing luteolin pigment) giving brilliant and fast colours on both wool and silk [4].

5.2.2.5 Dihydropyran Dyes

The substituted dihydropyrans, viz. haematin and its leuco form, haematoxylin are closely related to the chemical structure of the flavones. These are important natural dyes for dark shades on silk, wool, and cotton. Logwood, Brazil wood and sappan-wood are the common examples.

Anthocyanins are the most important flavonoid colorants in plants and mostly occur in floral tissues. The six main aglycone anthocyanin chromophores and their glycosides are pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin [24]. Some of them are covalently linked to flavonol glycoside co-pigments. This intermolecular co-pigmentation enhances and stabilizes the color. For example, the stable bluish color of Ceanothus and agapanthus praecox flowers is related to the delphinidin glycoside linked to a kaempferol triglycoside. The colorant has maximum absorption at 680 nm, as well as bands at 536, 576 and 615 nm. The reported ratio of flavonol to anthocyanin in the complex is 8:1.6. Pigment–co-pigment complexes are mostly linked together by hydrogen bonding but rarely via covalent linkage through organic acids [25]. Chelation between anthocyanin and metal cation can increase stability as well [24].

5.2.3 Classification Based on Application

Natural dyes are also classified based on the method of their application, viz. mordant dyes, direct dyes, vat dyes, acid dyes and basic dyes, and disperse dye.

5.2.3.1 Mordant Dyes

These essentially require a mordant for application because of their lack of affinity for the fiber. According to definition, these dyes form complexes with the mordant. Three types of mordants are used, viz. (i) metallic mordants such as metal salts of aluminum, copper, tin etc., (ii) tannic mordant such as tannic acid, e.g., myrobalan and sumach and (iii) oil mordant which forms complex with main metal mordant.

5.2.3.2 Vat Dyes

These are water insoluble and first reduced with sodium hydrosulphide followed by solubilisation with sodium hydroxide; in this state they show affinity for natural fibres. After application of the dye on the fiber, it is converted into parent insoluble form by oxidation to develop the true colour of the dye, e.g., indigo.

5.2.3.3 Direct Dyes

Direct dyes possess affinity for cellulosic fibres without any pretreatment to dye or to the fiber. Many natural dyes belong to this class. The most common example is turmeric; others are harda, pomegranate rind, and annatto.

5.2.3.4 Acid Dyes

These possess either sulphonic or carboxylic groups in structure and are most suitable for dyeing of wool and silk from acidic medium. After-treatment with tannic acid, known as back tanning improves the colour-fastness, e.g., saffron.

5.2.3.5 Basic Dyes

Basic dyes on ionization develop coloured cations and form electrovalent bond with the –COOH groups of wool and silk. These are applied from neutral to mildly acidic pH and shows poor light fastness, e.g., berberine.

5.2.3.6 Disperse Dyes

Previously no natural dye was classified as disperse dye, but after the introduction of disperse dyes; it was felt that some of the natural dyes are structurally similar to disperse dyes. These dyes have relatively low molecular weight, low aqueous solubility and no strong solubilising groups. These dyes can be post-mordanted with chromium, copper or tin salt and are applied on synthetic fibres at neutral to mild acidic pH. They can also be applied to silk and wool. One such dye could be Lawsone or henna and many other flavone as well as anthraquinone dyes.

5.2.4 Classification Based on Origin

There are primarily three sources from which natural dyes are extracted, viz. plants, minerals, and animals.

5.2.4.1 Plants

Various parts of many plants are found potentially rich in natural dye; parts like root, bark, stem, seeds, and fruit can be used to extract colour. Some plants may possess more than one colour depending upon from which part of the plant they are extracted [4, 20].

5.2.4.2 Minerals

These colourants are derived from the natural mineral sources. Mineral colours are produced from purified natural organic compounds. Some of the important mineral colourant are chrome yellow, iron buff, nankin yellow, prussian blue, and manganese brown. However, these are produced *in situ* making handling of textile stiffer.

5.2.4.3 Animals

Animals are also rich source of natural dyes. Dyes normally are being extracted from the dried body of the insects; common examples are lac, cochineal and chemical structures, botanical names as well as C I specification of a few popular natural animal dyes are cited by many authors. [1–5, 26, 27].

5.3 Extraction of Natural Dyes

5.3.1 Extraction Methods

As natural dye-bearing materials contain only a small percentage of coloring matter or dye along with a number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, among others, extraction is an essential step not only for preparing purified natural dyes but is also required to be carried out by users of crude dye-bearing materials. As natural coloring materials are not a single chemical entity and the plant matrix also contains a variety of non-dye plant constituents, extraction of natural dyes is a complex process. The nature and solubility characteristics of the coloring materials need to be ascertained before employing an extraction process. The different methods for extraction of coloring materials are:

- Aqueous extraction
- Alkali or acid extraction
- Microwave and ultrasonic assisted extraction
- Fermentation
- Enzymatic extraction
- Solvent extraction
- Super critical fluidextraction

5.3.1.1 Aqueous Extraction

Aqueous extraction was traditionally used to extract dyes from plants and other materials. In this method, the dye-containing material is first broken into small pieces or powdered and sieved to improve extraction efficiency. It is then soaked with water in earthen, wooden, or metal vessels (preferably copper or stainless steel) for a long time usually overnight to loosen the cell structure and then boiled to get the dye solution, which is filtered to remove nondye plant remnants. The process of boiling and filtering is repeated to remove as much dye as possible. When the extraction is to be carried out on a larger scale for preparation of purified dye powders, stainless steel vessels are used and the time of soaking the materials in water may be reduced by boiling the solution for an extended time period. Generally, centrifuges are used to separate residual matter. Use of trickling filters can ensure removal of fine plant material particles and ensure better solubility of the purified natural dye. As most of the dyeing operations are carried out in aqueous media, the extract obtained by this method can be easily applied to the textile materials. Disadvantages of this extraction method are long extraction time, large water requirement, use of high temperature, and low dye yield as only water-soluble dye components get extracted whereas many dyes have low water solubility. Also, along with dye, other water-soluble substances such as sugars and the like get extracted that may have to be removed if the extract is to be concentrated and converted to a powder form. Yield of heat-sensitive dye substances gets reduced at boiling temperature; therefore a lower temperature should be used for extraction in such instances.

5.3.1.2 Acid and Alkali Extraction Process

As many dyes are in the form of glycosides, these can be extracted under dilute acidic or alkaline conditions. The addition of the acid or alkali facilitates the hydrolysis of glycosides resulting in better extraction and higher yield of coloring materials. An acid hydrolysis process is used for the extraction of dye from tesu (Buteamonosperma) flowers. Acidified water is also used for extracting some flavone dyes to prevent oxidative degradation. Alkaline extraction is suitable for dyes having phenolic groups as they are soluble in alkali, which improves the dye yield. Dyes can be later precipitated by the use of acids. Dye from annatto seeds can be extracted by this technique. This process is also used to extract lac dye from lac insect secretions and red dye from safflower petals. The disadvantage of this process is that some coloring materials may be destroyed under alkaline conditions considering the fact that some of the natural dyes are pH sensitive. As many natural dyes are usually a mixture of different chemical constituents, changing the pH of the extraction medium by adding acid or alkali can lead to the extraction of different dye constituents which can lead to different hues upon subsequent dyeing and differences in colorfastness properties. Many researchers have studied the extraction of natural dyes under various pH conditions and compared the color and fastness properties of dyed fabric to find out the optimum dye extraction conditions and further additions to this information continue to be made every year in the scientific literature.

5.3.1.3 Ultrasonic and Microwave Extraction

These are actually microwave- and ultrasound-assisted extraction processes where extraction efficiency is increased by the use of ultrasound or microwaves, thus reducing the quantity of required solvent, time, and temperature of extraction. When the natural dye containing plant materials is treated with water or any other solvent in the presence of ultrasound, very small bubbles or cavitations are formed in the liquid. These increase in size but upon reaching a certain size, they cannot retain their shape. When this happens, the cavity collapses or the bubbles burst creating high temperature and pressure. Millions of these bubbles form and collapse every second. The creation of very high temperature and pressure during extraction increases the extraction efficiency within a short time. Also the process can be performed at lower temperature and therefore extraction of heat-sensitive dye molecules is better. As exploration of new dye sources and attempts to optimize the dye extraction process is continuing, use of this extraction technique has been recently reported by many researchers.

In microwave extraction, the natural sources are treated with a minimum amount of solvent in the presence of microwave energy sources. Microwave increases the rate of the processes so the extraction can be completed in a shorter time with better yield. Sinha *et al.* have reported extraction of annatto colorant with microwave energy. Earlier their group had reported microwave-assisted extraction of blue pigment from the butterfly pea. Microwave and ultrasound extractions can be considered as green processes due to reduction of extraction temperature, solvent usage, and time which results in lower consumption of energy.

5.3.1.4 Fermentation

This method of extraction uses the enzymes produced by the microorganisms present in the atmosphere or those present in the natural resources for assisting the extraction process. Indigo extraction is the most common example for this type of extraction. Freshly harvested indigo leaves and twigs are soaked in warm water (about 32 °C). Fermentation sets in and the colorless indigo containing glucosideindican present in the leaves is broken down into glucose and indoxyl by the indimulsin enzyme also present in the leaves. Fermentation is complete in about 10–15 h and the yellow liquor containing indoxyl is then taken to beating vats where indoxyl gets oxidized by air to the blue-colored insoluble indigotin which settles down at the bottom. It is collected, washed, and after removing excess water, it is pressed into cakes. Extraction of indigo from other indigo-containing plants such as woad is also carried out by fermentation. This process can also be used for extraction of certain other colorants such as annatto. The fermentation method is similar to aqueous extraction with the exception that this method does not require high temperatures. The microorganisms disintegrate the coloring matter binding substances in natural way. Long extraction time, need for immediate extraction of pigments after harvesting, foul smell due to microbial action, and so on, are some of the disadvantages of this method.

5.3.1.5 Enzymatic Extraction

As plant tissues contain cellulose, starches, and pectins as binding materials, commercially available enzymes including cellulase, amylase, and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions. This process may be beneficial in the extraction of dye from hard plant materials such as bark, roots, and the like.

5.3.1.6 Solvent Extraction

Natural coloring matters depending upon their nature can also be extracted by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol, and so on. The water/alcohol extraction method is able to extract both water-soluble and water-insoluble substances from the plant resources. The extraction yield is thus higher as compared to the aqueous method as larger number of chemicals and coloring materials can be extracted. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and release of coloring matter. Purification of extracted color is easier as solvents can be easily removed by distillation and reused. Extraction is performed at a lower temperature thus chances of degradation are fewer. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect. Another disadvantage of this method is that the extracted material is not readily soluble in water and the subsequent dyeing process has to be carried out in an aqueous medium.

5.3.1.7 Supercritical Fluid Extraction

Extraction is an emerging area in natural product extraction and purification. A gas functions as a supercritical fluid above its critical values of temperature and pressure. Such a fluid has physical properties somewhere between those of a liquid and a gas. They are able to spread out along a surface more easily than a true liquid because they have much lower surface tension than liquids. As their viscosity is also low, they have very good diffusivity and thus better interaction with the substrate. At the same time, a supercritical fluid is able to dissolve many substances like a liquid, as solubility of a substance in any solvent is higher at higher pressure and temperature and such conditions are needed to maintain a gas in the supercritical state. Supercritical fluid extraction using carbon dioxide (CO_2) is a good alternative to solvent extraction as it is nontoxic, cheap, easily available, and does not leave residues. Critical temperature and pressure values for carbon dioxide are 31.4 C and 1,070 pounds per square inch (psi) or 73.8 bars, respectively. Supercritical extractions using CO_2 typically operate at temperatures between 32 and 49 C and pressures between 1,070 and 3,500 psi. As the CO_2 is a nonpolar molecule it behaves as does a nonpolar organic solvent. A cosolvent or a modifier may be added to improve the solubility of slightly polar solutes. The advantage of the process is that the extract is free from residual solvent traces and heavy metals and is light colored due to the absence of polar polymerizing substances. Hence the process has gained popularity in extraction of purified natural products for food and pharmaceutical applications. The disadvantage of the method is the high cost of the equipment and poor extraction of polar substances.

5.4 Natural Dyes Application

5.4.1 Textile, Medicinal and Herbal Applications

Natural colorants can be grouped based on their sources, methods of application, colors, and chemical structures. They are mainly in the category of phenolic compounds, which play an important role in the growth and reproduction of plants and serve as defense systems against pathogens and predators.

Many of them possess antioxidant activity and have shown remarkable antibacterial, anti-inflammatory and anticancer functions. In fact, many of the plants that can produce natural colorants have been known for their medicinal and herbal applications. These phenolic compounds based on their various structural moieties can be categorized into groups such as quinones, flavonoids, tannins, lignanes, curcuminoids, coumarins, stilbenes, and their subgroups [4, 9, 28, 29].

5.4.1.1 Quinones

Quinone-type compounds including anthraquinones, naphthoquinones, phenanthraquinones and benzoquinones (Figure 5.1) are naturally occurring in plants with remarkable therapeutic applications. These compounds are the basis of many of the ancient natural dyes [4]. In addition, they have been used as medicines due to their antibacterial, antiviral or antifungal activities [4, 5, 29].

5.4.1.2 Anthraquinones

Anthraquinones are the largest class of naturally occurring quinones and contain some of the most important natural colorants such as alizarin, purpurin, munjistin, emodin, chrysophanol, aloe-emodin, physcion, rhein, etc.

They exist in the form of hydroxyanthraquinones and usually have 1–3 hydroxyl groups. These quinone dyes could form complexes with different metal salts resulting in very good color fastness [15].

Alizarin and purpurin are two main anthraquinone-type colorants found in the root and tubers of *Rubiatinctorum* (Common Madder), *R. peregrine* (Wild Madder) and *R. cordifolia* (Indian Madder). Madder has been cultivated and used as a source of red dyes in Asia, Europe, and America. In fact, the oldest sample of madder dyed cotton found in Egypt belongs to the third millinium BC [30]. Other colorants found in these plants include munjistin, pseudopurpurin, xanthopurpurin, ruberythric acid, and rubiadin [31].

Madder has been used to dye wool, leather, and cotton and can also be used as a food colorant. Alizarin and purpurin have antimicrobial and antifungal activity against different pathogenic bacteria [32]. Wool fibers dyed

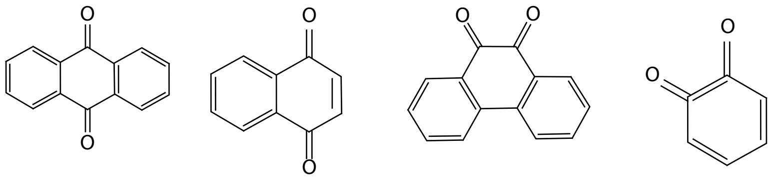

Figure 5.1 Structures of quinones.

with madder have shown higher insect resistance against carpet beetles. Purpurin even reveals an antigenotoxic effect against a range of different environmental carcinogens such as hetrocyclic amines. In medicinal application, madder has been used in skin care products with astringent, tonic, vulnerary, and antiseptic functions. It can be used to clean open wounds and treat skin diseases, especially tubercular conditions of the skin and mucous tissues [21, 22, 33].

Carminic acid is another important hydroxyanthraquinone based colorant, which is derived from cochineal and has been used to dye wool, silk, and cotton fabrics. Its brilliant red color with great light fastness could overcome many similar synthetic ones used in textiles [34].

Although cochineal has shown antimicrobial activity against *S. aureus*, the dyed wool fabric did not provide any antimicrobial activity. However, the wool fabrics dyed with cochineal and some metal mordant revealed up to 100% antimicrobial functions depend on the type of metals [35].

5.4.1.3 Naphthoquinones

Another main class of quinone colorants are naphthoquinones, including shikonin, alkannin, juglone and lawsone [4]. Shikonin is a naturally occurring naphthoquinone found in the dried root of the plant *Lithospermumerythrorhizon*. The S-enantiomer form of this pigment known as alkanninwas also identified in the root of the plant *Alkannatinctoria* [36]. These two red pigments have traditionally been used as natural colorants in textile, food, and cosmetic industries. Besides their use as pigments, shikonin and its derivatives have been used as a medicine for antimicrobial, anti-inflammatory, and anti-tumor purposes. They also have shown ability to heal wounds, burns, and hemorrhoids via proliferation of granulation tissue [37]. Shikonin is the first natural colorant that has been commercially produced by a plant cell culture method to supply the cosmetic industry in Japan since 1983. Lawsone, a major colorant component extracted from *Lawsoniainermis* (Henna), and Juglone, extracted from walnut (Juglans), are the two most prominent members of naphthoquinone-type dyes [38, 39]. This compound is well known for its cosmetic use to dye hair, nails, and skin while it has been used to color textiles including leather, wool and silk [4, 38].

Lawsone and juglone, as members of the quinone-type compound family are found to possess antibacterial, antifungal, antiviral, and antineoplastic activities. They could also inhibit tumor cell growth [38].

Their bioactivities are considered to be related to their high protein binding ability. They can covalently bind to the proteins, especially keratin in hair and skin through Michael addition reactions. Henna in particular, has antiinflammatory effects and traditionally has been used as a cooling agent and astringent to treat skin infections such as boils, burns, and bruises. Juglone traditionally has been used for many years as a treatment for localized, topical fungal infections such as ringworm [5, 38, 39].

5.4.1.4 Anthocyanins

Hundreds of studies support the use of anthocyanins, both dietary sources and as supplements, for improving health and warding off disease. Anthocyanins have a wide range of biological activities including: redox/ antioxidant, anti-inflammatory, antimicrobial, anti-carcinogenic, fostering eye health, neuroprotective, prevention of LDL oxidation, improvement of capillary stability, supporting collagen, and increasing intercellular levels of vitamin C. Anthocyanins have variety of colors and high abundance in nature, hence they were used as textile colorants. Cotton and silk fabrics dyed with anthocyanins extracted from grape pomace using tannic acid as mordant, and the combination of the mordant with anthocyanins provided different red-violet color with good washing fastness. Silk dyed fabrics have good light fastness, however it was not the same for cotton ones [1–4, 6].

5.4.1.5 Usnic Acid

Usnic acid is the most common yellow colorant extracted from lichens. Lichens are a combination of fungi and algae and have been used to dye fabrics for a long time. Like anthocyanins, they have different color shades from yellows, oranges and browns to reds, pinks and purples, but their washing and light fastness is better. The colorant extracted from *Roccellatinctoria* was used as an alternative for royal purple from shellfish [4, 16]. The main natural colorants from the lichen extracts, *Leconoratartarla*, *Ochrolechiatartarea* and *R. tinctoria*, are depsides.

Usnic acid and depsides have shown antimicrobial activities against gram-positive bacteria and some pathogenic fungi [40]. It also has anti-inflammatory, anti-insect, and preserving properties and can absorb UV light. Usnic acid has been used as an herbal medicine and recently has been marketed in the USA as an ingredient for weight reduction [41].

Phycocyanobilin is a colorant from spirulina, a blue-green algae, which has been used for many years to dye fabrics. Research on bacterial production of prodigiosin compounds showed that fabrics dyed with this compound, including wool, nylon, silk, and acrylic fibers, exhibited good antibacterial activities [42].

5.4.1.6 *Tannins*

Tannins are concentrated in bark, wood, leaves, fruit, roots, and seeds of different plants. Their production is increased in plants with sickness, so it is assumed to provide protection against infections and insects. Tannins are natural water-soluble polyphenolic compounds with light yellow or white color. In textiles, they are well-known mordant dyes for brown and black colors [43, 44].

Tannins are applied on fabric as cationic dyes and have also been used in the production of inks (iron gallate ink). Tannins are widely used as tanning agents in preparing leather, herbal medicine, textile dyes, and antioxidants in the food industry [44]. They have antiviral, antimicrobial, anti-inflammatory, and especially, anti-tumor activity and could be used as astringent, antiseptic, and haemostatic agents [45]. Tannins divide into four major groups based on their chemical structure: gallotannins, ellagitannins, complex tannins, and condensed tannins. The first three groups contain galloyl moieties and their derivatives are attached to a variety of polyol-, catechin and triterpenoid core structures. Many types of tannins in these categories can be hydrolyzed after treatment with hot water [44].

Pomegranate (*Punicagranatum* L.) is rich in hydrolyzable tannins including punicalagin 80–85% w/w), ellagic acid (EA; 1.3% w/w), punicalin and EA-glycosides (hexoside, rhamnoside and pentoside) [46]. Besides its use as fruit and juice, pomegranate fruit husk/peels have been used in dyeing wool, silk and cotton fabrics for 1000 years. In addition, it has shown antimicrobial activities on cotton and wool fabrics with good laundry durability and light fastness [45].

5.4.2 Natural Dyes in Food Coloration

As a consequence of growing worldwide concern for food quality and safety, a set of standards have been brought in by different governments. Market pressure brought about by changes in legislation and consumer preferences have necessitated the foods to be formulated with more natural ingredients. The use of natural pigments for food coloring is receiving growing interest from both food manufacturers as well as consumers and there has been much interest in the development of new natural colorants for use in food industry continuing the replacement of synthetic food dyes, because the natural products are associated with quality and health promotion whereas synthetic pigments are critically assessed by consumers [47, 48]. Standardized methods of collection, extraction, purification, stabilization, and standardization for a variety of natural food colorants are available such as anthocyanins [49], betalains [4, 50] chlorophylls [51], carotenoids [52], tannins [43, 44], *Monascus* [53], quinones [4], safflower [54], turmeric [4] etc. They have different groups of chemical compounds which may be used directly as colorants or in chemically modified form to produce different hues ranging from green through yellow, orange, red, blue, and violet, depending on the source of colorant or increased stability. Researchers willing to experiment and expand this interesting palette of natural food color choices to give distinguished look and quality to a variety of food preparations.

A number of reports are available on exploitation of the potential of new sources of plants [1–5] and insect [4] origin as well as other biological sources such as fungi [55], and algae [53] in addition to those covered by existing legislations. Most of the currently used natural pigments are highly sensitive to pH change, temperature and prone to light, heat, and oxygen disintegration [56]. Establishing the color stability of natural colorants as requirement for their successful application, a number of researchers focused on improving color stability of different classes of natural food colorants [57].

Pigments producing microbes such as fungi, bacteria, and microalgae are quite common in nature. Among the molecules produced are carotenoids, melanins, flavins, quinones and more specifically monascins, violacein, phycocyanin or indigo [4]. A great upsurge has been seen in recent times in biotechnological production of food grade pigments [56]. The use of fungi to color foodstuffs is not new; *Monascus* pigments are being traditionally used in food in the Orient for hundreds of years. Fungi provide a readily available alternative source of naturally derived food colorants. The recent approval of a fungal food colorant has vastly increased the prospects of research to explore the extraordinary chemical diversity and biodiversity of fungi for the biotechnological production of pigments as natural food colorants. Recent statistics indicate that with an appropriate selection of suitable fungus using chemotaxonomic tools and *a priori* knowledge of fungal extrolites, fungi can be used as cell factories for pigment production and could be developed to tailor functionality and expand the color palette of existing natural food colorants; the fungal natural colorants could be produced in high yields by using the available cultivation technology without potential genetic manipulation.

Microalgae are also seen as a major natural source for a huge variety/array of natural colors. Carotenoid production has been proved to be one of the most successful branches of biotechnology of microalgae.

Innumerable associated benefits and innumerable healing properties are linked with the use of natural colorants in food industry [58]. For example, in addition to coloring property, anthocyanin extracts may act as quality control marker for foodstuffs; improve the nutritional quality of foods and beverages, possibly play an important role in reducing the risk of coronary heart disease, cancer, and stroke [52–56]. Carotenes are also used for nutritional purposes an essential vitamin source (provitaminA agents) or as dietary supplements [52]. Paprika is a source of vitamin C, whereas riboflavin contains vitamin B [59]. Many of the natural food colorants possess excellent antioxidant properties. Flavonoids and tannins are recognized as colorants with high pharmacological value [58]. Thus, in addition to their primary function of improving the visual quality of food products, naturally derived food colorants may improve the nutritional value of the target food.

5.4.3 UV-Protective Finishing

Ultraviolet radiation (UVR) from the sun causes sunburns, tanning, premature skin aging and wrinkling and its overexposure leads to skin cancer [4]. Exposure to the sun is an occupational hazard to outdoor workers such as construction industry workers, recreation workers, sportspersons, agricultural and horticultural workers, and fishermen as they have no choice about the duration of their exposure to sunlight. This necessitates the development of UV-protective clothing and coverings to minimize the effect of harmful UVR. UVR transmission properties of textiles are influence by many factors such as structure and physiochemical nature of fibre, dyes and finishes, fabric thickness, porosity and moisture content [60]. The sun rays blocking properties of a textile are enhanced when a dye, pigment, delustrants, or ultraviolet absorber finish is present that absorbs UVR and blocks its transmission through a fabric to the skin; thus dyed fabrics protect more than undyed ones and their protection levels rise with the increase in dye concentration [61].

Sarkar [62] characterized Ultraviolet Protection Factor (UPF) of plain, twill or sateen weave cotton fabrics dyed with colorants of plant (madder and indigo) and insect (cochineal) origins with respect to fabric construction, weight, thickness, and thread count. A positive correlation exists between the weight, thickness, and shade depth of the naturally dyed fabric and their UPF values; however thread count appears to negatively correlate with UPF.

Grifoni *et al.* [9, 63] studied the effect of color on UVR transmission of cotton, flax, hemp, and ramie fabrics with different construction parameters dyed with some common natural dyes by *in vitro* and outdoor assessments. The comparison between two methods applied to measure fabric transmittance pointed out that the UPFs calculated by *in vitro* measurements were generally lower than those based on outdoor data, indicating an underestimation of actual protection level of tested fabrics assessed by *in vitro* test. Metallic salt mordants have been reported to enhance UV-protective properties of naturally dyed cotton [64], wool and silk [65] fabrics to a substantial account depending on nature of fibre, mordant, and natural dye used. Very recently, Hou *et al.* [66] used natural dyes extracted from orange peel (OP), an abundant, cheap, and readily available agricultural byproduct, for producing highly durable UV-protective wool fabrics. They reported that UPF value of OP treated wool fabric was six times higher than that of the wool fabric dyed with normal synthetic dyes with similar shade and depth of shade and even after 30 home laundering cycles, the *UPF* value of the OP dyed wool was found 4 times higher than wool dyed with synthetic dyes.

Textile industries see a promising future for UV-protective fabrics, with the environmental and energy conservation benefits, in developing high performance materials for the world market. Therefore, it is contemporary need to develop a proper treatment to increase the UV protection property to fabrics. Promising research findings obtained from laboratory scale and outdoor experiments show that naturally dyed fabrics with UV-protective properties seem to have bright future after some laborious research and development.

5.4.4 Insect Repellent Finishing

Insect damage on textile products such as carpets, garments, upholstered furniture, blankets, and priceless heirlooms is a serious problem faced during storage and results in significant economic losses, especially in warehouses and showrooms. Even a small amount of fibre eaten from a valuable suit or a rug can ruin its functional and/or aesthetic properties. Insect repellents that discourage insect damage in textile industry are in great demand. Kato *et al.* [67] studied damage to wool fabrics dyed with ten different natural dyestuffs by the larvae of varied carpet beetle, *Anthrenusverbasci*. Eight among the ten natural dyestuffs were found effective against *A. verbasci* and strength of their repellent effect in feeding preference test was in the order of lac dye, gallnut, catechu, red cabbage, *Cricula* cocoon extract > cochineal, indigo, Amur cork tree extract. The anthraquinone dyes, such as cochineal and madder, were found to be very effective in protecting wool fabric against black carpet beetles. Madder resulted in the lowest weight loss and the best effect of insect deterrence against black carpet beetles.

5.4.5 Natural Dyes in Dye-Sensitized Solar Cells

Solar energy has emerged as one of the promising renewable energy sources for eco-friendly and cost-effective conversion of solar energy to electricity,due to the use of inexpensive materials, simple fabrication process and low environmental impact, especially those sensitized by natural dyes [68]. Dye-sensitized solar cells (DSSC) are innovative solar cells that mimic photosynthesis in plants. Unlike traditional solar cells, dye-sensitized cells can work effectively in low light conditions and are less susceptible to losing energy to heat. The efficiency of DSSC is determined mainly by the sensitizer used. The dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electrical energy [69]. DSSCs with efficiencies of up to 11% have been designed using ruthenium (Ru) based dyes but the limited availability and high cost of these dyes together with their undesirable environmental impact have led to the search for cheaper and safer dyes [70].

There have been some interesting explorations of natural dyes in the context of the DSSC application using pigments obtained from biomaterials. Several reports have emphasized on exploration into natural dyes, such as cyanine, anthocyanins, cyanidins, tannins, chlorophyll and their derivatives, carotenoids, betalains, chalcones, and many others as a cheaper, faster, low-energy requiring and environment-friendly alternative for use in DSSCs [68–74]. Although these natural dyes often work poorly in DSSCs, these are expected as low cost and prepared easily when compared to ruthenium complex based dyes.

Different types of natural dyes showed different solar conversion efficiencies depending on the source and chemical structure of dye and interaction between dye molecule and photo-electrode i.e., TiO_2, ZnO, etc. Natural dye-sensitized DSSCs usually perform poorly in DSSC because of weak binding energy with the metal oxide film (photo-electrode) and low charge-transfer absorption in the whole visible range. Based on investigation on the structure and properties of dye molecules, the best photosensitized effect in some of the tested natural dyes is obtained due to the better interaction between the different binding groups of dye molecule and the TiO_2 film on cathode in DSSCs. Heera and Cindrella [75] theoretically evaluated ten natural pigments: caffeic acid, ferulic acid, ellagic acid, deoxysantalin, resveratrol (plant source), carminic acid, kersemic acid, ommatin D (insects), methoxatin and caulerpinic acid (microbes), as photosensitizers for their possible application in DSSC. They also concluded that resveratrol, ferulic acid, caffeic acid and methoxatin can prove potential pigments for efficient application in DSSC due to their favorable maximum wavelength, much compatible with TiO_2 and their high oscillator strength. Gomez-Ortiz *et al.*

(2010) investigated the use of bixin and norbixin obtained from achiotes seeds in DSSCs based on TiO_2 and ZnO substrates and confirmed that the efficiencies obtained with TiO_2 are much higher than for ZnO substrates, in agreement with the general trends observed for these two substrate materials. Yamazaki *et al.* [76] assembled DSSCs by using natural carotenoids, crocetin and crocin, as sensitizers and demonstrated that, crocetin can attach effectively to the surface of TiO_2 film due to the presence of carboxylic groups in the molecule and perform the better photosensitization effect than crocin that has no carboxylic group in the molecule. Extracting temperature, extracting solvent and pH of the extract solution also have very prominent role in determining efficiency and stability of DSSCs [77]. Energy conversion efficiencies and maximum power output for solar cells sensitized by mixed pigments were much higher than that achieved by the linear superposition of the cells sensitized by individual pigments.

The efficiency of natural DSSCs is determined by a number of factors that include selection of the appropriate natural dye, quantitatively significant and stable electronic anchorage of the dye to the surface of the metal oxide nanostructure, choice of photoanode, counter electrodes, electrolyte, and solvent system. It is therefore highly desirable to standardize these critical factors in the context of making natural DSSCs, a commercially viable option. The advantages of natural dyes as photosensitizers are large absorption coefficients, high light-harvesting efficiency, no resource limitations, low cost, simple preparation techniques and no harm to the environment. Although the efficiencies obtained with these natural dyes are still below the current requirements for large scale practical applications, these interesting explorations of fabrication of DSSC using dyes obtained from bioresources invoked participation of researchers around the globe to engage in research to search for new sources of natural dye systems that are stable, non-toxic, biocompatible and have desirable opto-electronic properties. Some serious efforts in natural dye sensitizers may spring up a perspective of commercial feasibility for inexpensive and environmentally friendly DSSCs.

5.5 Other Applications of Natural Dyes

In addition to the above mentioned applications, there is a growing interest for using natural dyes to dye leather [78], to stain wood [79], pulp [80], and some plastics [81] to add color to cosmetics [4]; to dye hair [4]; to impart color to some pharmaceutical preparations [82]; and also in histological staining [83]. Natural pigments derived from different sources with active functional components have shown high biological activities, and exhibited different properties depending on each kind of pigments which make them excellent coloring materials for natural cosmetics and functional health foods [4, 56]. Siva *et al.* [84] reported an easy, practical and reliable procedure for using *Bixaorellana* L. natural dye as an alternative tracking dye for gel electrophoresis in place of regularly used dye marker bromophenol blue. Another very common aspect of natural dye application is their use as pH indicator [85] developed by thermo-regulating natural indigo dyed fabrics through the fixation of the Microcapsules (MCs) containing *n*-octadecane and *n*-eicosane on the back side of the fabrics using the dot-screen printing method. They obtained relatively good latent heat storage capacity and color durability to rubbing, laundering, and ironing.

Researchers have lately explored the promise of some historical pigments such as indigo and madder in designing novel organic electronics devices successfully. Recent explorations on thin films of indigo and Tyrian purple have shown their good charge transport properties for use in organic electronics as natural and sustainable semiconductors. Indigo and Tyrian purple form highly ordered thin films that afford ambipolar charge transport with relatively high mobilities. Inspiring results have shown that these biomaterials can compete with the best organic electronic materials and in conjunction with other biomaterials, (i.e., substrate, dielectric) they demonstrate the possibility of creating fully biocompatible/biodegradable electronics for many low-cost applications. Reddy *et al.* [86] reported reversible lithium ion storage properties of a naturally occurring and abundant organic compound purpurin, a non-toxic dye derived from widely available plant madder, to develop sustainable and eco-friendly lithium ion batteries. The lithium batteries assembled using purpurin and chemically lithiated purpurin as working electrode showed good charge/discharge characteristics with very good reversible lithium ion storage properties. Future large-scale application of sustainable organic electronics based on biodegradable materials would have a positive impact on the current problem of electronic waste.

These interesting findings on newly discovered panoramas of natural dye applications invoke great expectations for further research on utilization of natural dyes in a wide variety of fields with focus on the future industrial application.

5.6 Conclusion and Future Outlook

Natural dyes, generally supposed to be cheap, non-toxic, worthwhile, and sustainable resource with minimal environmental impact, have attracted the attention of the scientific community to use them in a variety of traditional and newly discovered application disciplines. Although, past few years have witnessed substantial growth in our understanding of technological details required for efficient utilization of colorants obtained from natural sources, but still there are number of technical challenges in each area of natural dye application that must be overcome before these technologies can be adopted on a practical large scale. Improving methodologies of extraction and application and generating cost-effective processes are currently challenging because of the large diversity of natural dye sources. Enthusiastic studies discussed in the present article assert that current incompatibility of commercial exploitation of laboratory scale results can be carried off with some serious efforts. The data generated from these studies may device the basis for the economic viability of natural dye production in commercial scale for sustainable utilization of bioresources. Extensive R&D in the area of natural dye applications is underway worldwide, but practical implementation to adopt new technologies for making natural dyes, a compatible co-partner with synthetic dyes in different spheres of our life is a long-term prospect.

References

1. Adeel, S., Ali, S., Zsila, F., Dyeing of cotton fabric using pomegranate (*Punica granatum*) aqueous extract. *Asian J. Chem.,* 21, 3493–3496, 2009.
2. Adeel, S., Bhatti, IA., Kausar, A., Osman, E., Influence of UV radiations on the extraction and dyeing of cotton fabric with Curcuma longa L. *Indian J. Fibre Text Res*., 37, 87–90, 2012.
3. Yusuf, M., Shahid, M., Khan, MI., Khan, MA., Mohammad, F., Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant. *J. Saudi Chem. Soc.* 19, 64–72, 2015.
4. Yusuf, M., Shabbir, M., Mohammad, F., Natural colorants: Historical, Processing and Sustainable Prospects. *Nat. Prod. Bioprospect.,* 7(1), 123–145, 2017.
5. Aggarwal, BB., Kumar, A., Bharti, AC., Anticancer potential of curcumin: Preclinical and clinical studies. *Anticancer Res*., 23, 363–398, 2003.
6. Mansour, R., Haouas, N., Ben Kahla-Nakbi, A., Hammami, S., Mighri, Z., Mhenni, F., Babba, H., The effect of Vitisvinifera L. leaves extract on Leishmania infantum. *Iranian J. Pharmaceut Res.,* 12, 349–355, 2013.
7. Khan, SA., Ahmad, A., Khan, MI., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., Antimicrobial activity of wool yarn dyed with Rheum emodi L. (Indian Rhubarb). *Dyes Pigm*., 95, 206–214, 2012.
8. Al-Sehaibani, H., Evaluation of extracts of henna leaves as environmentally friendly corrosion inhibitors for metals material. *Materialwissenschaft Werkstofftechnik,* 31, 1060–1063, 2000.

9. Grifoni, D., Bacci, L., Zipoli, G., Carreras, G., Baronti, S., Sabatini, F., Laboratory and Outdoor Assessment of UV Protection Offered by Flax and Hemp Fabrics Dyed with Natural Dyes. *Photochem. Photobiol.,* 85, 313–320, 2009.
10. Dawson, TL., Biosynthesis and synthesis of natural colours. *Color Technol.,* 125, 61–73, 2009.
11. Dweck, AC., Natural ingredients for colouring and styling. *Int. J. Cosmetic Sci.*, 24, 287–302, 2002.
12. Hao, S., Wu, J., Huang, Y., Lin, J., Natural dyes as photosensitizers for dye-sensitized solar cell. *Sol. Energy,* 80(2), 209–214, 2006.
13. Tousson, E., Al-Behbehani, B., Black mulberries (Morusnigra) as a natural dye for animal tissues staining. *Anim. Biol.,* 61, 49–58, 2011.
14. Mishra, PK., Singh, P., Gupta, KK., Tiwari, H., Srivastava, P., Extraction of natural dye from Dahlia variabilis using ultrasound. *Indian J. Fibre Text. Res.,* 37(1), 83–86, 2012.
15. Shahid, M., Mohammad, F., Recent advancements in natural dye applications: a review. *J. Clean Prod.,* 53, 310–331, 2013.
16. Gulrajani, ML., Gupta, DB., Agarwal, V., Jain, M., Some studies on natural yellow dyes, part 1: CI Natural Yellow 3 (turmeric). *Indian Text. J.,* 102(4), 50–56, 1992.
17. Paul, R., Jayesh, M., Naik, SR., Natural dyes: classification, extraction and fastness properties. *Text. Dyer Printer,* 29(22), 16–23, 1996.
18. Teli, MD., Paul, R., Pardesi, PD., Natural dyes: classification. chemistry and extraction methods. part 1. *Colourage,* 60, 43–48, 2000.
19. Vankar, P.S., Chemistry of natural dyes. *Resonance,* 5(10), 73–80, 2000.
20. Sinha, K., Saha, P.D., Datta, S., Response surface optimization and artificial neural networmodeling of microwave assisted natural dye extraction from pomegranate rind. *Ind. Crops Prod.,* 37(1), 408–414, 2012.
21. Tayade, P.B., Adivarekar, R.V., Adsorption kinetics and thermodynamic study of Cuminum cyminum L. dyeing on silk. *J. Environ. Chem. Eng*., 1(4), 1336–1340, 2013.
22. Kamel, M.M., El-Shishtawy, R.M., Youssef, B.M., Mashaly, H., Ultrasonic assisted dyeing. IV. Dyeing of cationised cotton with lac natural dye. *Dyes Pigm.,* 73(3), 279–284, 2007.
23. Yusuf, M., Mohammad, F., Natural colorant from Lawsonia Inermis leaves: Reflectance spectroscopy-induced optimal conditions of extraction and dyeing,in: *Plant-Based Natural Products: Derivatives and Applications,* S-U. Islam (Ed.), pp.89–101, John Wiley-Scrivener, Hoboken, USA, 2017.
24. Stintzing, F.C., Carle, R., Functional properties of anthocyanins and betalains in plants, food, and in human nutrition. *Trends Food Sci. Technol.,* 15(1), 19–38, 2004.
25. Harborne, J.B., Williams, C.A., Anthocyanins and other flavonoids. *Nat. Prod.Rep.,* 18(3), 310–33, 2001.
26. Kharbade, B.V., Agrawal, O.P., Analysis of natural dyes in Indian historic textiles. *JSTOR Studies Conserv*., 33, 1–8, 1988.

27. Zhang, X., Laursen, R.A., Development of mild extraction methods for the analysis of natural dyes in textiles of historical interest using LC-diode array detector-MS. *Analytical Chem.*, 77(7), 2022–2025, 2005.
28. Dweck, A.C., Nature provides huge range of colour possibilities. *Personal Care June,* 61–73, 2009.
29. Alihosseini, F., Sun, G., (Eds.) Antibacterial colorants for textiles, in: *Functional Textiles for Improved Performance, Protection and Health*, pp. 375–391, Woodhead, Publishing Ltd Cambridge, UK, 2011.
30. De, Santis, D., Moresi, M., Production of alizarin extracts from *Rubia tinctorum* and assessment of their dyeing properties. *Ind. Crops Prod.*, 26(2), 151–62, 2007.
31. Yusuf, M., Mohammad, F., Shabbir, M., Eco-friendly and effective dyeing of wool with anthraquinone colorants extracted from Rubia cordifolia roots: Optimization, colorimetric and fastness assay. *J. King Saud. University-Sci.,* 29(2), 137–144, 2017.
32. Bechtold, T., Mussak, R., Natural colorants–quinoid, naphthoquinoid and anthraquinoid dyes,in: *Handbook of Natural Colorants,* T. Bechtold, R. Mussak (Eds.), pp. 151–82, John Wiley & Sons, Chichester, UK, 2009.
33. Han, S., Yang, Y., Antimicrobial activity of wool fabric treated with curcumin. *Dyes Pigm.,* 64(2), 157–161, 2005.
34. Taylor, G.W., Natural dyes in textile applications. *Rev. Prog. Color. Relat. Top.,* 16, 53–61, 1986.
35. Bae, J.S., Huh, M.W., The Dyeability and Antibacterial Activity of Wool Fabric Dyed with Cochineal. *Text. Color. Finishing,*18(5), 22–29, 2006.
36. Papageorgiou, V.P., Assimopoulou, A.N., Couladouros, E.A., Hepworth, D., Nicolaou, K.C., The chemistry and biology of alkannin, shikonin, and related naphthazarin natural products. *Angew. Chemie. Int. Ed.*, 38(3), 270–301, 1999.
37. Ordoudi, S.A., Tsermentseli, S.K., Nenadis, N., Assimopoulou, A.N., Tsimidou, M.Z., Papageorgiou, V.P., Structure-radical scavenging activity relationship of alkannin/shikonin derivatives. *Food Chem.,* 124(1), 171–6, 2011.
38. Singh, D.K., Luqman, S., Mathur, A.K., Lawsonia inermis l.–a commercially important primaeval dying and medicinal plant with diverse pharmacological activity: A review. *Ind. Crops Prod.,* 65, 269–286, 2015.
39. Kapadia, G.J., Rao, G.S., Sridhar, R., Ichiishi, E., Takasaki, M., Suzuki, N., Konoshima, T., Iida, A., Tokuda, H., Chemoprevention of skin cancer: effect of Lawsonia inermis L.(Henna) leaf powder and its pigment artifact, lawsone in the Epstein-Barr virus early antigen activation assay and in two-stage mouse skin carcinogenesis models. *Anti-Cancer Agents Med. Chem.,* 13(10), 1500–1507, 2013.
40. Dawson, T.L., Examination, conservation and restoration of painted art. *Color Technol.,*123(5), 281–292, 2007.
41. Rangno, A.L., Hobbs, P.V., Microstructures and precipitation development in cumulus and small cumulonimbus clouds over the warm pool of the tropical

Pacific Ocean. *Quarterly J. Royal Meteorological Soc.,* 131(606), 639–673, 2005.

42. Ghaheh, F.S., Mortazavi, S.M., Alihosseini, F., Fassihi, A., Nateri, A.S., Abedi, D., Assessment of antibacterial activity of wool fabrics dyed with natural dyes. *J. Clean Prod.,* 72, 139–145, 2014.
43. Ferreira, E.C., Nogueira, A.R., Souza, G.B., Batista, L.A., Effect of drying method and length of storage on tannin and total phenol concentrations in Pigeon pea seeds. *Food Chem.,* 86(1), 17–23, 2004.
44. Khanbabaee, K., van, Ree, T., Tannins: classification and definition. *Nat. Prod. Rep.,* 18(6), 641–649, 2001.
45. Joshi, M., Ali, S.W., Purwar, R., Rajendran, S., Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products. *Indian J. Fibre Text. Res.*, 34, 295–304, 2009.
46. Sarkar, A.K., Dhandapani, R., Study of natural colorants as antibacterial agents on natural fibers. *J. Nat. Fibers*, 6(1), 46–55, 2009.
47. Dawson, T.L., It must be green: meeting society's environmental concerns. *Color Technol.,* 124(2), 67–78, 2008.
48. Downham, A., Collins, P., Colouring our foods in the last and next millennium. *Int. J. Food Sci. Technol.,* 35(1), 5–22, 2000.
49. Wrolstad, R.E., Anthocyanin pigments—Bioactivity and coloring properties. *J. Food Sci.,* 69(5), C419-C425, 2004.
50. Azeredo, H., Betalains: properties, sources, applications, and stability–a review. *Int. J. Food Sci. Technol.,* 44(12), 2365–2376, 2009.
51. Humphrey, A.M., Chlorophyll as a color and functional ingredient. *J, Food Sci.,* 69(5), 2004.
52. Mortensen, A., Carotenoids and other pigments as natural colorants. *Pure Appl. Chem.,* 78(8), 1477–1491, 2006.
53. Dufossé, L., Galaup, P., Yaron, A., Arad, S.M., Blanc, P., Murthy, K.N., Ravishankar, G.A., Microorganisms and microalgae as sources of pigments for food use: a scientific oddity or an industrial reality? *Trends Food Sci. Technol.,* 16(9), 389–406, 2005.
54. Cho, M.H., Paik, Y.S., Hahn, T.R., Enzymatic conversion of precarthamin to carthamin by a purified enzyme from the yellow petals of safflower. *J. Agric. Food Chem.,* 48(9), 3917–21, 2000.
55. Velmurugan,P.,Kamala-Kannan,S.,Balachandar,V.,Lakshmanaperumalsamy, P., Chae, JC., Oh B.T. Natural pigment extraction from five filamentous fungi for industrial applications and dyeing of leather. *Carbohydrate Polym.*, 79(2), 262–268, 2010.
56. Delgado-Vargas, F., Jiménez, A.R., Paredes-López, O., Natural pigments: carotenoids, anthocyanins, and betalains—characteristics, biosynthesis, processing, and stability. *Crit.Rev.Food Sci.Nutr.*, 40(3), 173–289, 2000.
57. Castañeda-Ovando, A., de, Lourdes, Pacheco-Hernández, M., Páez-Hernández, M.E., Rodríguez, J.A., Galán-Vidal, C.A., Chemical studies of anthocyanins: A review. *Food Chem.,* 113(4), 859–871, 2009.

58. Chattopadhyay, P., Chatterjee, S., Sen, S.K., Biotechnological potential of natural food grade biocolorants. *Afr. J. Biotechnol.,* 7(17), 2972–2985, 2008.
59. Burrows, J.D., Palette of our palates: a brief history of food coloring and its regulation. *Comprehen. Rev. Food Sci. Food Safety*, 8(4), 394–408, 2009.
60. Gies, P., Elix, R., Lawry, D., Gardner, J., Hancock, T., Cockerell, S., Roy, C., Javorniczky, J., Henderson, S., Assessment of the UVR protection provided by different tree species. *Photochem. Photobiol.,* 83(6), 1465–1470, 2007.
61. Crews, P.C., Hustvedt, G., The ultraviolet protection factor of naturally-pigmented cotton. *Clothing Design J. Cotton Sci.,* 9, 47–55, 2005.
62. Sarkar, A.K., An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants. *BMC Dermatol.*, 4(1), 15, 2004. https://doi.org/10.1186/1471-5945-4-15
63. Grifoni, D., Bacci, L., Zipoli, G., Albanese, L., Sabatini, F., The role of natural dyes in the UV protection of fabrics made of vegetable fibres. *Dyes Pigm.*, 91(3), 279–85, 2011.
64. Gulrajani, M.L., Deepti, G., Emerging techniques for functional finishing of textiles. *Indian J. Fibre Text. Res.,* 36, 388–397, 2011.
65. Mongkholrattanasit, R., Kryštůfek, J., Wiener, J., Viková, M., UV protection properties of silk fabric dyed with eucalyptus leaf extract. *J. Text. Institute,* 102(3), 272–279, 2011.
66. Hou, X., Chen, X., Cheng, Y., Xu, H., Chen, L., Yang, Y., Dyeing and UV-protection properties of water extracts from orange peel. *J. Clean. Prod.,* 52, 410–419, 2013.
67. Kato, H., Hata, T., Tsukada, M., Potentialities of natural dyestuffs as antifeedants against varied carpet beetle, Anthrenus verbasci. *J. Japan Agric. Res. Quart.,* 38(4), 241–251, 2004.
68. Narayan, M.R., Dye sensitized solar cells based on natural photosensitizers. *Renew. Sust. Energy Rev.*, 16(1), 208–215, 2012.
69. Zhou, H., Wu, L., Gao, Y., Ma, T., Dye-sensitized solar cells using 20 natural dyes as sensitizers. *J. Photochem. Photobiol. A: Chem.,* 219(2), 188–194, 2011.
70. Campbell, W.M., Jolley, K.W., Wagner, P., Wagner, K., Walsh, P.J., Gordon, K.C., Schmidt-Mende, L., Nazeeruddin, M.K., Wang, Q., Grätzel, M., Officer, D.L., Highly efficient porphyrin sensitizers for dye-sensitized solar cells. *J. Phys. Chem. C.,* 111(32), 11760–11762, 2007.
71. Hao, S., Wu, J., Huang, Y., Lin, J., Natural dyes as photosensitizers for dye-sensitized solar cell. *Solar Energy,* 80(2), 209–214, 2006.
72. Fernando, J.M., Senadeera, G.K., Natural anthocyanins as photosensitizers for dye-sensitized solar devices. *Curr. Sci.,* 95(5), 663–666, 2008.
73. Chang, H., Wu, H.M., Chen, T.L., Huang, K.D., Jwo, C.S., Lo, Y.J., Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea. *J. Alloys Comp.*, 495(2), 606–610, 2010.
74. Chang, H., Lo, Y.J., Pomegranate leaves and mulberry fruit as natural sensitizers for dye-sensitized solar cells. *Sol. Energy,* 84(10), 1833–1837, 2010.

75. Heera, T.R., Cindrella, L., Molecular orbital evaluation of charge flow dynamics in natural pigments based photosensitizers. *J. Molecul. Model,* 16(3), 523–533, 2010.
76. Yamazaki, E., Murayama, M., Nishikawa, N., Hashimoto, N., Shoyama, M., Kurita, O., Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells. *Sol. Energy*, 81(4), 512–516, 2007.
77. Wongcharee, K., Meeyoo, V., Chavadej, S., Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers. *Sol. Energy Mater. Sol. Cells,* 91(7), 566–571, 2007.
78. Sivakumar, V., Vijaeeswarri, J., Anna, J.L., Effective natural dye extraction from different plant materials using ultrasound. *Ind. Crops Prod.,* 33(1), 116–22, 2011.
79. Goktas, O., Duru, M.E., Yeniocak, M., Ozen, E., Determination of the color stability of an environmentally friendly wood stain derived from laurel (Laurus nobilis L.) leaf extracts under UV exposure. *Forest Prod. J.,* 58(1/2), 77, 2008.
80. Savvidou, M.I., Economides, D.G., Colour gamut produced by applying mixtures of natural dyes on de-inked mechanical pulp. *Color Technol.*, 123(2), 119–23, 2007.
81. van, Dam, J.E., van, den, Oever, M.J., Keijsers, E.R., van, der, Putten, J.C., Anayron, C., Josol, F., Peralta, A., Process for production of high density/high performance binderless boards from whole coconut husk: Part 2: Coconut husk morphology, composition and properties. *Ind.Crops Prod.,* 24(2), 96–104, 2006.
82. Chigurupati, N., Saiki, L., Gayser, C., Dash, A.K., Evaluation of red cabbage dye as a potential natural color for pharmaceutical use. *Int.J. Pharmaceut.,* 241(2), 293–299, 2002.
83. Tousson, E., Al-Behbehani, B., Black mulberries (Morus nigra) as a natural dye for animal tissues staining. *Animal Biol.*, 61(1), 49–56, 2011.
84. Siva, R., Mathew, G.J., Venkat, A., Dhawan, C., An alternative tracking dye for gel electrophoresis. *Curr. Sci.*, (00113891). 94(6), 765–767, 2008.
85. Khan, P.M., Farooqui, M., Analytical Applications of Plant Extract as Natural pH Indicator: A Review. *J. Adv. Scientific Res.,* 2(4), 20–27, 2011.
86. Reddy, M.S., Sivaramakrishna, L., Reddy, A.V., The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *J. Hazard Mater.,* 203, 118–127, 2012.

6

Lichen Derived Natural Colorants: History, Extraction, and Applications

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Abstract
Color makes human life more aesthetic and fascinating as it is one of the basic elements of nature in the world. Dyes from plants, animals, and minerals have been used as primary sources for coloration of textile substrate from ancient times. However, lichens form a group of more peculiar natural colorants in dyeing violet and purple colors, widely used in Europe and other parts of the world during the period from ancient times to the beginning of the Middle Ages. Mollusk and shellfish dyestuffs were very expensive and difficult to obtain. It was a unique dyeing tradition for the Mediterranean and European cultures. This chapter gives a detailed account of the history, extraction, and applications of lichen based natural colorants along with the chronological developments in dyeing processes and the origins of lichen dyes used from ancient times.

Keywords: Natural colorants, lichens, mollusk, shellfish, purple, violet

6.1 Introduction

Lichens are curious plants, composed of fungi and algae that often resemble splotches of paint peeling from rocks or wood. They have been used to create brilliant, versatile dyes for over 4,000 years. Lichens form a group

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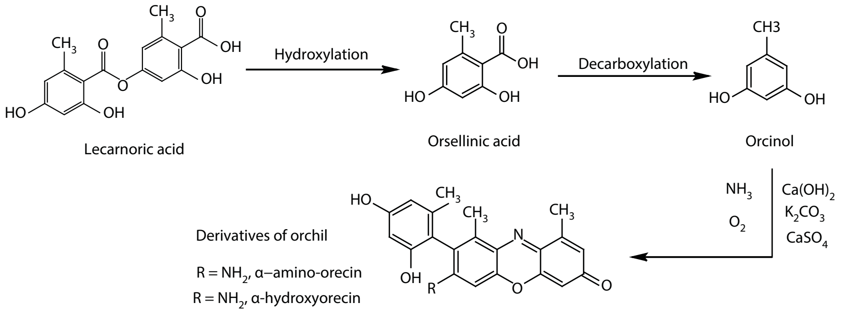
of more peculiar natural colorants. They have been widely used in Europe and also in other parts of the world as sources of natural colorants, especially in dyeing violet and purple colors [1]. In the times of Mediterranean civilizations, violet and purple colors were most commonly obtained from mollusks and were very expensive due to the tedious extraction and purification processes. However, lichen dyes were easier to collect as they were found everywhere on coastal areas and the dyeing with lichen colorants was much simpler with only disadvantage of poor light-fastness properties [2]. Hence, lichen dyes were used for cheaper textile materials. In that way the precious mollusk colorants were economized [1–3]. Lichen dyes were occasionally used to produce 'false shellfish purples.' The ammonia fermentation of lichen dye extracts of different species and subsequent oxidation in air produces orchillichen dyes. The lichens were prepared by immersion in ammonia-rich aqueous solution (e.g., urine) and during the resulting fermentation, depside or depsidone were hydrolyzed to orsellic acid. Decarboxylation of orsellic acid yields orsinol which reacts by a sequence of condensation reactions incorporating nitrogen from ammonia to give various orcein derivatives (Scheme 6.1). Depending on the pH and the presence of mordants, these can give bright red, purple or orange dyes [4].

Among the other uses of lichens, medicinal attributes are often related to the lichen secondary compounds that are abundant in most lichen thalli. Different lichens produce a wide variety of these unique compounds many of which are antibiotic. Many lichen extracts have been found to have bactericidal effects which include bacterial species that cause boils, scarlet fever, and pneumonia. One of the most potent lichen antibiotics is usnic acid which is most commonly used in traditional medicines [5]. There are records of lichens being used as food by many different human



Scheme 6.1 Chemical reactions occurring in purple dyeing procedure.

cultures across the world. Lichens are eaten by people in North America, Europe, Asia, and Africa, and perhaps elsewhere. Often lichens are merely famine foods eaten in times of dire needs, but in some cultures lichens are a staple food or even a delicacy [6]. However, in this particular chapter, we review the applications of lichen species for producing innumerable natural colorants to develop colored textile materials of varying hue and tone. The information reported in this review will help researchers to utilize lichens more effectively and convince them to use lichens as commercial dyes that has ability to duplicate colors produced from natural dyes.

6.2 History

Ethnolichenology is the study of relationship between lichens and people. Lichens have been used for many different purposes by human cultures across the globe. Most commonly lichens have been used for dyeing purposes in addition to medicine, food, and other purposes. The use of lichens in embalming dates to the 18th Dynasty, where *Pseudeverniafurfuracea* was found in an Egyptian vase. *P.furfuracea* was employed for its preservative and aromatic qualities. It was also used simply as a highly absorbent, light-weight packaging material. It also contains antibiotic substances. These qualities helped to inhibit bacterial decay of the mummies. Another discovery is that the Egyptians would grind and mix *P.furfuracea* with their flour for bread. *P.furfuracea* was imported shiploads from the Grecian archipelago to Alexandria [7]. *Rocellatinctoria* D.C. and *Rocellafuciformis* D.C. were the most important lichens which can be found in the East Indies, South and Central America, Cape Verde Islands (West Coast of Africa), Madagascar and Europe. *Pertusariadealbescens*Erichs from France and *Orchrolechiatartarea* L. (‘cudbear’) from Scandinavian and Celtic countries were also used for lichen dyes [4, 8, 9]. Today embalming fluids are colored from the lichen dye orchil into a product called Cudbear, illustrating how a historical procedure can influence future practices.

In North America, the most significant yellow lichen dye is *Letharia vulpine* extracted in boiling water. Many of the traditional dyes of the Scottish Highlands were made from lichens including red dyes from the cudbear lichen (*Lecanoratartarea*), the common orange lichen (*Xanthoriaparietina*), and several species of leafy *Parmelia* lichens. Tartans were extensively produced from red, brown and yellow lichen dyes from *Parmeliasaxatilis*. Purple lichen dyes were historically important throughout Europe from the 15th to 17th centuries. They were generally extracted from *Roccella* spp. Orchil dye was also produced from *Ochrolechia* spp. in

Britain and was called cudbear. Both *Roccella* and *Ochrolechia* species contain the lichen substance orcin. Litmus, a water-soluble pH indicator dye mixture, is extracted from *Roccella* species. In Northern Europe, Scotland and Scandinavia yellowish, brownish, and reddish brown colors were obtained using a simpler dyeing method in which lichens were boiled in water together with mordanted or un-mordanted wool [1, 2, 9–12]. Similar dyeing methods were applied by the American Indians in their traditional textiles [1, 2]. Recent investigations reveal that there is more information than suspected about the use of fungi for dyeing textiles. It seems that fungi have been used as a source of color on all continents, Europe, North Africa and America as well as Asia [1]. The American Indians obtained red color from the fungus *Echinodontiumtinctorium*. Sometimes Americans dyed with colorants obtained from mushrooms pretreated with alum mordants giving furs luxurious golden hues [10, 11]. Fungi belonging to *Polyporales* were used to dye wool in Italy and France. In Northern Europe several authors refer to lichen and fungal colorants [12–16]. During the Second World War, some experiments were carried out in Europe aiming at the use of fungi as a source of textile colorants [13].

6.3 Lichen Dyes and Industrial Revolution

Due to the recent debate on diminishing fossil resources and ecological design natural dyes have gained growing interest [17–21]. Research has been done to promote the use of natural dyes in several fields of food, cosmetics and textile industries [22–25]. Lichen dyes played a significant role in industrial revolution. Dyeing of textile materials is commercially most valued application of lichens and lichen dyes had high economic value for many centuries until the discovery of synthetic dyes in 1950s. British dye industries although lagged behind that of European dye industries due to political and economical pressure to develop natural dyes from indigenous plants. The big limitation to the establishment of lichen dye industry was that even large amounts of lichen dyes weigh little; an entire family has to work for many hours to collect small amounts of lichens. The discovery of cudbear, a native dye yielding plant was found to be cheaper than orchil and lead to the first improvement and progress toward natural dyeing. The urban people saved urine by shifting themselves toward cudbear industries; which even draw the city dwellers into cudbear industry. Cudbear became popular because of its low prize. Carelessness in collecting lichen dyes and economical problem lead to the decline in the quality of lichen dyes [26].

6.4 Extraction

Orhil is obtained by fermenting lichen with ammonia, water, and oxygen in warm atmospheric conditions. A greenhouse or low sunny window-seat is good place in summertime. The temperature needs to be in between 56–75 °F throughout the fermentation period, which varies from three to four weeks. Although household ammonia hastens orchil maceration as compared with the old and primitive methods [1, 2]. The addition of chalk or lime toward the end of the fermentation period is necessary to give consistency to the mass. Orchil dye was used to dye wool, silk, wood, feathers, marble, and even leather. Litmus is still used as a reagent for Orchil to react to alkalis and acids; Cudbear is now being used once more as an edible dye for foodstuffs [26].

Lichens containing usnic acid are likely to give good clear yellows, but this color may be altered by the presence of other chemicals (acids) in the plants. For instance, *Hypogymniaphysodes* contains usnic acid, but it also contains other acids which in boiling water yields yellow brown color. Ammonia fermentation and boiling water extract different acid colors from same plant [27]. Thus fermented *Everniaprunastri* will yield an orchil from the evernic acid which it contains, and a pale yellow from another acid, by the boiling-water method. Some lichens have proved to be chemical strains, which means that a lichen is capable of producing more than one acid, any one of which present itself in different geographic areas or localities [28]. *Everniafurfuracea* (known as *Parmeliafurfuracea*in the U.S.A.) gives an orchil dye because of lecanoric acid content. However, in Britain, it presents a non-orchil acid, or a different orchil acid 'olivetoric acid'. *Parmeliasaxatilis* and *P. omphalodes* contain two acids; atranorine and salacinic acids, but *P. omphalodes*contains one other, lobaric acid. *P. omphalodes* always dyes a darker and faster brown than *P. saxatilis* [29].

6.5 Dye Stuffs from Lichens

Lichens are cryptograms, symbiotic organisms comprised of alga and fungal partners. Due to this symbiotic origin, lichens and fungi contain similar types of colorants (Table 6.1). Lichens form a group of peculiar natural colorants. They have been used as colorants sources in Europe and also in other parts of world. Especially lichens were important for dyeing purple and violet colors. Lichens were used for the dyeing of wool and silk in ancient times and probably the most famous are the lichens known collectively as the orchil lichens [1]. Yellowish, brownish, and reddish brown colors were obtained using simple dyeing method in which lichens were

Table 6.1 Chemical structures of some coloring compounds obtained from different lichen species.

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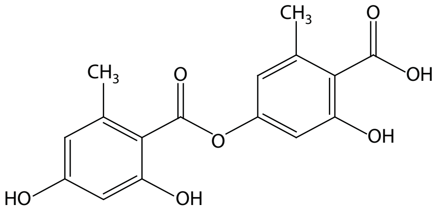

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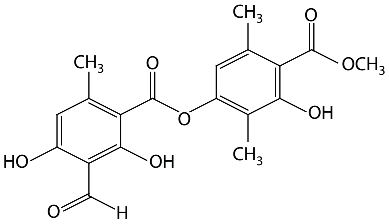

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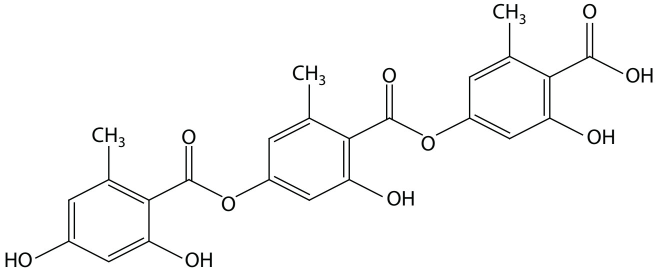

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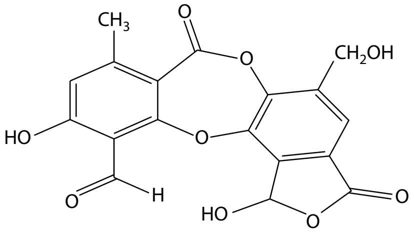

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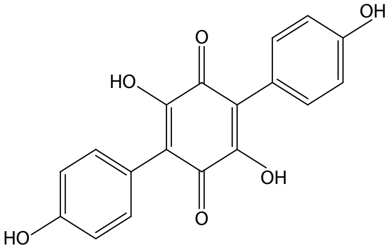

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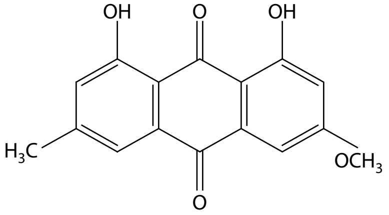

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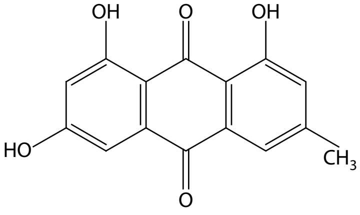

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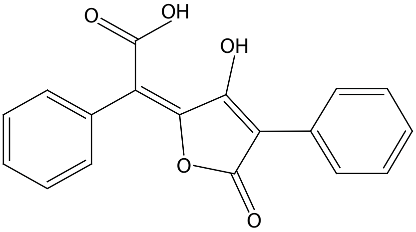
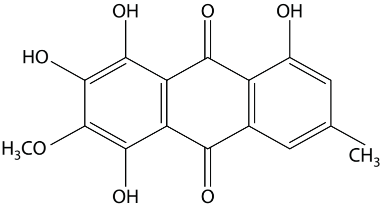
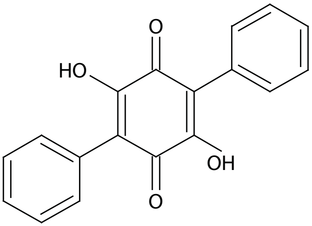
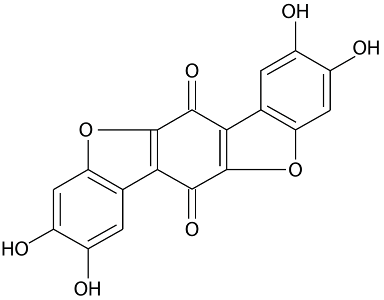
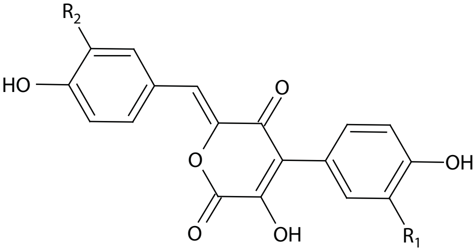
 Pulvinic acid	 Dermocybin
 Polyphoric acid	 Telephoric acid
 $R_1 = R_2 = H$: Grevillin A $R_1 = H, R_2 = OH$: Grevillin B $R_1 = R_2 = OH$: Grevillin C	

boiled in water together with mordanted and un-mordanted wool [27]. Figure 6.1 shows the color wheel obtained from lichens. Many colorants in lichens and fungi are benzoquinone derivatives particularly terphenylquinone [30]. Some species, e.g., Sarcodon, Phellodon, Hydnellum, and

Figure 6.1 Color wheel for lichen dyes.

Telephora containing these chemical compounds are known to give blue color, which is rare in nature, to wool fibers [1, 30, 31].

6.5.1 Lichen Dyestuffs: Orchils and Litmus

Both orchil and litmus are colorants not found in plants. Although, they are formed from their colorless precursors through enzymatic hydrolysation, decarboxylation, and oxidation processes (Scheme 6.1). Precursors of orchil and litmus exist in several species of lichen, e.g. Roccella and Lecanora spp. [30]. The color of both litmus and orchil are pH-dependent; in acidic conditions the dyestuffs form red cations while in the basic conditions they give bluish violet colors in their anionic forms [1, 30]. Lichens from Rocella sp. contain lecanoric acid up to 3–4 % on dry weight basis [30]. Orchil is a complex mixture of several other orceins e.g. β- and γ-aminoorcein, β- and γ-hydroxyorcein and β- and γ-aminoorceimine [1].

6.5.2 Yellowish, Brownish and Reddish Colorants from Lichen

Atranorinis found in *Parmelia* sp. and *Xanthoriaparietina* where as gyrophoric acid in *Ochrolechiatartarea* and *Lasalliapustulata*. Salizinic acid, the derivative of atranorin, is found in *Parmeliasaxatilis* and several other *Parmelia* spp. In Scottish Highlands, woolen materials used in tweeds are dyed in yellowish, reddish, and brownish hues by these lichens [1, 9, 30].

6.6 Ways of Dyeing with Lichens

Traditionally, there are two ways of dyeing with lichens. The first method demonstrates the extraction of lichen colorants with acidified boiling water. However, acid and peat-stained mountain water may give even better results. After boiling point is reached, heat is lowered and left for simmer for three hours. The well-wetted wool fibers/fabrics are entered next day, brought up to boiling point and simmered until the desired depth of color has been obtained. The second method demonstrates the use of lichen dyes along with that of wool fibers in which the dye-bath is nearly three quarters filled with alternate layers of wool and lichens. The bath is then filled with acidified soft water, and the mixture simmered until the desired shade is obtained. Fleece can be dyed by this method. However, more recently DEM extraction method has been found to provide green, brown, and yellow shades [32].

These lichen dyes can be applied without use of mordant on wool, but wool can be dyed in yellow hues with *Peltigeracanina* when mordanted with alum. White or natural carpet wool takes the brown lichens very well, and a rug woven with the wool will always have an attractive aroma. A very beautiful red-brown can be got by using an orchil dye over a dark *P. omphalodes* brown, or by bottoming with orchil. *Xanthoriaparietina* will yield a golden brown in boiling water and various shades of pink or purplish pink in alkaline environment. Chrome mordanted wool takes a dusky pink color [33, 34].

6.7 Future Prospectus and Conclusion

Recently, significant advances have been made to exploit other unique properties of natural compounds. Fungi and lichens have been used for centuries for their high medicines attributes and now these medicinal properties have been recognized as a growing opportunity in textile and healthcare applications [35]. Emodin, the most widely distributed anthraquinone being present in moulds, higher fungi, lichens, flowering plants and insects has been obtained from fungi that have been cultivated on culture medium [36]. Recently, natural compounds have been found to have UV-protective properties and when applied to textiles could help humans from hazardous solar ultraviolet radiation [37]. Also, the antimicrobial activity of natural colorants brings new ideas to be considered when developing protective clothing or home textiles such towels and carpets. Modern textiles are required to have high degrees of chemical and photolytic stability in order to maintain their structure and color.

However, it is important to test the dyes also for their cytotoxicity and carcinogenic properties. For example, some anthraquinones, such as emodin and its chloro-derivatives, have been found to have slightly toxic or carcinogenic properties [38–40].

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References

1. Cardon, D., *Natural Dyes: Sources, Tradition, Technology and Science*, Archetype Publications, London, 2007.
2. Casselman, K.D., *Lichen Dyes and Dyeing: The New Source Book*, Dover Publications, Mineola, New York, 2001.
3. Casselman, K.D., *Magic, mystery and mayhem: lichen dyes old and new, in Publication of the Natural Dyes Product Research and Development Project*, EVTEK Institute of Art and Design, Vantaa, 2002.
4. Ferreira, E.S., Hulme, A.N., McNab, H., Quye, A., The natural constituents of historical textile dyes, *Chem. Soc. Rev.,* 33(6), 329–336, 2004.
5. Lauterwein, M., Oethinger, M., Belsner, K., Peters, T., Marre, R., In Vitro Activities of the Lichen Secondary Metabolites Vulpinic Acid, (+)-Usnic Acid, and (-)-Usnic Acid against Aerobic and Anaerobic Microorganisms, Antimicrob. *Agents Chemother.*, 39, 2541–2543, 1995.
6. Edwards, R.Y., Soos, J., Ritcey, R.W., Quantitative Observations on Epidendric Lichens Used as Food by Caribou, *Ecology*, 41, 425–431, 1960.
7. Kosanić, M., Ranković B., Lichen secondary metabolites as potential antibiotic agents, in: *Lichen Secondary Metabolites*, B. Ranković (Ed.), pp. 81–104, Springer, Cham, 2015.
8. Cardon, D., *Le monde des teinturesnaturelles*, Belin, Paris, 2003.
9. Knecht, E., Rawson, C., Loewenthal, R., *A manual of dyeing, (9th Edition)*, Griffin, C. and Co, London, 1933.
10. Grierson, S., Duff, D.G. Duff, Sinclair, R.S., Natural dyes of the Scottish Highlands, *Tex. History,* 16, 23–43, 1985.
11. Taylor, G.W., Reds and purples: from the Classical World to Pre-Conquest Britain, in: *Textiles in Northern Archaeology, NESAT III:* Textile Symposium

in York, Northern European Symposium for Archaeological Textiles, P. Walton, J.P. Wild, (Eds.), IAP Archetype Publications, London, 1990.

12. Wallart, A., Fluorescent assay of quinone, lichen and redwood dyestuffs, *Stud. Conser.,* 31, 145–155, 1986.
13. Hall, A.R., Tomlinson, P.R., Dye plants from Viking York, *Antiquity*, 58, 58–60, 1984.
14. Fasidi, I.O., Kadi, M., Use of agricultural wastes for the cultivation of *Lentinussuhnudus* (*Polyporales: Polyporaceae*) in Nigeria, *Rev. Biol. Trop.*, 41, 411–415, 1993.
15. Linder, J., *SvenskaFarge-konst. Med InlandskaOrter, Gras, Blommor, Blad, Laf, Barkar, Rotter, WarterochMineralier*, 2nd edition, Lars Salvius, Stockholm, 1749.
16. Westring, J.P., *SvenskaLafvarnasFarghistoriaellerSattetattAnvandadem till FargningochannanHushallsnytta*, Delen, C., Stockholm, 1805.
17. Palmstruch, J.W., *Svenskbotanik,*Delen, C., Stockholm, 1802–1819.
18. Rather, L.J., Islam, S., Akhter, S., Hassan, Q.P., Mohammad, F., Chemistry of Plant dyes: Applications and Environmental Implications of Dyeing Processes, *Curr. Env. Eng.*, 4, 103–120, 2017.
19. Rather, L.J., Akhter, S., Padder, R.A., Hassan, Q.P., Hussain, M., Khan, M.A., Mohammad, F., Colorful and semi durable antioxidant finish of woolen yarn with tannin rich extract of *Acacia nilotica* natural dye, *Dyes Pigm.*, 139, 812–818, 2017.
20. Rather, L.J., Islam, S., Shabbir, M., Bukhari, M.N., Shahid, M., Khan, M.A., Mohammad, F., Ecological dyeing of Woolen yarn with *Adhatodavasica* natural dye in the presence of biomordants as an alternative copartner to metal mordants, *J. Env. Chem. Eng.*,4, 3041–3049, 2016.
21. Rather, L.J., Islam, S., Azam, M., Shabbir, M., Bukhari, M.N., Shahid, M., Khan, M.A., Haque, Q.M.R., Mohammad, F., Antimicrobial and fluorescence finishing of woolen yarn with *Terminaliaarjuna*natural dye as an ecofriendly substitute to synthetic Antibacterial agents, *RSC Adv.*, 6, 39080–39094, 2016.
22. Rather, L.J., Islam, S., Khan, M.A., Mohammad, F., Adsorption and Kinetic studies of *Adhatodavasica* natural dye onto woolen yarn with evaluations of Colorimetric and Fluorescence Characteristics, *J. Env. Chem. Eng.*, 4, 1780–1796, 2016.
23. Yusuf, M., Ahmad, A., Shahid, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsoniainermis*), *J. Clean. Prod.*, 27, 42–50, 2012.
24. Yusuf, M., Shahid, M., Khan, S.A., Khan, M.I., Islam, S., Mohammad, F., Khan, M.A., Eco-dyeing of wool using aqueous extract of the roots of Indian madder (*Rubiacordifolia*) as natural dye, *J. Nat. Fibers*, 10, 14–28, 2013.
25. Rather, L.J., Islam, S., Mohammad, F., Study of the application of *Acacia nilotica* natural dye on wool using Fluorescence and FTIR-Spectroscopy, *Fibers Poly.,* 16, 1497–1505, 2015.

26. Khan, S.A., Islam, S., Shahid, M., Khan, M.I., Yusuf, M., rather, L.J., Khan, M.A., Mohammad, F., Mixed metal mordant dyeing of wool using root extract of *Rheum emodi* (Indian Rhubarb/Dolu), *J. Nat. Fibre*, 12, 243–255, 2015.
27. Devkota, S., Chaudhary, R.P., Werth, S., Scheidegger, C., *J. Ethnobiol. Ethnomed.*, 2017. https://doi.org/10.1186/s13002–017-0142–2
28. Fernández-Moriano, C., Divakar, P.K., Crespo, A., Gómez-Serranillos, P.M., Protective effects of lichen metabolites evernic and usnic acids against redox impairment-mediated cytotoxicity in central nervous system-like cells, *Food Chem. Toxicol.*, 105, 262–277, 2017.
29. Llano, G.A., Economic uses of lichens, *Econ. Bot.*, 2, 15–45, 1948.
30. Schweppe, H., *Handbuch der Naturfarbstoffe,*Ecomed, Landsberg/Lech, 1993.
31. Rice, M., Mushrooms for Color, (2nd eds.), Mad River Press, Eureka, California, 1980.
32. Shukla, P., Upreti, D.K., Nayaka, S., Tiwari, P., Natural dyes from Himalayan lichens, *Ind. J. Trad. Knowl.*, 13, 195–201, 2014.
33. Upreti. D.K., Tiwari, P., Shukla, P., Dwivedi, A., Natural thalli and cultured mycobiont of *U. ghattensis*G. Awasthi: A potential source of purple dye yielding lichen from India, *Ind. J. Nat. Prod. Resour.*, 3, 489–492, 2012.
34. Upreti, D.K, Divakar, P.K., Nayaka, S., Commercial and Ethnic Use of Lichens in India, *Econ. Bot.,* 59, 269–273, 2005.
35. Duran, N., Teixeira, M.F.S., Conti, R.D., Esposito, E., Ecological-friendly pigments from fungi, *Crit. Rev. Food Sci. Nutr.*, 42, 53–66, 2002.
36. Thomson, R.H., *Naturally Occurring Quinones,* 2nd edition, Academic Press, London, 1971.
37. Feng, X.X., Zhang, L.L., Chen, J.Y., Zhang, J.C., New insights into solar UV-protective properties of natural dye, *J. Clean. Prod.*, 15, 366–372, 2007.
38. Gross, M., Levy, R., Toepke, H., Zumvorkommen und zurAnalytik des MycotoxinsEmodin, *Nahrung*, 28, 31–44, 1984.
39. Cohen, P.A., Hudson, J.B., Towers, G.H.N., Antiviral activities of anthraquinones, bianthrones and hypericin derivatives from lichens, *Experientia*, 52, 180–183, 1996.
40. Von Wright, A., Raatikainen, O., Taipale, H., Karenlampi, S., Maki-Paakkanen, J., Directly acting geno- and cytotoxic agents from a wild mushroom Cortinariussanguineus, *Mutation. Res.*, 269, 27–33, 1992.

7

Chlorophylls as Pigment: A Contemporary Approach

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Abstract

Abundantly available chlorophylls are found in nature with primary function photosynthesis, which is the fundamental process for life on Earth. However, their use as colorants is not more common due to their chemical instability and high production costs. Chlorophylls are showing the possibility of excellence alternatives with a real potential of usage are water-soluble, metal-chelated chlorophyll derivatives. Due to the unique physicochemical and photochemical characteristics and biological activities, these pigments are used as food colorants and in the wide range of other industrial applications and also have beneficial effects on human health. Natural chlorophyll-derived pigments are marketed in different pharmaceutical forms for a variety of dietary and medicinal uses for therapeutic purposes, which include anti-inflammatory activity, the stimulator of wound healing, and the regulator of immunity. Chlorophylls and chlorophyllins are capable of reducing the number of dietary mutagenic and environmental carcinogenic activity, but copper-complexed chlorophyllins seem to be more effective in all chlorophyllins. Chlorophyllin is more effective antimutagen than β-carotene, retinol, vitamins C and E against certain dietary and environmental carcinogens as reported in several literatures. But there are still some controversial results reported in the literature for the variable composition and purity of commercial preparations. This is the reason behind the expectation of further investment in research for the future development of stable chlorophylls.

Keywords: Pigment, chlorophyll, chlorophyllin, green plants.

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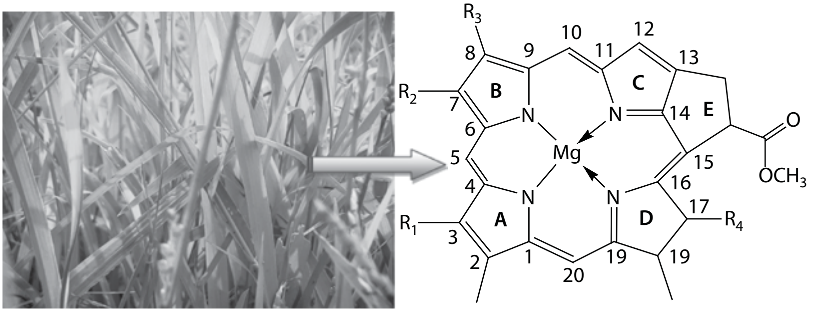
7.1 Introduction

Environmental toxicants level is increased, which shows the bad effect on human population and these bad effects have led to an intensive search for naturally occurring plant products to reduce genotoxic effects. The principal component of plant extract is chlorophyll, which is omnipresent in all green plant parts. The primary function of chlorophylls is photosynthesis, which is the fundamental process for life on Earth. Chlorophylls absorb light most strongly in the blue portion of the electromagnetic spectrum, followed by the red portion [1, 2]. Inversely, it is a poor absorber of green and near-green portions of the spectrum, which gets reflected and produces the green color of chlorophyll-containing tissues. Chlorophyll molecules are specifically arranged in and around photo systems that are embedded in the thylakoid membranes of chloroplasts [2, 3]. The planar porphyrin has 'head' with magnesium and a long phytol 'tail'. Chlorophyllins are derivatives of chlorophyll in which the magnesium is replaced by other metals like copper, iron or cobalt. However, abundantly present in nature, their use as colorants is not more common due to their chemical instability and high production costs. Chlorophylls are showing the possibility of excellence alternatives with a real potential of usage are water-soluble, metal-chelated chlorophyll derivatives. Due to the unique physicochemical and photochemical characteristics and biological activities, these pigments are used as food colorants and in the wide range of other industrial applications and also have beneficial effects on human health. Natural chlorophyll-derived pigments are marketed in different pharmaceutical forms for a variety of dietary and medicinal uses in therapeutic purposes, which include anti-inflammatory activity, the stimulator of wound healing, and the regulator of immunity. Chlorophylls and chlorophyllins are capable of reducing the number of dietary mutagenic and environmental carcinogenic activity, but copper-complexed chlorophyllins seem to be more effective in all chlorophyllins. Chlorophyllin is more effective antimutagen than β-carotene, retinol, vitamins C and E against certain dietary and environmental carcinogens as reported in several literature [2–5]. But there is still some controversial results reported in the literature for the variable composition and purity of commercial preparations. This is the reason behind the expectation of further investment in research for future development of stable chlorophylls [4–7].

7.2 Molecular Structure and Physico-Chemical Characterization

The basic chemical structure of chlorophylls contains porphyrin macrocycle, which is a cyclic tetrapyrrole derivative. It has four pyrrole rings which are joined via one carbon bridges to an aromatic macrocycle with shared electron density of 18 electrons around the tetrapyrrole unit. It is a system of coplanar conjugated double bonds that form an aromatic structure with delocalization of electron density in π-orbitals. In the centre of chlorophylls, four nitrogen faces inward creating a hole that is ideal for binding metal ions which is almost always magnesium (Mg). Beside four pyrrole rings (A, B, C, and D), Chlorophylls carry a characteristic iso-cyclic five-membered ring E. A monounsaturated isoprenoid alcohol (phytol) esterified to propionic acid located at C-17 gives chlorophyll *a* hydrophobic character. There are three main classes of chlorophylls divided by the degree of unsaturation of the macrocyle. Porphyrins with a completely unsaturated macrocycle are mainly present in chlorophyll *c*, present in chromophyte algae and in some prokaryotes. The most common chlorophylls are the chlorins, which present a saturated bond between C17 and C18. Chlorins are chlorophyll *a*, *b*, and *d* (oxygenic organisms), and bacterio-chlorophylls *c*, *d*, and *e* (green anoxygenic bacteria). Structurally, chlorophyll *a* and chlorophyll *b* differ from each other due to a substituent on the second pyrrole ring (ring B) at the C-7 position [8]. Chlorophyll *a* has a methyl group ($-CH_3$) at the C-7 position, whereas chlorophyll *b* has a formyl group (–CHO). Chlorophyll *d* has a very similar structure with chlorophyll *a*, except that it contains formyl group instead of vinyl group ($-HC{=}CH_2$) at the C-3 position. Apart from them, chlorophyll *f* has been identified in recent years, also with a chlorin structure, in stromatolites of cyanobacteria. Chlorophyll *a* is found in all photosynthetic organisms, except some groups of bacteria. Chlorophyll *b* is present in all higher plants, and in algae of the divisions Chlorophyta and Euglenophyta, always accompanying chlorophyll *a* as an accessory pigment in the photosynthetic process. Chlorophyll *a* and chlorophyll *b* are the most abundant types in higher plants. They are generally present at ratios between 3:1 and 1:1. This ratio varies depending on genetic and environmental factors such as ripening stage, species, luminosity, stress, and other factors [9]. The molecular structures of major chlorophylls are shown in Figure 7.1 [10]. The conjugated electronic structure of chlorophyll leads to a high probability of electronic transitions from the highest occupied molecular



Chlorophylls	R_1	R_2	R_3	R_4
Chlorophyll *a*	$CH=CH_2$	CH_3	CH_2CH_3	$(CH_2)_2COOC_2$0H39
Chlorophyll *b*	$CH=CH_2$	CHO	CH_2CH_3	$(CH_2)_2COOC_2$0H39
*Chlorophyll c_1	$CH=CH_2$	CH_3	CH_2CH_3	CH_2=CHCOOH
*Chlorophyll c_2	$CH=CH_2$	CH_3	CH=CH2	CH_2=CHCOOH
*Chlorophyll c_3	$CH=CH_2$	$COOCH_3$	CH=CH2	CH_2=CHCOOH
Chlorophyll *d*	CHO	CH_3	CH_2CH_3	$(CH_2)_2COOC_2$0H39

#double bond occur in all chlorophylls c (c_1,c_2,c_3) between C-17 and C-18

Figure 7.1 Structure of some natural chlorophylls.

orbitals to the lowest unoccupied molecular orbitals and ensures absorbance spectrum. Chlorophylls show two absorption regions corresponding to the first excited state (red band) and to the second one (blue or Soret band). Different chlorophyll derivatives will present differences in the relative absorbance intensity (red to blue band) and in the position of the respective band. This is due to structural characteristics of the macrocycle, the peripheral groups, and the nature of the central metal ion that may have different effects on each resonance form and strongly influence the profile of their UV-Vis absorption spectra [11, 12].

Chlorophyll *a* has two characteristic bands in the 432 and 669 nm regions that correspond to the Soret band and Q-band, respectively. The corresponding bands for chlorophyll *b* are located at 455 and 644 nm, respectively. Although chlorophyll *b* is similar to chlorophyll *a*, except for having an aldehyde group in place of the methyl group at C-7, this small structural difference between both molecules generates significant differences in absorption spectra. Chlorophyll *c* has characteristic bands between 578 and 630 nm and between 443 and 450 nm. The absorbance spectrum of chlorophyll *d* is very close to that of chlorophyll a due to its structural similarity. It has a formyl group instead of a vinyl group at C-3 but is otherwise identical with chlorophyll *a*. [13]. Epimerization and allomerization reactions do not change the chromophore and therefore do not change the UV/Vis spectrum of the corresponding chlorophyll derivatives. Consequently, caution must be taken when identification of chlorophyll derivatives is performed solely on the basis of the UV/Vis characteristics. The complete quantitative spectroscopic data of most chlorophyll derivatives were compiled by Scheer (1988) [14] with references to λ_{max} values in different solvents and the corresponding molar extinction coefficients. In chloroplasts, chlorophylls are found bound to carotenoids, lipids, and lipoproteins *via* non-covalent bonds. For that reason, chlorophylls are easily extracted with organic solvents, especially polar solvents such as acetone, methanol, and ethanol [15].

7.3 Coloring Aspects

Different chlorophyll preparations are used in the industry as food colorants to reinforce green color to a manufactured product. General administrations in different countries delegate the mission of regulating and controlling food safety to food agencies, such as the European Food Safety Authority (EFSA) in Europe or the Food and Drug Administration (FDA) in the United States. Specifically, in food colorants legislation, European and American legislations are very different [16]. Certain colors that are permitted for use in Europe or Asia may not be acceptable in the United States and vice versa. Therefore, it is important to consider international implications regarding color additive regulations when working on products for international markets [17].

Unmodified chlorophylls are too labile for most practical use, but some derivatives are used as dyes for cosmetics and food (Cu-chlorophyllin), and in photodynamic tumor therapy (chlorins and bacteriochlorins). The chlorophyll used, for example, in certain health care products is a complex mixture of degradation products [18, 19]. In addition to their use as foods and pharmaceutical colorants, chlorophylls play a vital role in photosynthesis, creating the basis for the animal food chain on which most living organisms depend. The initial step of photosynthesis involves absorption of light by the light-harvesting antennae complexes and funneling the resulting electronic excitation to the photosynthetic reaction center, where the energy is used for the conversion of carbon dioxide and water into carbohydrates with the liberation of oxygen. The high levels and ubiquity of chlorophylls in a variety of leafy green vegetables raise questions about their bioavailability and metabolism and whether they may exert any biological function. Currently, there is considerable interest in studying chlorophylls, not only because of their coloring properties but also for their

Table 7.1 Some algae based pigments.

Class of the pigment	Colour	Chief source
Phycoerythrin	red	*Porphyridium cruentum*
Phycocyanin	blue green	*Spirulina platensis*
b-carotene	yellow orange	*Dunaliella salina*
Chlorophylls	green	*Chlorella sp.*
Fucoxanthin	brown	*Ascophyllum nodosum, Sargassum sp., Macrocystis pyrifera*

health-related biological activities [20]. Despite being the most abundant pigments in nature, chlorophylls have rarely been included in biological experiments, first due to the difficulty in purifying these pigments and the chemical instability of the molecules, and also because of the high costs involved. Natural chlorophylls are so unstable that in most research the commercially available semi-synthetic copper chlorophyllin, a saponified mixture of natural chlorophylls, has been used as a model for several experimental designs. Cu-chlorophyllin is easily available, water-soluble, and significantly more stable than natural chlorophyll [3, 5].

Literature revealed that algae contain a wide range of photosynthetic pigments such as chlorophylls, carotenoids (carotenes and xanthophylls) and phycobilins (Table 7.1) [1–5, 8, 10]. Due to the green color of chlorophylls and their derivatives, they are being used as dyes and pigments for dyeing fabrics such as wool and cotton [21].

Today, different nature-derived colorants and functional agents for textiles have been under consideration based on renewable sources (flora and fauna). Kadir *et al.* elucidated the dyeing mechanisms to understand dye–fiber interactions arising during the dyeing process with respect to natural renewable sources. In this study, colorimetric characteristics of colorants derived from *Sargassum sp.* was investigated on polyester fabric with dendrimer at different concentrations with and without mordants, and found brilliant outcome as *Sargassum sp.* extract is suitable to be used as natural dye for textile dyeing [22].

7.4 Characterization and Quality Control

Spectroscopic assays techniques are widely used for the determination of natural chlorophylls; however it is inadequate for correct determination of each component as all components have similar absorption spectra. Analytical results obtained from the Spectroscopic analysis are not close agreements with the data obtained by elemental analysis. There are no standards for the quantification of chlorophyllin and also lack of officially approved analytical methods to monitor the quality control. In studies where Chlorophylls spectrophotometric analysis was accompanied by elemental analysis of copper and nitrogen, a significant overestimation by the spectrophotometric analysis was found. Further this can be explained by the optical properties of the chlorophyllin in the blue region of the spectrum where measurements take place. If other colouring compounds like carotenoids and metal-free chlorophyll analogues are present in the sample, absorption is enhanced significantly. The ratio between copper and nitrogen contents has been used frequently as an indicator of the purity of chlorophyllin; however, studies have also shown inconsistent results. For an optimized quality control, the copper/nitrogen index should be accompanied by measurement of the percentage of absolute copper and nitrogen. The interference of carotenoids can be avoided by obtaining the total absorption in the red region of the spectrum [23]. This heterogeneity of commercial samples of chlorophyll–copper complexes may explain the different biological responses observed when administered to laboratory animals in 95 *in vitro* and *in vivo* tests. In addition, proper methods of analysis are needed for quality control [24].

7.5 Conclusion and Future Outlook

So far on the basis of the information related to the chlorophylls it can be concluded as part of a vegetable extract, especially green parts occur in complexed form instead of isolated compounds. The green plant extracts and chlorophyll-derived pigments are marketed for a variety of dietary and medicinal uses by several pharmaceutical companies. However, chlorophylls have been observed to show outstanding biological activities, which created a shift of emphasis to exert potential beneficial effects on human health such as anti-inflammatory, wound healing, immune modulator activities etc. However, cumulative scientific evidence is strengthening the assumption that natural chlorophylls and semi-synthetic water-soluble derivatives possess minimal toxicological and abortive effects [25, 26]. Conversely, published studies demonstrate that there is a limited research performed on chlorophyll as colorant. Therefore, in view of the above description, considerable research should still be invested for risk assessment in order to identify adverse health effects related to semi-synthetic chlorophyll derivatives as well as coloring potential.

References

1. Sarkar, D., Sharma, A., Talukder, G., Chlorophyll and chlorophyllin as modifiers of genotoxic effects, *Mut. Res.,* 318, 239–247, 1994.
2. *Photosynthetic Pigments. UCMP Glossary* (online). University of California Museum of Paleontology. http://www.ucmp.berkeley.edu/glossary/gloss3/pigments.html
3. Breinholt, V., Hendricks, J., Pereira, C., Arbogast, D., Bailey, G., Dietary chlorophyllin is a potent inhibitor of aflatoxin B1 hepatocarcinogenesis in rainbow trout, *Cancer Res.*, 55, 57–62, 1995.
4. Ritchie, R.J., Universal chlorophyll equations for estimating chlorophylls a, b, c, and d and total chlorophylls in natural assemblages of photosynthetic organisms using acetone, methanol, or ethanol solvents. *Photosynthetica*, 46(1), 115–126, 2008.
5. Kamat, J.P., Boloor K.K., Devasagayam, T.P.A., Chlorophyllin as an effective antioxidant against membrane damage *in vitro* and *ex vivo*, *Biochim. Biophys. Acta*, 1487, 113–127 2000.
6. Boloor, K.K., Kamat, J.P., Devasagayam, T.P.A., Chlorophyllin as a protector of mitochondrial membranes against gamma-radiation and photosensitization. *Toxicol.*, 155(1–3), 36–71, 2000.
7. Kumar, S.S., Shankar, B., Sainis, K.B., Effect of chlorophyllin against oxidative stress in splenic lymphocytes *in vitro* and *in vivo*, *Biochim. Biophys. Acta*, 1672(2), 100–111, 2004.
8. Marquez, U.M.L., Sinnecker, P., Chlorophylls: properties, biosynthesis, degradation and functions, in: *Food Colorants – Chemical and Functional Properties, Chemical and Functional Properties of Food Components Series,* C. Socaciu (Ed.), CRC Press, Boca Raton, Florida, 2008.
9. Chen, M., Schliep, M., Willows, R., Cai, Z., Neilan, B., Scheer, H., A red-shifted chlorophyll. *Sci.*, 329, 1318–1319, 2010.
10. Steer, J., *Structure and Reactions of Chlorophyll.* http://www.ch.ic.ac.uk/local/projects/steer/chloro.htm
11. Hendry, G.A.F., Chlorophylls and chlorophyll derivatives, in: *Natural Food Colorants, 2nd edition*, G. A. F Hendry, J. D. Houghton (Eds.), Chapman & Hall, London, 1996.[12] Nonomura, Y., Igarashi, S., Yoshioka, N., Inoue, H., Spectroscopic properties of chlorophylls and their derivatives. Influence of molecular structure on the electronic state. *Chem. Phys.,* 220(1–2), 155–166, 1997.
13. Rüdiger, W., Chlorophyll metabolism: from outer space down to the molecular level, *Phytochem.*, 46, 1151, 1997.
14. Scheer, H., Chromatographic methods for the separation of chlorophylls. in: *Handbook of Chromatography*, G. Zweig, J. Sherma, (Eds.), *Plant Pigments, vol. 1*, H.P. Köst, (Ed.), pp. 261–307CRC Press, Boca Ratón, Florida, 1988.

15. Delgado-Vargas, F., Jiménez, A.R., Paredes-López, O., Natural pigments: carotenoids, anthocyanins, and betalains—characteristics, biosynthesis, processing, and stability. *Crit. Rev. Food Sci. Nutr.*, 40(3), 173–289, 2000.
16. Timberlake, C.F. and Henry, B.S., Plant pigments as natural food colours. *Endeav.*, 10(1), 31–36, 1986.
17. Wang, X.F., Xiang, J., Wang, P., Koyama, Y., Yanagida, S., Wada, Y., Hamada, K., Sasaki, K.,Tamiaki, H., Dye-sensitized solar cells using a chlorophyll a derivative as the sensitizer and carotenoids having different conjugation lengths as redox spacers, *Chem. Phys. Lett.*, 408, 409–414, 2005.
18. Chernomorsky, S.A., Segelman, A.B., Biological activities of chlorophyll derivatives, *New Jersey Med.*, 85(8), 669–673, 1988.
19. US Food and Drug Administration,Listing of color additives exempt from certification: sodium copper chlorophyllin, 21 CFR Part 73, 67 Federal Register, 35429, May 20, 2002.
20. Pangestuti, R., Kim, S.K., Biological activities and health benefit effects of natural pigments derived from marine algae. *J. Funct. Foods*, 3(4), 255–266, 2011.
21. El-Khatib, E.M., Ali, N.F., El-Mohamedy, R.S.R., Enhancing dyeing of wool fibers with colorant pigment extracted from green algae. *J. Chem. Pharmaceut. Res.,* 8(2), 614–619, 2016.
22. Kadir, A., Ismail, M., Ahmad, M.R.,Ismail, A., Partial Characterisation and Colorimetric Characteristics of Sargassum sp. Colorant on Treated Polyester Fabric with Dendrimer. *In Key Eng. Mater.,* 737, 329–334, 2017.
23. Chernomorsky, S., Chlorophyllin copper complex: quality control, *J. Soc. Cosmetic Chemists*, 44, 235–238, 1993.
24. Chernomorsky, S., Variability of the composition of chlorophyllin, *Mut. Res.*, 324(4), 177–178, 1994.
25. Kephart J.C., Chlorophyll derivatives—Their chemistry? commercial preparation and uses. *Econ. Bot.*, 9, 3–38, 1955.
26. FAO/WHO, Toxicological evaluation of some food colours, enzymes, flavour enhancers, thickening agents and certain other food additives, Joint FAO/WHO Expert Committee on Food Additives, WHO Food Additives Series 6, pp. 74–77, Geneva, 1975.

8

Contemporary Revolutions in Natural Dyes: Extraction and Dyeing Methodology

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Abstract

Recent studies on the effect of harmful and venomous effects of man-made dyes urge the worldwide researchers and manufacturer to resuscitate the use of natural dyes in various walks of life. As these hold several beneficial properties, including their non-carcinogenic affects on human with enormous biological activities that make their use viable so their economic aspects are also considered to be the main factor for their revitalization and practiced by industrialists. Although natural dyes can be obtained from plants, animals, minerals, microorganisms etc., plants are the biggest source of natural colorant because the presence of colorant in almost all plants. . Currently, the wide spread usage of modern tools in extraction of natural dye and their dyeing processes are gaining popularity due to their cost, time, and labor effectivenesses and also helpful in exploration of new plants as a source as well as improve their dyeing behavior on natural fibers. Hope this chapter contains valuable information that will indulge the research readers, students, industrialists who intend to reconnoiter natural dye in applied fields.

Keywords: Arjun, Conventional extraction methods, Harmal, modern extraction methods, Neem

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8.1 Introduction

Nature has wonderful source of natural colorant and these colorants have their own attraction since history of mankind. These colorants are isolated from different sources such as plants, animals, minerals, and microorganisms without any chemical processing [1]. Even different parts of single plant species such as root, bark, stem, leaves, shoot, flowers, fruits etc. can also supply surplus amount of colorant. Examples of some common sources which are used to get color from them are lac (*Kerria lacca*), kermes (*Kermes vermilio*), madder (*Rubia tinctorium*), brazilwood (*Caesalpinia echinata*), Henna (*Lawsonia inermis*), Turmeric (*Curcuma longa*), Indigo (*Indigofera tinctoria*), Baptisia (*Baptisia australis*) etc. [2, 3]. These sources are responsible to give red, crimson red, orange, yellow, blue, purple, black color etc. and their usage are very old as the history of mankind. These dyes were used for diverse purposes such as in cosmetics, food, pharmaceutical, cloth coloring and printing, for decoration of their walls, caves, and painted their body [4, 5]. They had some superstitious belief that coloring their body will give them some mystic control. Hence in that immemorial time, these dyes kept a great importance for them and for their society. Egypt, China, Phoenicians and Mediterranean etc. were the largest producers and consumers of such dyes [6]. However, the use of natural dyes has been eclipsed by the accident discovery of synthetic dyes "Mauviene" by W.H.Perkin in 1856. Synthetic dyes become prominent over its counterpart as it is claimed through applications that preparative dyes are cheap, easily to attach on fabric and good fastness properties. They also have ability to give bright and charming appearance to fabric, having good performance and time effective during processing and application [7]. In view of all these beneficial aspects related to synthetic dyes, a question which arise in our mind is that "why does we need to regain and contemplating the importance of natural dyes"? The answer is the harmful aspects and indiscriminate exploitation of synthetic dyes that are destroying our climate day by day. As the studies reveal that genotoxic precursors of dye e.g., benzidine, beta-nephthylamine etc. and genotoxic product such as azo dye having mutagenic, carcinogenic, and toxicological effects on ecosystem and also a cause of global warming [8]. By product and remains of hazardous chemicals when loaded into the rivers and streams, will disrupt the aquatic life and also contaminate water for domestic, industrial, and agriculture use [9]. It has been estimated that about 50,000 tons of dye and 200,000 tons of metal salts are discarded each year into the streams. During manufacturing and application on textile many toxic chemicals like dioxins, formaldehyde and metals i.e., chrome, copper, zinc, cobalt etc. pose severe health hazards. They cause dermatitis problem like skin allergy and also responsible for nausea, breathing, and mental health problems [10, 11]. Dyes in darker color and their heavy loads prevent the penetration of sunlight into the river and streams. These effluents resist the bacteria to do useful job in nature. Similarly, salt makes the water too much alkaline and saline that these may kill the aquatic life. Furthermore, these dyes are made from non-renewable sources i.e., petroleum product that make the life non-sustainable. These carcinogenic effects regulate pressure on people from all over the world and motivate to revitalize natural dyes. Because natural dyes are less toxic, non-carcinogenic, biodegradable, eco-friendly and have healthy effects that makes the dyes viable at global mart [12]. Many beneficial properties i.e., antimicrobial, antioxidant, antimalarial, anti-inflammatory, UV protective, anti-hemolytic, flame retardant properties etc. present in natural dyes make them valuable again [13]. These properties exhibit due to chemical constituents that not only provide color but also have therapeutic effects as well. Thus, natural dyes are perfect and sustainable source for application in different fields, especially in textile due to their ecological point of view [14].

8.2 Pros and Cons of Natural Dyes

There are some beneficial points regarding natural dyes that make it viable in different fields. These aspects have compelled the world environmental associations, researchers, traders and consumers to use eco-friendly products in applied fields.

1. The use of natural dyes familiarizes us to experience its beautiful, charming, and attractive color and give the soothing sensation to our eyes.
2. There are five sources of natural colorants that give any color we need. These are also good resistance to fade such as madder (*Rubia cordifolia*), cochineal (*Dactylopius coccus*), weld (*Reseda luteola*), cutch (*Acacia catechu*) and indigo (*Indigofera tinctoria*).
3. Such dyes also give some sort of social benefits. This can increase the economy of country by providing the job opportunity for poor people [15].
4. Use of natural colorants helps to decrease the need to import some costly chemicals that are used in textile finishing process. As natural dye yielding plants which are alternative to synthetic finishing agents can grow within the country [16].
5. Unlike synthetic dyes, wastes of natural dyes does not cause any sort of problems to environment as these are easily

biodegradable. Effluents of dye can become the part of fertilizer, being able to restore the environment and to improve the fertility of soil for cultivation [17].

6. Synthetic dyes are prepared from non-renewable resources such as petroleum product, while, natural dyeing plants are sustainable source of colorants [18].
7. Increasing the plantation for obtaining natural colorant, helps to increase forest and safe biodiversity.
8. Natural dyes provide us a wide range of spectra of shades by employing different mordants. Furthermore, different parts of a single plant are also offering sufficient shades.
9. Handling and processing of natural dyes do not cause problem to skin and environment.
10. Natural dyes not only offer different colors but also have some therapeutic and medicinal properties. For example, tannin rich plants such as myrobalan (*Terminalia Chebula)* act as antiseptic. Turmeric and Indigo provide freshness and relaxing effect to skin.
11. These dyes possess different functionalities and have properties such as antimicrobial, antioxidant, anti-inflammatory, de-odorizing, insect repellent, UV protection etc. These inherent properties in textile for finishing process also eliminate or reduce the need of toxic chemicals [19, 20].

In spite of all these useful effects of natural dyes, there are also some drawbacks which are under observation to be removed.

1. Poor light fastness is the main drawback of natural colorants
2. Non continuous supply of these dyes
3. High consumption of natural dyes in textile sector damages the natural resources and environment.
4. Mordant used in natural dyeing to increase its affinity towards fabric harm the environment especially chrome and copper.
5. Extraction of natural colorant and its dyeing process consume a lot of time, energy and cost. Because much heat and time is required to extract the dye molecule from plant source.
6. Reproducibility and poor fastness properties will limit its application at industrial scale.
7. There is a lack of knowledge of technical and standard procedure about its useful application [21, 22].

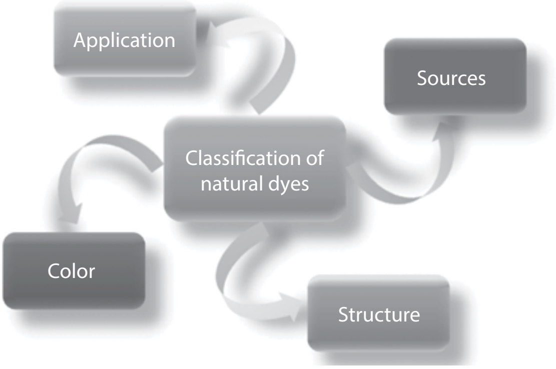


Figure 8.1 Classification of natural dyes.

8.3 Classification of Natural Dyes

8.3.1 Plant Based Natural Dyes

Natural dyes are classified on the basis of color, structure and method of application, however plant based dyes are well known to global community. Although, many sources can be used for obtaining natural colorants and have remarkable results on textile and other fields, yet plant based sources of natural dyes are in abundance. A single plant species can offer different shades as its various parts i.e., bark, leaves, stem, root, fruit, flowers etc. have bear surplus amount of colorant [23]. It is good to know that plants are biocompatible, greener, sustainable and renewable sources, and have less toxicity. Their presence in many products is eco-friendly to environment. There are many plants which are either being used for coloration or under investigation to act as natural colorant [24, 25]. Details of some plants which are frequently used in all fields are as follows.

8.3.1.1 Pomegranate

Common name: Pomegranate (Figure 8.2a); Botanical name: *Punica granatum;* Family: *Punicaceae*; Distribution: Iran, Himalayas, Northern India, Mediterranean region; Part used: Rind; Chemical constituent: Granatonine (Figure 8.2b) ; Color yield: Yellow, brown and black color; Medicinal properties: Anticancer, antibacterial, improve memory; cure arthritis, and Joint pain etc. [26].

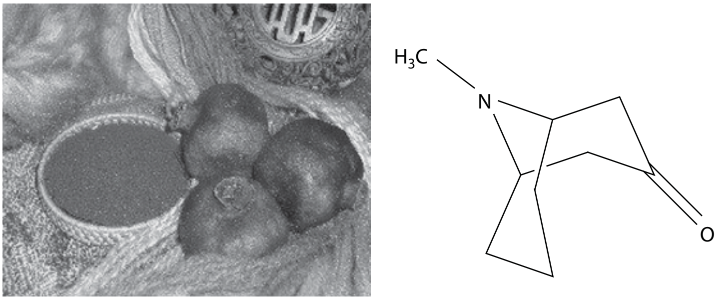


Figure 8.2 (a) Pomegranate and its bark powder (b) Granatonine.

8.3.1.2 *Australian Pine*

Common name: Australian pine (Figure 8.3a); Botanical name: *Casuarina equisetifolia*; Family: *Casurainaceae*; Distribution: Australia, Indian subcontinent, Southest Asia, Island of Pacificdepicts the place of its origin; Part used: Bark; Chemical constituent: Ellagic acid, gallic acid, kaemferol and quercetin (Figure 8.2b–e); Color yield: Brown; Medicinal properties: Astringent, antioxidant, anticancer and anthelmintic properties etc. [27]

8.3.1.3 *Bush Grape*

Common name: Bush grape (Figure 8.4 a); Botanical name: *Cayratia carnosa*; Family: *Vitaceae*; Distribution: Australia, Asia; Part used: Fruits; Chemical constituent: Pelargonidin, cyanidin, delphinidin, peonidin, petunidin, malvidin etc (Figure 8.4b–g) ; Color yield: Blue and purple; Medicinal properties: Treat anemia, dysentery, and jaundice and have been reported as anti-oxidant agent [28].

8.3.1.4 *Butterfly Pea*

Common name: Butterfly pea (Figure 8.5a); Botanical name: *Clitoria ternatea*; Family: *Fabaceae*; Distribution: Asia, Africa, Australia and America; Parts used: Roots; Chemical constituents: Tannin, taraxerol (Figure 8.5b), starch, taraxerone (Figure 8.5c), flavonol glycosides and delphinidin glycosides. ; Color yield: Black, blue, red; Advantages: It is used as pH indicator because it produces red color in acidic media and blue color in alkaline media; Medicinal properties: To cure goiter and whooping cough and shows anxiolytic, antidepressant, anticonvulsant, antistress properties etc. [29]

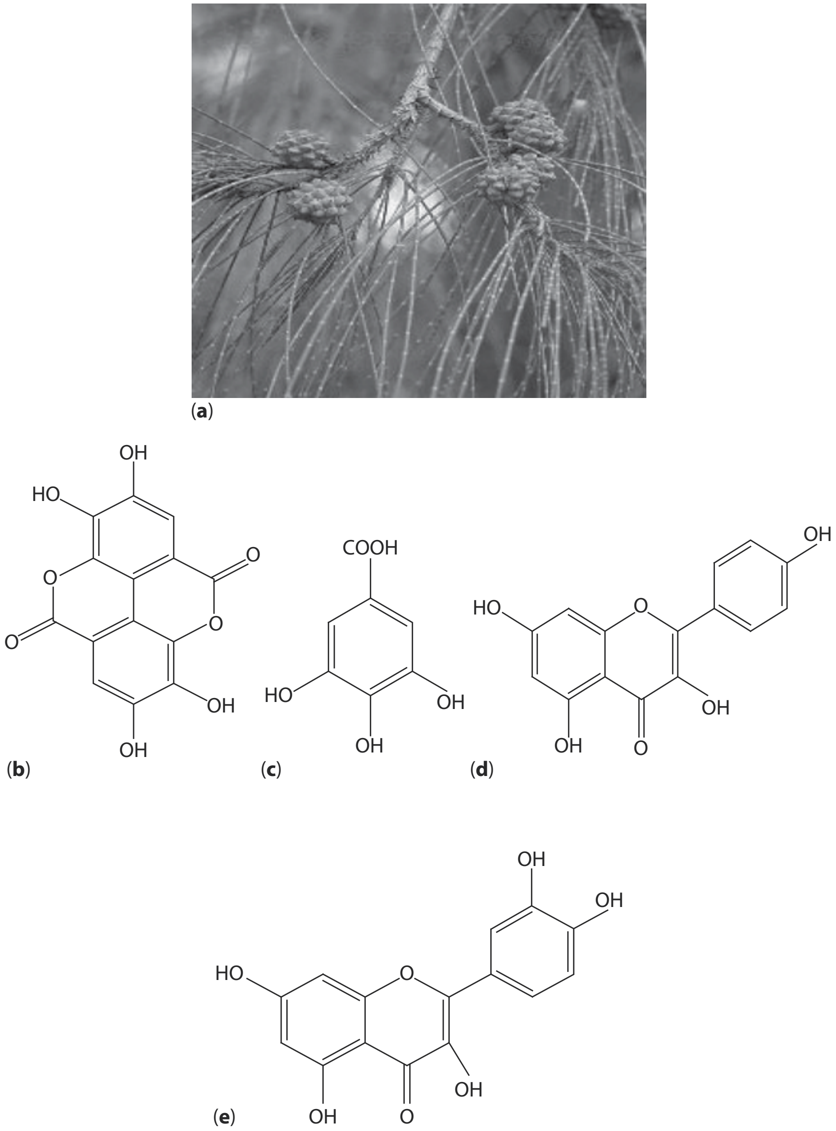


Figure 8.3 (a) Australian Pine and its important compounds (b) Ellagic acid (c) Gallic acid (d) Kaempferol (e) Quercetin.

8.3.1.5 Mugavu

Common name: Mugavu (Figure 8.6a); Botanical name: *Albizia coriaria*; Family: *Fabaceae*; Distribution: Uganda; Part used: Bark; Colorant: Tannin, coumarins (Figure 8.6b), triterpenoids, reducing sugar and alkaloids;

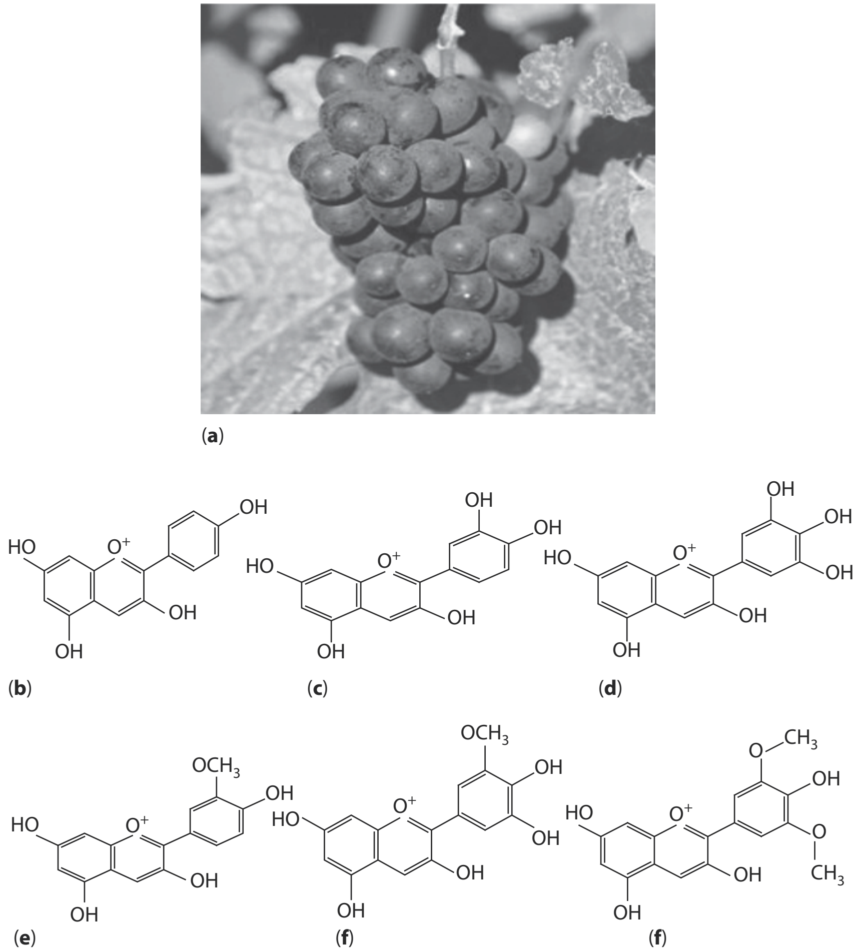


Figure 8.4 (a) Bush grape (b) Pelargonidin (c) Cyanidin (d) Delphinidin (e) Peonidin (f) Petunidin (g) Malvidin.

Color yield: Brown; Medicinal properties: Treat different ailments such as cancer, insomnia, sore throat, abdomen pain and also helps to diagnose anxiety disorders and depression [30].

8.3.1.6 *Jackfruit*

Common name: Jackfruit or kathal (Figure 8.7a); Botanical name: *Artocarpus heterophyllus*; Family: *Moraceae*; Distribution: Southeast Asia; Part used: Wood; Colorant: Morin, arotonin and Isocycloheterphyllin moieties (Figure 8.7b–d) respectively; Color yield: Yellow; Medicinal

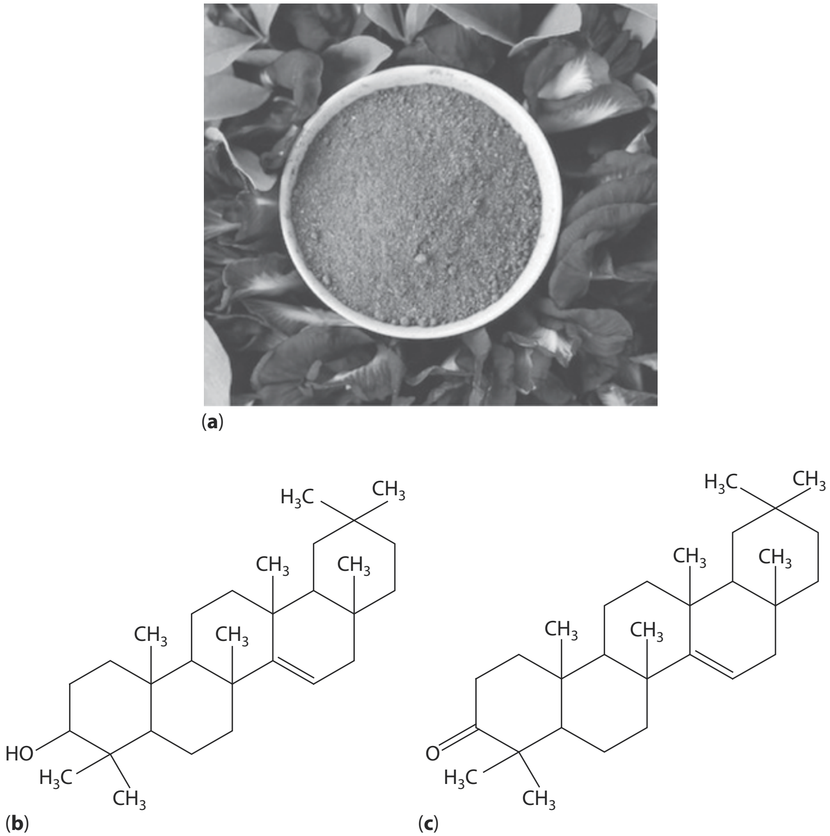


Figure 8.5 (a) Butterfly pea (b) Taraxerol (c) Taraxerone.

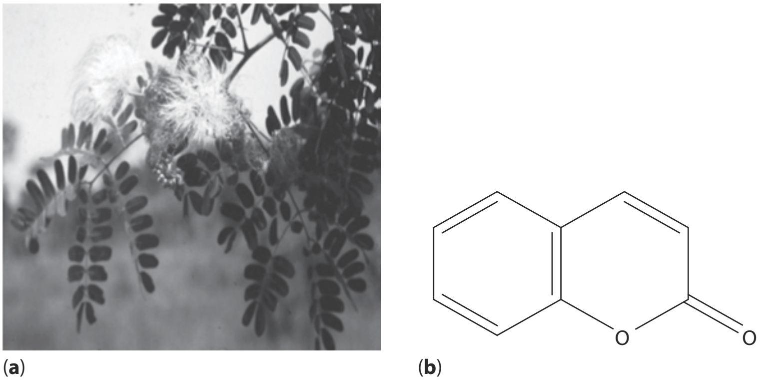


Figure 8.6 (a) Mugava (a) and one of the colorants (b) Coumarin.

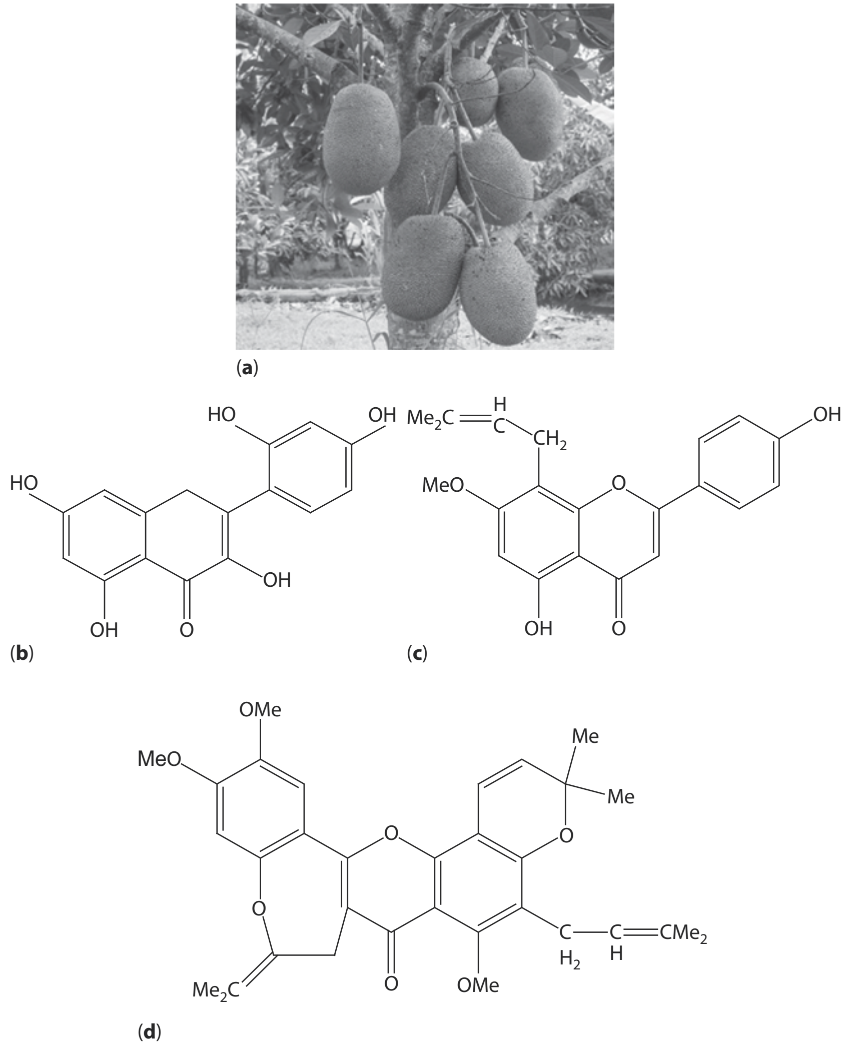


Figure 8.7 (a) Jack Fruit (b) Morin (c) Arotonin (d) Isocycloheterophyllin.

properties: Cure swelling, wounds, dysentery and skin diseases etc. and show anti-inflammatory activities [31].

8.3.1.7 Larkspur

Common name: Larkspur (Figure 8.8a); Botanical name: *Delphinium zalil*; Family: *Ranunculaceae*; Distribution: in California, Siberia, Syria, Iran and Indian; Part used: Flower; Colorant: Isorhamnetin (Figure 8.8b), quercetin, kaempferol and apigenin (Figure 8.8c); Color yield: Yellow color;

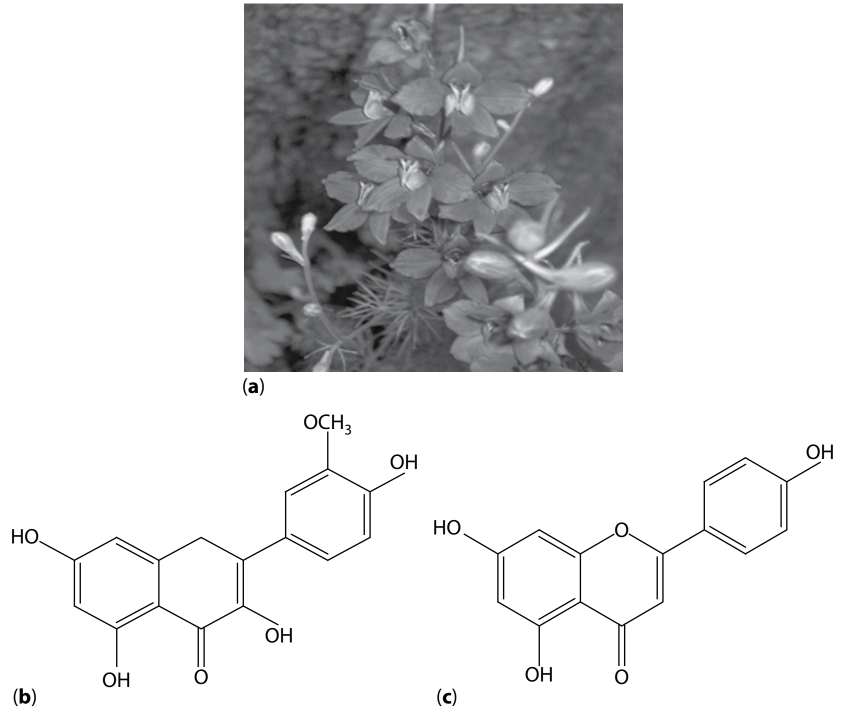


Figure 8.8 (a) Larkspur and colorants can be obtained are (b) Isorhamnetin (c) Apigenin.

Figure 8.9 Tea Oil Plant.

Medicinal properties: Anthelmintic, cathartic, emetic, narcotic, parasitcide and purgative [32].

8.3.1.8 Tee Oil Plant

Common name: Tea oil plant Figure 8.9; Botanical name: *Camellia oleifera*; Family: *Theaceae*; Distribution: China; Part used: Fruit shell;

Colorant: Tannin and flavonoids; Color yield: Yellow or brown; Medicinal properties: Shows antioxidant, cicatrizant, antiaging, antimicrobial, antimutaion, astringent, anti-inflammatory properties etc. [32].

8.3.1.9 Chaste Tree

Common name: Chaste tree (Figure 8.10a); Botanical name: *Vitex Negundo*; Family: *Verbenaceae*; Distribution: India; Part used: Leaves; Colorant:

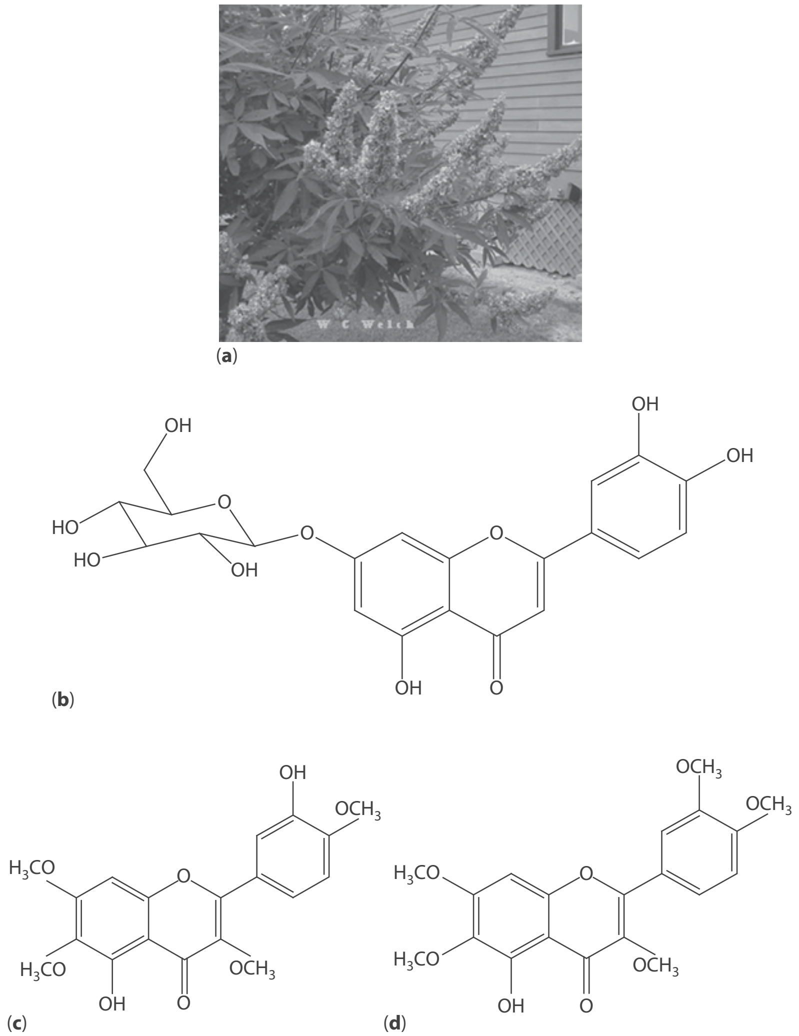


Figure 8.10 (a) Chaste tree (b) Luteolin-7-glucoside (c) Casticin (d) Artemetin.

Luteolin-7-glucoside, casticin and artmetin (Figure 8.10 b-d); Color yield: Yellow; Medicinal properties: Show anti-inflammatory, antipyretic, tranquilizer, antiarthritic, antihelmintic, antimicrobial, antioxidant activity [33].

8.3.1.10 Chinese Sumac

Common name: Chinese sumac (Figure 8.11); Botanical name: *Rhus pentaphylla*; Family: *Anacardiaceae*; Distribution: Tunisia; Part used: Bark; Colorant: Tannin, flavonoids and coumarin; Color yield: Brown; Medicinal properties: Act as antifibrogenic, antifungal, anti-inflamation, antimalarial, antimicrobial, antimutagenic, antioxidant, and luekopenic [34].

8.3.1.11 Limoniastrum Monopetalum

Common name: Limoniastrum (Figure 8.12a); Botanical name: *Limoniastrum monopetalum;* Family: *Plumbaginaceae*; Distribution: Mediterranean region, Africa and Southern Europe; Part used: Stem; Colorant: Gallic acid, myrecetin (Figure 8.12b), protocatechuic acid (Figure 8.12c), chlorogenic acid (Figure 8.12d), methyl gallate and trans-cinnamic acid (Figure 8.12e) ; Color yield: Brown; Medicinal properties: Having antidysentry, antioxidant, antimicrobial and wound healing properties [35].

8.3.1.12 Yerba Mate

Common name: Yerba mate (Figure 8.13a); Botanical name: *Ilex paraguariensis;* Family: Aquifoliaceae; Distribution: South America; Part used: Stem and leaves; Colorant: Flavonoids, rutin (Figure 8.13b), quercetin; Color yield: Yellowish brown; Medicinal properties: Have antioxidant, anticancer,

Figure 8.11 Chinese sumac.

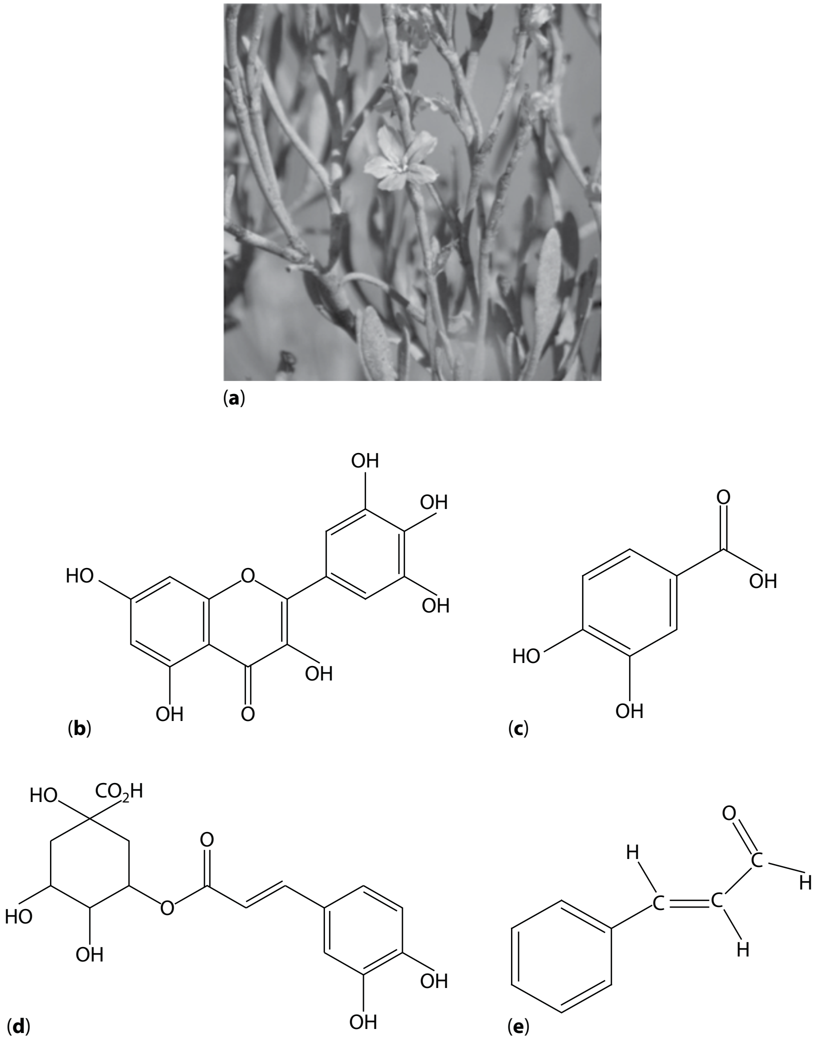


Figure 8.12 (a) Limoniastrum (b)Myrecetin (c) Protocatechuic acid (d) Chlorogenic acid (e)Trans-cinnamic acid.

central nervous system stimulant, hypocholesterolemic, hepatroprotective benefits [36].

8.3.1.13 Camphor Tree

Common name: Camphor tree or Camphor wood (Figure 8.14); Botanical name: *Cinnamomum camphora;* Family: *Lauraceae*; Distribution: China;

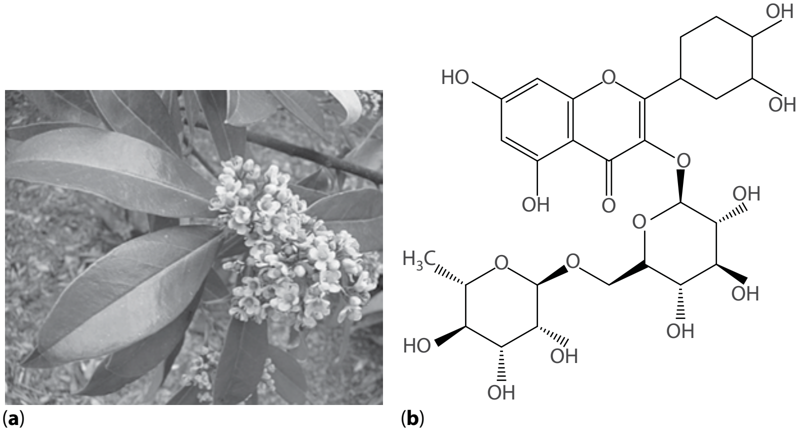


Figure 8.13 (a) Yerba mate (b) Rutin.

Figure 8.14 Camphor tree or Camphor wood.

Part used: Fruit; Colorant: Peonidin; Color yield: Red; Medicinal properties: Antifungal, antibacterial, mosquito repellent and treat ophthalmic disorders [37].

8.3.1.14 Basil

Common name: Basil or Tulsi (Figure 8.15a); Botanical name: *Ocimum basilium;* Family: *Lamiaceae*; Distribution: Indian and Africa; Part used: Stem and leaves; Colorant: Salvigenin (Figure 8.15b); Color yield: Purplish gray; Medicinal properties: Antiviral, antimicrobial, antioxidant, anti-inflammatory, treat headaches, and cough [38].

8.3.1.15 Fennel

Common name: Fennel (Figure 8.16); Botanical name: *Foeniculum vulgare;* Family: *Apiaceae*; Distribution: Mediterranean region; Part used:

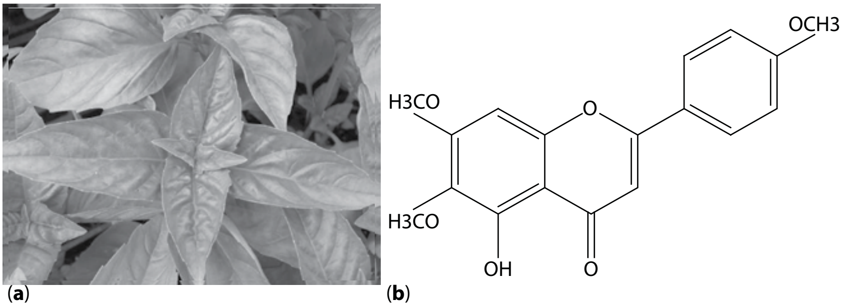


Figure 8.15 (a) Basil or Tulsi (b) Salvigenin.

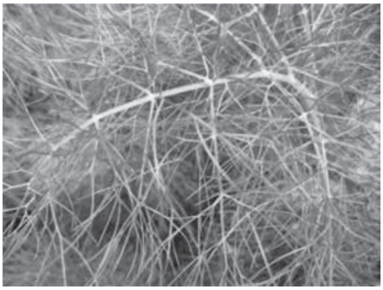


Figure 8.16 Fennel.

Leaves; Colorant: Quercetin, kaempferol; Color yield: Yellow; Medicinal properties: Anti-inflammatory, antispasmodic, analgesic, antidiabetic and treat asthma, cough etc. [39].

8.3.1.16 Indian Paper Plant

Common name: Indian paper plant (Figure 8.17a); Botanical name: *Dephne papyracea;* Family: *Thymelaeaceae*; Distribution: Asia, Europe, North Africa; Part used: Stem and leaves; Colorant: Genkwanin, dephnetin 8-glucoside and yuanhuanin (Figure 8.17 b–d); Color yield: Yellow, orange, brown; Medicinal properties: Febrifuge and purgative [40].

8.3.1.17 Guava

Common name: Guava (Figure 8.18a); Botanical name: *Psidium guajava;* Family: *Myrtaceae*; Distribution: Central America and South America; Part used: Leaves; Colorant: Quercetin, hyperin (Figure 8.18b&c), myrecetin-3-O-β-D-glucoside; Color yield: Brown; Medicinal properties: Exhibits

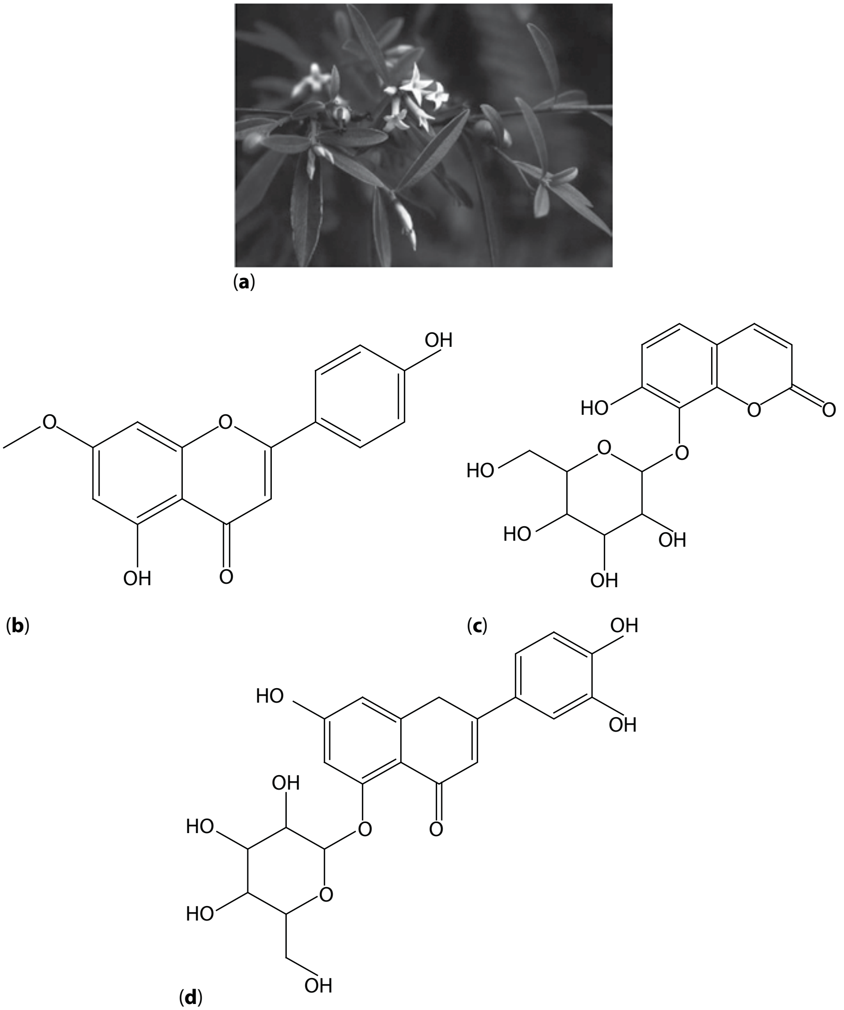


Figure 8.17 (a) Indian Paper Plant (b) Genkwanin (c) Dephnetin-8-glucoside (d) Yuanhuanin.

as antifungal, antioxidant, antimicrobial, antiseptic, homeostasis and narcotic properties etc. [41].

8.3.1.18 Scarlet Sage

Common name: Scarlet sage or red salvia (Figure 8.19a); Botanical name: *Salvia splendens;* Family: *Lamiaceae*; Distribution: Brazil and India; Part

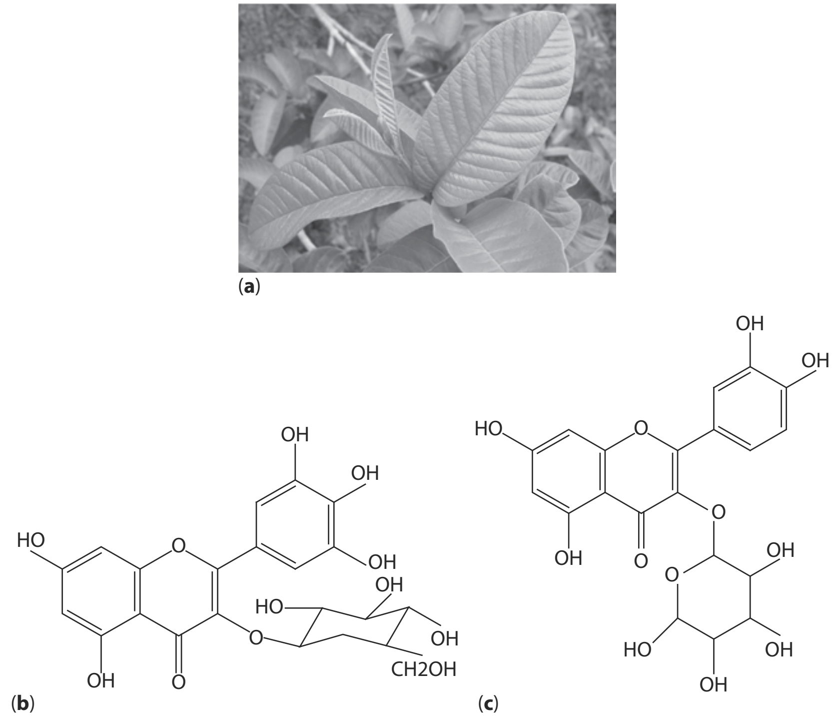


Figure 8.18 (a) Guava (b) Myrecetin-3-O-β-D-glucoside (c) Hyperin.

used: Flowers; Colorant: Salvianin, monardaein (Figure 8.18b&c); Color yield: Red; Medicinal properties: Antihyperglycemic and anticougulant [42].

8.3.1.19 Sandalwood

Common name: Sandalwood (Figure 8.20a); Botanical name: *Pterocarpus santalinus;* Family: *Fabaceae*; Distribution: South India; Part used: Wood; Colorant: Santalin (Figure 8.20b), deoxysantalin; Color yield: Maroonish red; Medicinal properties: Antioxidant, antimicrobial, anticancer, anti-inflammatory and antidiabetic etc. [43].

8.3.1.20 Centaury

Common name: Centaury (Figure 8.21a); Botanical name: *Hypericum scabrum*; Family: *Hypericaceae*; Distribution: Turkey, Europe, North Africa, Asia and Persia; Part used: Flower; Colorant: Quercetin and hypericin (Figure 8.21b); Color yield: Yellow; Medicinal properties: Wound healing,

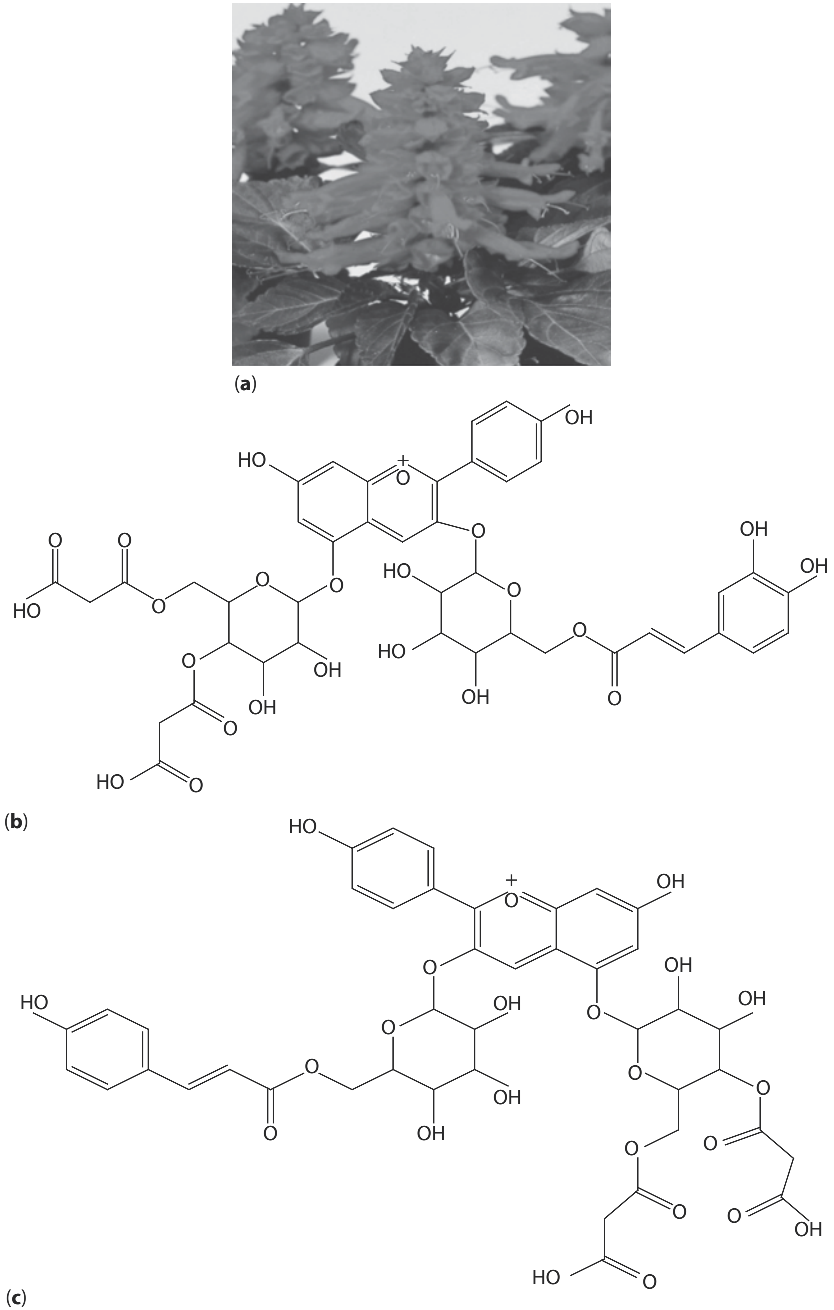
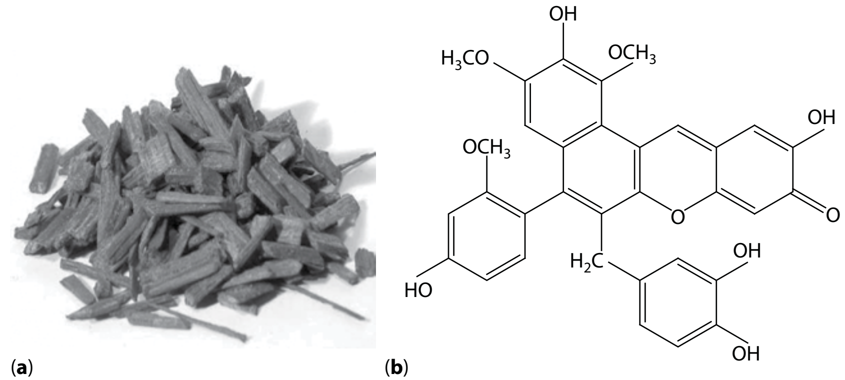
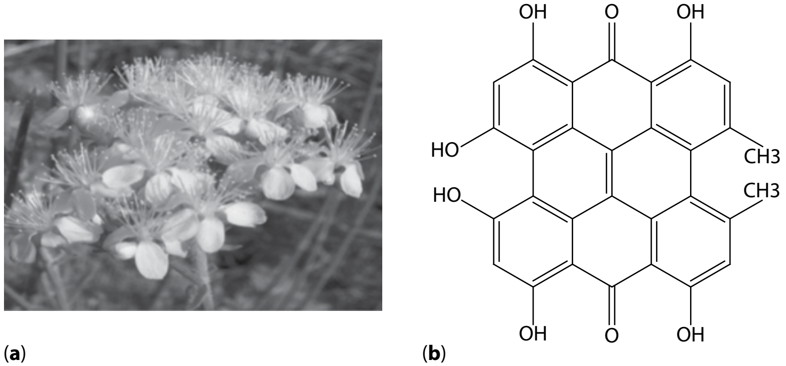


Figure 8.19 (a) Scarlet sage or red salvia (b) Salvianin (c) Monardaein.



(a) (b)

Figure 8.20 (a) Sandalwood (b) Santalin.



(a) (b)

Figure 8.21 (a) Centaury (b) Hypericin.

antimicrobial, antioxidant, antidepressant, anti-inflammatory properties and treat intestinal disorders [44].

8.4 Extraction Methodology

Extraction methodology is not an innovative term and has been employed since the discovery of fire. Extraction is basically a method to isolate the desired component from central core of the material. In natural dyeing process, it has a fundamental role and is the key step for processing and implementation of natural dyes into textiles [45]. As natural dyes have no such good binding property with fabric and get easily washed off, these have reproducibility problem. These limitations make natural dyes inferior to its synthetic competitor but ecological concern related to natural dyes urge to introduce natural dyes at industrial level. Hence, till now several techniques have been developed and practiced to standardized methods to increase productivity of the colorant [46]. The choice of appropriate method helps to improve high color strength, fastness characteristics with bright color bearing maximum functional properties on fabric [47].

There are two methods that are being employed for the extraction purposes i.e.,

1. Conventional methods
2. Modern methods

8.4.1 Conventional Methods

There are several methods included in conventional or traditional methods like boiling method, maceration method, soxhlet method, solvent method etc. Many studies have revealed their useful application in different field especially in textile sector where natural dyes were extracted through these phenomena [48].

In solvent method, different solvent media i.e., aqueous, alkali, acid or organic media are being employed which depend upon the solubility power of the dye component. All natural dye sources are organic in nature and some of them can solubilize in water. However, some chemical constituents such as flavonoids, aglycones, anthraquinones present in plant material have poor solubility in aqueous media [49]. Singh and Gahlot [50] printed silk fabric with natural dye obtained from flowers of wax mellow (*Malvaviscus arboreus*). They extracted dye component using different solvent media i.e., aqueous, alkali, and acid. In boilingprocess, the dye material is immersed in a liquid and then heated at reflux [51]. Ebrahimi and Gashti [52] used immersion and boiling method to obtain juglone colorant from leaves of Caucasian Walnut (*Pterocarya fraxinifolia*). This colorant was then applied to dye wool fabric and its antifungal and UV-protected properties have also been evaluated. Rym *et al.* [53] also used boiling method to extract cyaniding-3-oglycoside from leaves of grape wine (*Vitis* vinifera) and dye on cationized and non-cationized cotton fabric. Maceration method involve soaking of dye material in different solvent for many hours until the material become soften and dye component can easily come out of the material [54]. Chattopadhyay *et al.* [55] has employed maceration process to evolve colorant from madder (*Rubia tinctoria*), annatto (*Bixa orellana)*, ratanjot (*Alkanna tinctoria*) and babool

(*Acacia nilotica*) and used to dye jute fabric. Soxhlet process is used when solubility of dye material is limited and thus difficult to extract through thermal process, solvent, and maceration process. It is a continuous process where the material is washed several times with organic solvents e.g., hexane, alcohol or benzene etc. until the maximum color is extracted [56]. Jha *et al.* [57] extracted colorant from marigold (*Tagetes eracta)* through boiling and soxhlet method and evaluated their fastness properties on dyed fabric.

There are some limitations that are attached with the conventional extraction methods which are discussed above. It is very difficult to provide enough heat to hardy plant material such as bark, wood, stem or root of cassia, ratanjot (*Alkanna tinctoria)* or brazilwood (*Caesalpinia echinata)* etc. [58]. Therefore, the extracted product has low yields, low results of fastness properties on dyed fabric. Process of extraction is time consuming, with consumption of huge amount of energy (i.e., fuel), water, and chemicals. Thus, these techniques are very expensive, non-sustainable and less efficient and need to be replaced by methods which are cost and time effective [59].

8.4.2 Modern Methods

Due to less efficiency, prolong time for extraction, more consumption of energy and chemicals derive a force to researchers to introduce effective technology. For such purpose many intensification techniques have been developed and practiced for extraction of natural colorants. The techniques involve supercritical fluid, microwave (MW) radiation, Ultraviolet radiation, Gamma radiation, Ultrasonic treatment and plasma treatment [60]. These techniques have following advantages:

1. Minimized the amount of water, chemicals and energy which are to be consumed using conventional method.
2. Reduced processing time and give the better result in short moments
3. These tools help to improve the productivity and quality of the extracted colorant by increasing the kinetic and transfer rate [61].
4. They also minimized the emission of greenhouse gases that pollute the environment. Thus, these are clean and safest methods.
5. These tools also improve the functional and fastness properties of dyed fabric [62].

Supercritical carbon dioxide is a technique where gas is heated and pressurized above its critical point. This CO_2 then acquire the property like liquid and selectively extract the desired component from the dye material. This technique has advantages such as cost effective, non-toxic, non-flammable, recycled process, and consumes less amount of solvent. Talib *et al.* [63] extracted dye material from brown seaweed (*Sargassum spinosum)* with supercritical fluid method and ultrasonic method. They found that brownish green color has been obtained with maximum yield by employing SCF-method. Ultrasound energy has a frequency greater than the human audible range. The formations of mechanical waves through ultrasonic field produce micro-cavitations around the dye material (Figure 8.22). When these bubbles are provided enough heat they collapse near the interface that improves the transfer of colorant from solid to liquid. The mechanical effect of ultrasound minimized the need of high temperature, power, amount of dye material, and chemical auxiliaries [64]. Ticha *et al.* [65] extracted the dye material from red cabbage (*Brassica oleracea*) and dyed modified cotton fabric using ultrasonic technique. They estimated the effect of ultrasound on color strength and fastness properties of dyed fabric. Benli and Bahtiyari [66] pretreated cotton fabric with ozone and ultrasonic treatment to improve the dyeability of fabric. They dyed with the extract of pomegranate peel (*Punica granatum*), nutshell, orange tree (*Citrus sinensis*) leaves and roots of alkanet (*Alkanna tinctoria*) as sustainable dye source. Similarly, Guesmi *et al.* also practiced ultrasound for extraction of indicaxanthin from prickly pear cactus (*Opuntia ficusindica*)and dyed modified acrylic fiber using sonicator [67].

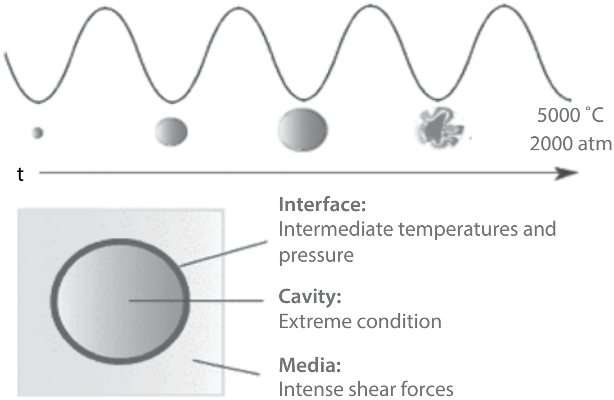


Figure 8.22 Cavitation effect of ultrasonic energy.

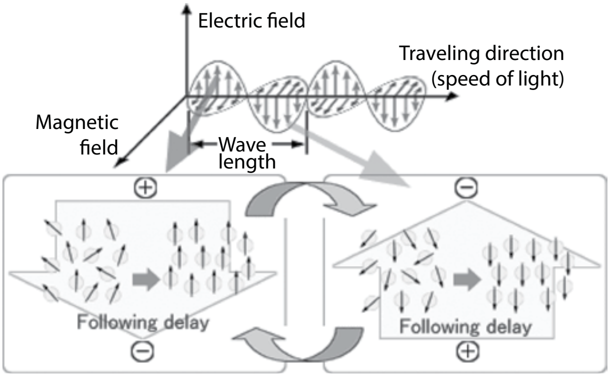


Figure 8.23 Effect of electromagnetic radiation on polar molecules.

Microwave radiation is a volume heating compared to the conventional heating which heats the surface of material only. When the fields of electromagnetic radiations such as MW are varied, it affects the polarized molecule (i.e., water) to reorient according to field. Their orientation causes interfacial friction with other molecule and produce heat in large amount (Figure 8.23). This heat penetrates the dye material and enables the dye component to transfer and dissolve in solvent conveniently. It has the advantages of having fastest control, produce high yield, reduce time, and transfer energy to the material faster to get desired color characteristics [68]. Various examples depicted its application for extraction of natural dyes. Ali *et al.* [69] used this technology to extract coloring component from saffron (*Cracus sativus*) and found remarkable results. Dayioglu *et al.* [70] pretreated silk fabric with plasma radiation and then dyed with elderberry(*Sambucus ebulus*) which was extracted using MWradiation. They found that microwave has increased the color strength of the dyed substrate and gave darker shade. Mosquera *et al.* [71] also employed microwave technology for extraction of coloring component from achiote (*Bixa orellana)* and carajuru (*Arrabidaea chica).* They examined that microwave has bettered the extraction of pigment and gave the intense and stable red color.

Plasma is being practiced in textile industry for modification of textiles substrate. It removes the hydrophobic layer from the surface of fabric that cause barrier for the penetration of dye. It is soft and dry process that deprived of the use of water and chemicals (Figure 8.24). Plasma treated fabric reduce the dyeing time and improve the dye ability and color strength and also in antimicrobial properties. For example, the antimicrobial activity of plasma treated knitted fabric dyed with bloodwort(*Achillea*

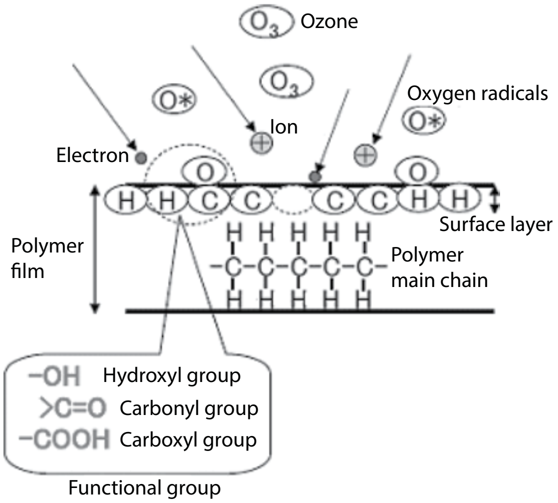


Figure 8.24 Principle of plasma treatment (Ref).

millefolium)and knotweed (*Raynoutria japonica*)has been dramatically increased [72].

Ultraviolet radiation is a form of electromagnetic radiation that has shorter wavelength and high energy than visible light. Due to its high penetration power, it is being applied for the alternation of substrate used for coloring and degradation of dye molecule. This improves the dyeability, color strength, fastness, and functional characteristics with reduction of time, cost, and energy. Baliarsingh *et al.* [73] investigated the effect of UV-radiation on cotton fabric dyed with natural dye plant i.e., Indian almond (*Terminalia catappa*), ashoka tree (*Saraca asoca*), lebbeck tree(*Albizia lebbeck*)and kumbhi(*Careya arborea*). Gamma radiation is also a form of electromagnetic radiation. However, its energy is higher than other radiation based technology i.e., higher than 100 keV. Due to its high penetration power, it has a remarkable role in textile dyeing and efficient extraction of colorant. This radiation has been utilized to achieve better hydrophilicity, dye ability, color yield, color strength, and color stability on substrate. It also has advantages of less consumption of water and toxic chemicals i.e., metallic mordants. A study of Kim *et al.* [74] revealed that high absorbed dose of gamma radiations to turmeric (*Curcuma longa*) and wild turmeric (*Curcuma aromatic*) yielded bright yellow color.

Thus, in view of all these beneficial aspects related to innovative tools, researchers have successfully practiced these techniques for extraction and textile dyeing.

8.5 Exploration of New Plants Using Modern Tools to Maintain Sustainability

There is an increase in demand of eco-friendly product from consumer as they are well aware of the toxic effects of synthetic dyes. Therefore, natural dyes are being studied in all over the world to make them applicable at industrial level. However, the high demand and less productivity have limited the natural dyes at industrial level. For such reason, the scientist, researchers, and those who have keen interest in natural dyeing are trying to find the new source of natural colorant [75]. They are also applying novel technology for sustainability and to increase the yield of the desired colorant. In this regard, the researchers of Chemistry, Applied Chemistry, Biochemistry and Botany Departments, Government College University Faisalabad, Pakistan have successfully explored new dye yielding plants. They have studied novel plants and explored their coloring behavior using modern tool such as Ultraviolet, MW, Gamma, Plasma, and Ultrasonic radiations. The new plants that are under study for coloration of natural fabrics are: Saffron, Safflower, Neem, Harmal, Arjun, Madder and Alkanet.

8.5.1 Harmal

Harmal (*Peganum harmala*) is one of the oldest medicinal plant and also known as “Asfand” and “Syrian rue” (Figure 8.25a). It is especially found in Mediterranean region and belongs to *Zygophyllaceae* family. The main phytochemical constituents present in the seed of harmala are β-carboline i.e., main alkaloid that includes harmane, harmine, harmaline and harmalol (Figure 8.25b–e). It has several pharmacological properties i.e., antihelmitic, antispasmodic, antipyretic, hypothermic, hallucinogenic, antioxidant, antimicrobial etc. It also has dyeing property as well and imparts brown coloration to substrate [76, 77].

Adeel *et al.* [78] is exploring the coloring wealth from new dye yielding plants. In his recent studies, Harmal is one of the novel sources which yield a firm color onto natural fabric. He employed microwave to enhance the extraction, color depth, and fastness characteristics using different solvents. Among three modes of extraction, he found that Microwave assisted extraction (MW) for 5 min gives high color strength on wool fabric. Similarly by irradiating the powder and extract 2 min. of Microwave has given dark shades. Upon optimization of conditions, he observed that 8 gm of powder gives maximum color strength by dyeing irradiated wool at 85 °C for 45 min keeping dye bath of 1 pH using 9% of salt as exhausting agent. He concluded that Microwave treatment has given good results

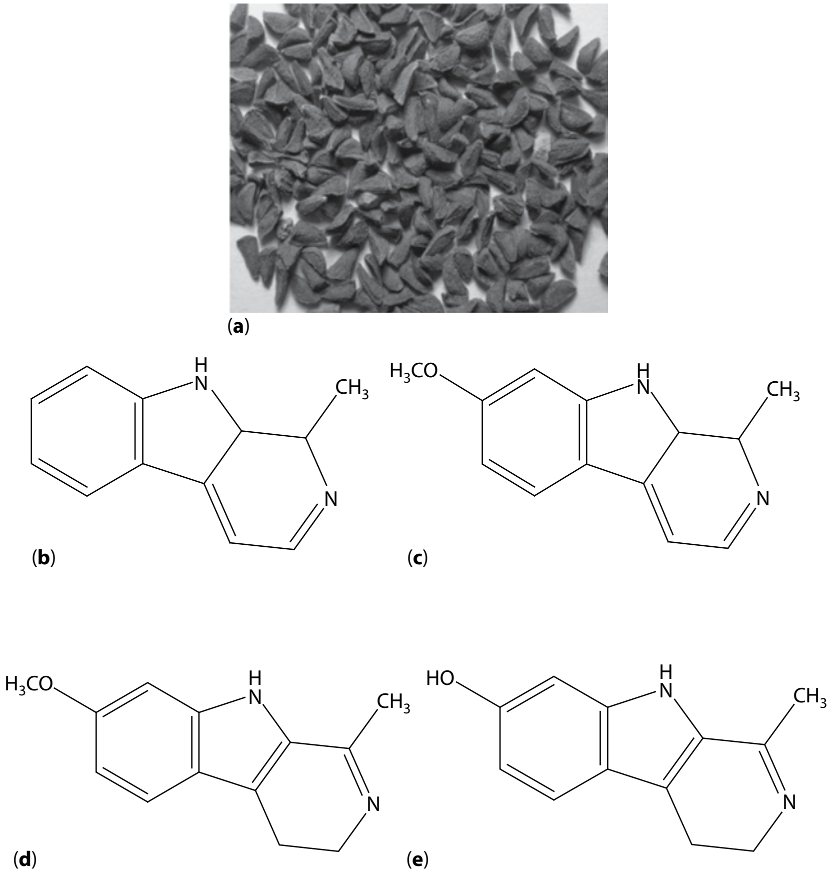


Figure 8.25 (a) Harmal (b) Harmane (c) Harmine (d) Harmaline (e) Harmalol.

under mild conditions of dyeing. Similarly, he also dyed cotton fabric using microwave radiation using different solvents and characterized the effects of different chemical and bio mordants on dyeing behavior. He found that exposure of microwave radiation to powder gave higher color strength value at 5 min and radiate the extract give maximum value at 4 min. While significant results have been obtained in simultaneous extraction i.e., MW assisted extraction where 3 min of radiation is an optimum dose to obtain higher color value. The dyeing condition gives the optimum results where 8 gm is an effective amount that provides maximum result at 85 °C for 45 min at pH of 9 using 9% of salt concentration. He also found that in chemical and bio mordanting 1% of alum and 10% acacia in pre mordanting and 7% of iron and 7% of acacia in post mordanting are optimized amount that helps to increase the fastness properties.

8.5.2 Saffron

Saffron (C.I. Natural Yellow 6) is basically known as “zafran” (*Crocus sativus)* and belongs to *Iridaceae*family that is native to Kashmire and Iran (Figure 8.26a). It is famous all over the world due to its charming appearance, fragrance, taste, and softy touch. The stigmas of the flower of saffron are responsible for yellow coloration in neutral and red coloration in acidic environment (Figure 8.26b). The yellow coloring component is obtained due to crocin component (Figure 8.26c); however after hydrolysis, it yields crocetin that produces red color. The violet appearance of flower of saffron is mainly due to the presence of anthocyanidin and kaempferol. Other constituents such as glucose, fructose, gentibose, xylose, ramnose, some minerals and vitamins i.e., thiamine and fiboflaving are also present. It also has therapeutic properties like helps digestion, cure tumors, insomnia, depression, blood pressure, respiratory disorders etc. It has also anti-oxidant, antitympanites, anticancer, anti-inflammation properties etc. It has been used in textile, medicinal and cosmetics [79, 80].

8.5.3 Madder

Madder (*Rubia cordifolia)* is also named as manjith and Indian madder (Figure 8.27a). It is an Indian perennial plant that belongs to *Rubiaceae*

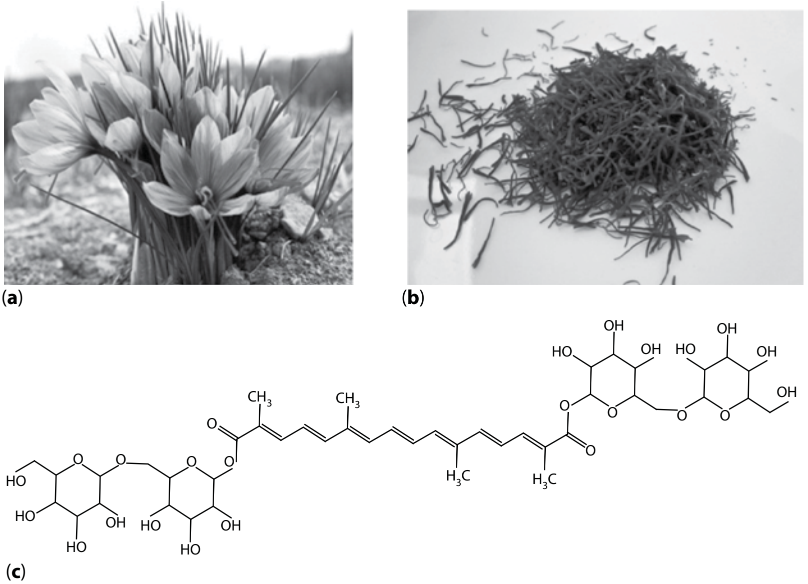


Figure 8.26 (a) Saffron petals (b) Saffron Stigma (c) Crocin.

family. It is dye yielding plant that imparts red coloration on substrate which is to be dyed. The color is due to the chemical constituents present in the root of madder such as alizarin (Figure 8.27d), purpurin, xanthopurpurin, pseudopurpurin, manjisthin, nordamnacanthal, and rubiadin. These coloring components are derivatives of anthraquinone structure in free or glucoside form. It behaves as anti-inflammatory, wound healing, antidiabetic, antimicrobial, antiulcer, anti-viral properties etc. [81].

8.5.4 Safflower

Safflower (*Carthamus tinctorius)* belongs to *Asteraceae* family and similar to saffron (Figure 8.28a), it yields yellow pigment (Figure 8.28c). The flower of safflower contains quinchalcones,which belongs to glycosylated flavonoids which on hydrolysis yields carthamin (Figure 8.28d) and precarthamin. Other components such as safflower yellow A, Safflower yellow B, Safflominc are also present. It also has pharmacological role like anticoagulant, antioxidant, reduces the response of immune, neuroprotector and UV protection properties etc. The yellow color produced is responsible for use in textile dyeing, food, and cosmetic industry [82].

Adeel *et al.* [83] dyed silk fabric with safflower using MW radiation in the presence of chemical and bio mordant. They found that 3 min of irradiation was the optimum time of gaining highest color strength on fabric.

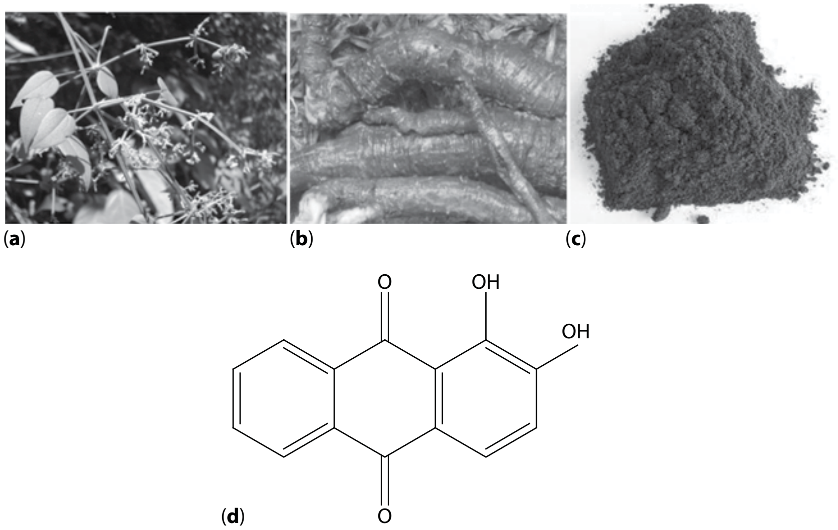


Figure 8.27 (a–c) Madder plant, its Roots and powder, respectively (d) Alizarin.

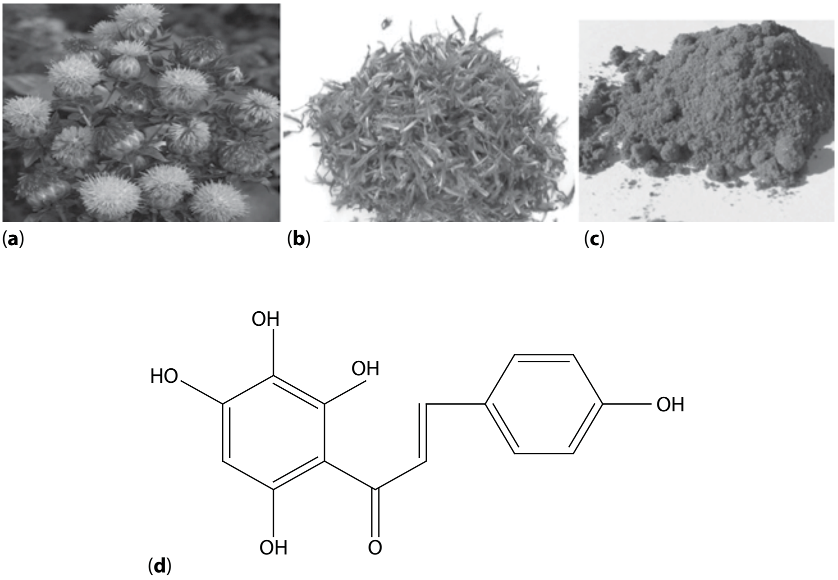


Figure 8.28 (a–c) Safflower, its dry petals and powder, respectively (d) Carthamin.

They also employed different pH and dyeing to get optimum dyeing condition. They observed that safflower provided good color strength at 2 pH for 60 min and 7% of turmeric and henna as eco-friendly bio-mordants provided good fastness properties as compared to chemical mordant.

8.5.5 Arjun

Arjuna (*Terminallia arjuna)* also known as "arnot" and is an evergreen tree that belongs to *Combretaceae* family. Its bark (Figure 8.29a) has been used in Ayurvedic system and has many therapeutic values. Various diseases have been cured by using arjuna i.e., diabetes, dysentery, cough, respiratory problems heart, and skin diseases. It also has antioxidant, anti-inflammatory, antibacterial, antiviral, antiacne, anticancer properties etc. The main constituent present in arjuna are, arjunetin, , arjungenin, arjunglycosides, arjunone, arjunolone, luteolin, bicalein (Figure 8.28b), ellagic acid (Figure 8.28c), arjunic acid (Figure 8.28d) arjunolic acid (Figure 8.28e), gallic acid, phytosterols, minerals etc. However, the main coloring components are bicalein and ellagic acid (tannin). Its bark is beingused for dyeing purposes as it yields brown color [84, 85].

Arjun bark also has a good potential to act as source of natural colorant under influence of MW and ultrasonic treatment. Upon using ultrasonic

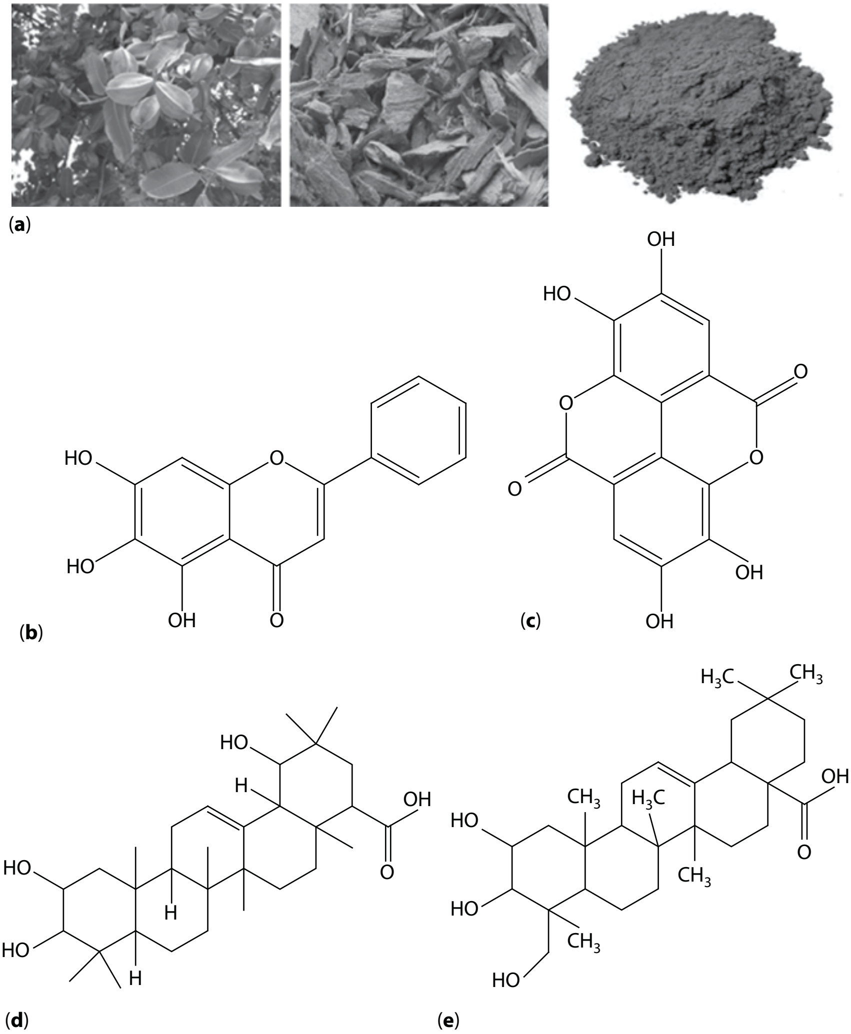


Figure 8.29 (a) Arjun bark (b) Baicalein (c) Ellagic acid (d) Arjunic acid (e) Arjunolic acid.

treatment in silk dyeing, it has been observed that irradiation of extract and powder gives significant result at 60 min. While simultaneous extraction i.e., ultrasonic assisted extraction (UAE) gave maximum results at 45 min. The optimized results revealed that 6 g of powder is a sufficient amount to gain optimized results at 65 °C for 65 min at pH of 1 using 3% of salt concentration. Similarly, in wool dyeing the maximum results has been obtained on 30 min for irradiation of extract, 15 min for irradiation

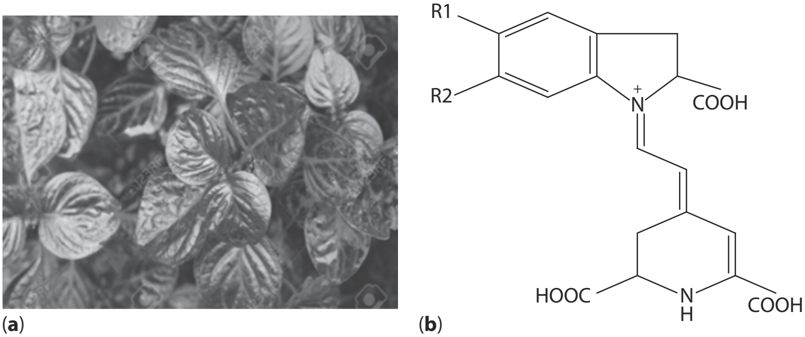


Figure 8.30 (a) Chicken gizzard Colored foliage (b) Betacyanin.

of powder while 45 min in UAE. The optimized condition was obtained using 10 g of powder and dyeing at 85 °C for 85 min at pH of 1 using 6 % of salt concentration. While wool dyeing using MWradiation gave higher color strength at 3 min for irradiating extract, powder and simultaneous extraction (MAE) [86].

8.5.6 Chicken Gizzard

Chicken gizzard (*Iresine herbstii*) also known as blood leaf due to its colored foliage (Figure 8.30a). It belongs to the *Amaranthaceae* and mainly found in American tropics. Chicken gizzard is also considered as bioactive plant that is bestowed with several medicinal properties such as astringent, relaxant, hallucingonic, antipyretic, anti-inflammatory etc. These properties are mainly depending on the presence of acylated betacyanin (Figure 8.30b), cylated betacyanin and iso-flavones. Due to the presence of betacyanin, this plant also has coloring property as well and gave green coloration. Batool *et al.* [87] utilized gamma radiation in dyeing of cotton with chicken gizzard leaves. They used different absorbed doses and found that 10 kGy was an effective dose for extraction and surface modification. The results of fastness rating revealed that gamma radiation is a promising tool in enhancement of color strength.

8.5.7 Red Calico

Red Calico (*Alternanthera bettzickiana*) also known as Baptist plant or border plant which is a perennial herb that has food and ornamental values (Figure 8.31). It belongs to *Amaranthaceae* family and native to South America. In phytochemical analysis, it has been observed that it has

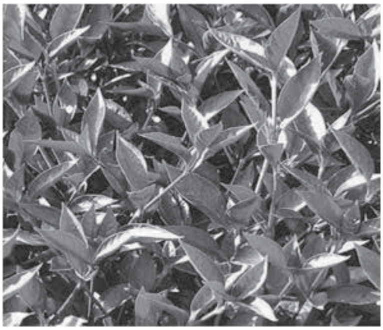


Figure 8.31 Calico plant Leaves.

antipyretic, wound healing, antimicrobial, and antifungal activity. Various chemical constituents such as alkaloids, saponins, flavonoids, tannin, terpenoids, steroid, anthocyanin, coumarin, and glycosides represent its bioactivity. Recently, it has been demonstrated by Khan *et al.* [88] that this plant can also have dyeing property as well. Cotton fabric is dyed with red calico leaves by employing different dose of gamma radiations. It is observed that 15 kGy was an optimized dose to get improved color strength.

8.5.8 Golden Duranta

Golden duranta (*Duranta repens*) is also known as sky blue or golden dewdrops which is flowering shrub (Figure 8.32). It belongs to *Verbenaceae* family and mainly native to South America.It is considered as ornamental plant. It has a remarkable role in agriculture as insecticidal and antifeedant due to the presence of terpenoids, coumarin, and phenols. It also exhibit antimalarial property due to the presence of quinone structure. Adeel *et al.* [89] studied the dyeing effect of golden duranta leaves on cotton fabric using microwave radiation. They also used chemical and biomordants to increase the affinity between the fabric and dye component. They observed that irradiation of extract and fabric for 1 min. gave maximum color strength and fastness characteristics. They also found that radiation could help to reduce the amount of mordant and gave maximum results at 3% in pre-mordanting and 5% in post mordanting.

8.5.9 Marigold

Marigold (*Tagetes erecta*) is an annual or perennial ornamental plant (Figure 8.32a). It belongs to *Asteraceae* family and found in North and

South America. It has medicinal importance as well that exhibit antioxidant, anticancer, antiseptic, and antifungal properties. It contains flavonoids, carotenoids, saponins, triterpenes, scopoletin, vitamins. However, it shows dyeing properties as well and has been used to dye eco-friendly textile. It has lutein as coloring component (Figure 8.32b) and imparts yellow color to the substrate. Adeel *et al.* [90] examined the effects of gamma radiation on extraction of marigold and pretreatment of cotton fabric to increase the dye uptake ability. They also employed chemical mordants as well to find the change in fastness rating. They found that 30 kGy was an optimized dose to obtain darker greenish yellow onto irradiated cotton fabric. They also found that 7% of tannic acid as pre mordanting and 5% of Cu as post mordanting was an optimized concentration in increment of

Figure 8.32 Golden Duranta.

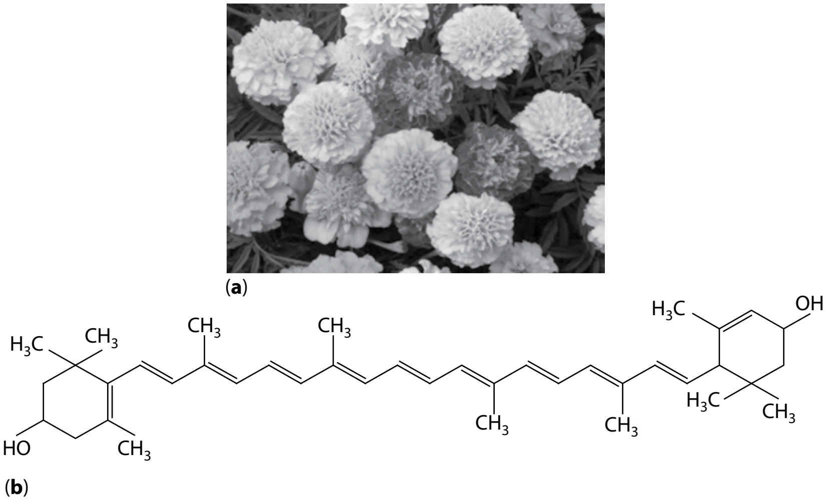


Figure 8.32 (a) Marigold Flowers (b) Structure of Lutein.

fastness characteristics. Similarly, Rehman *et al.* [91] investigated the role of UV radiation in dye uptake ability of cotton fabric that has been dyed with marigold. Upon investigation, it has been demonstrated that exposure of UV radiation for 90 min was an optimum time to modify the surface of fabric and increase the color strength.

8.5.10 Milk Weed

Milkweed (*Calotropis procera*) is named due to its milky sap nature (Figure 8.33a). It is a perennial shrub and belongs to *Asclepiadaceae* family that is mainly found in Middle East, Asia, and Africa. It has many therapeutic effects as well such as anticancer, activator or suppressor of nervous system, cardiovascular tonic, anti-inflammatory, antimicrobial activity. Several phytochemical constituents reveal properties such as alkaloids, terpenoids, phenolic, flavonoids, tannin and chlorophyll (Figure 8.33b) etc. Recent discovery of its dyeing properties revealed that it could be used as eco-friendly and abundant source of natural colorant due to the presence of chlorophyll moiety. Hassan *et al.* [92] utilized the leaves of milkweed to dye cotton fabric using different bio mordant. They investigated the role of MW assisted extraction of colorant from leaves of milkweed for different time and evaluate its dyeing behavior. They found that 4 min is an effective time to abstract the colorant in alkali media and obtain high color strength property. They also concluded that *Acacia nilotica* as premordant and *Curcuma longa* as post mordant gave maximum color fastness characteristics as eco-friendly alternative to metallic mordant.

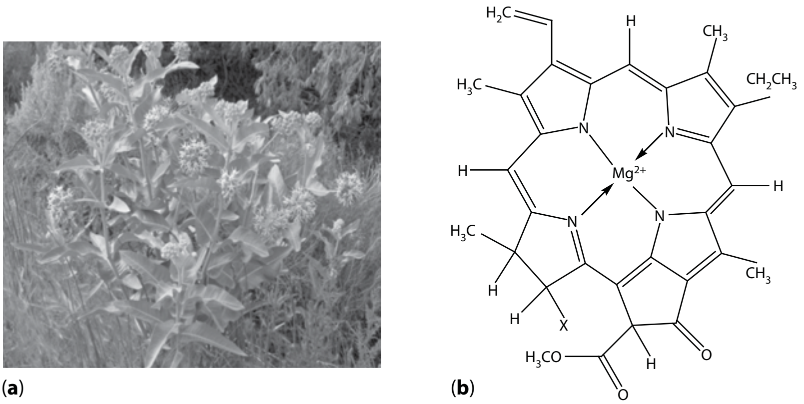


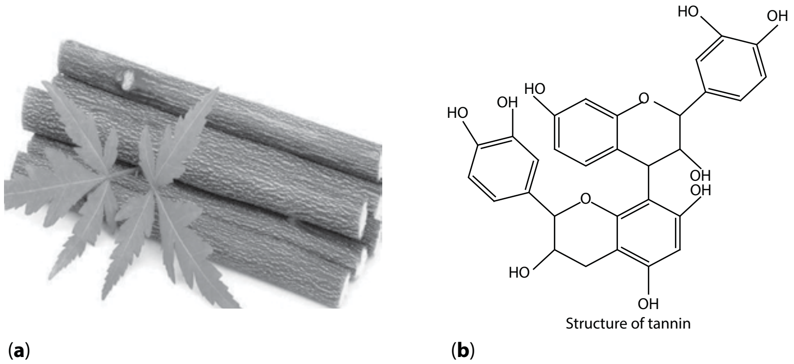
Figure 8.33 (a) Milkweed plant (b) Chlorophyll.

These results revolutionized the use of radiation based technology in exploring novel dye bearing plants as an eco-friendly and alternative source of harmful synthetic dyes.

8.5.11 Neem

Neem (*Azidirachta indica*) belongs to *Meliaceae* family (Figure 8.34a) and distributed throughout Southern Asia. Due to its non-toxic nature, it has been applied in cosmetic, agriculture, textile, and pharmaceutical industries. Neem is basically familiar as medicinal plant and has been used to treat various diseases such as inflammation infections, fever, skin diseases, and dental disorders. It is also bestowed with various functional properties known as anti-oxidant, anti-malarial, anti-bacterial, anti-inflammatory, anti-diabetic, anti-tumor etc. The main biologically active components such as alkaloids, minerals, steroids, flavonoids, tannin (Figure 8.34b), saponins, etc. present in neem are responsible for such therapeutic properties. Tannin in neem bark not only has medicinal value but also has coloring property as well and impart brown coloration to the substrate which is to be dyed [93, 94].

Adeel *et al.* [95] dyed silk fabric with neem bark using MW radiation from 1–6 min. They irradiated extract, powder and simultaneous extract (powder + solvent). The results they got demonstrated that 2 min for irradiation to both fabric and extract provided maximum results. While 1 min for simultaneous extraction and 5 min for powder was the optimum time they observed. Similarly, using ultrasonic treatment they examined that 30 min was the optimum time to irradiate both fabric and extract to gain darker shade. Hence from their studies, it is found that MW treatment



(**a**) (**b**)

Figure 8.34 (a) Neem Bark (b) Tannin.

has a great influence on extraction followed by dyeing using neem bark as source of natural colourant.

8.6 Conclusion

The resurge of natural colorant in many fields is due to their various unique benefits and their harmonization with nature has attracted the global community to use in textile. As natural colorants provide a wide spectrum of colors, the textile researchers are trying to explore new plants which can be the possible substitute of synthetic dyes. In the current chapter, the exploration of new plants has been discussed using green, clean, and modern technology which is not only cost, time effective but also gives high color characteristics onto natural fabrics. The results given in this chapter by our research group on exploration of new dye yielding plants can develop a new horizon for industrialist, traders, and researchers to make possible use of natural colorants in textiles.

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References

1. Zhang, B., Wang, L., Luo, L., King, M.W., Natural dye extracted from Chinese gall-the application of color and antibacterial activity to wool fabric. *J. Clean. Prod.*, 80, 204, 2014.
2. Yusuf, M., Shahid, M., Khan, M.I., Khan, S.A., Khan, M.A., and Mohammad, F., Dyeing studies with henna and madder: a research on effect of tin (II) chloride mordant. *J. Saudi Chem. Soc.*, 19, 64, 2015.

3. Mirjalili, M., Karimi, L., Antibacterial dyeing of polyamide using turmeric as natural dye. *Autex. Res J.*, 13, 51, 2015.
4. Gulmini, M., Idone, A., Diana, E., Gastaldi, D., Vaudan, D., Aceto, M., Identification of dyestuffs in historical textiles: Strong and weak points of a non-invasive approach. *Dyes Pigm.*, 98, 136, 2013.
5. Degani, L., Riedo, C., Gulmini, M., Chiantore, O., From plant extracts to historical textiles: characterization of dyestuffs by GC–MS.*Chromatographia*, 77, 1683, 2014.
6. Pauk, V., Bartak, P., Lemr, K., Characterization of natural organic colorants in historical and art objects by high-performance liquid chromatography. *J. Sep. Sci.*, 37, 3393, 2014.
7. Waring, D.R., Hallas, G., *The chemistry and application of dyes.*Springer Science & Business Media, 2013
8. Almeida, E.J.R., Corso, C.R., Comparative study of toxicity of azo dye Procion Red MX-5B following biosorption and biodegradation treatments with the fungi *Aspergillus niger* and *Aspergillus terreus*. *Chemosphere*, 112, 317, 2014.
9. Brillas, E., Martínez-Huitle, C.A., Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Appl. Catal B: Environ.,* 166, 603, 2015.
10. Chung, K.T., Azo dyes and human health: A review. *J. Environ. Sci. Health C.*, 34, 233, 2016.
11. Bladin, P.F., Azo dyes and the blood–brain barrier: Robert Aird's novel concept in chronic neurological disease (1903–2000). *J. Clin. Neurosci.*, 21, 33, 2014.
12. Rodriguez-Amaya, D.B., Natural food pigments and colorants. *Curr. Opin. Food Sci.*, 7, 20, 2016.
13. Ghaheh, F.S., Mortazavi, S.M., Alihosseini, F., Fassihi, A., Nateri, A.S., Abedi, D., Assessment of antibacterial activity of wool fabrics dyed with natural dyes. *J. Clean. Prod.*, 72, 139, 2014.
14. Pervaiz, S., Aziz, M., Khan, Z., Najeebullah, M., Floral Dyes: "An opportunity for punjab leather industry to promote sustainable fashion development."*Int. J. Res. Advent Technol.*, 4, 34, 2016.
15. Mongkholrattanasit, R., Saiwan, C., Klaichoi, C., Rungruangkitkrai, N., Sasivatchutikool, P., UV-protection property of silk fabric dyed with natural indigo by using padding technique: A focus on effect of ferrous sulfate mordant. *Int. J. Appl. Mech. Mater.*, 804, 217, 2015.
16. Shahid, M., Mohammad, F., Perspectives for natural product based agents derived from industrial plants in textile applications–A review. *J. Clean. Prod.*, 57, 2, 2013.
17. Mirjalili, M., Nazarpoor, K., Karimi, L., Eco-friendly dyeing of wool using natural dye from weld as co-partner with synthetic dye. *J. Clean. Prod.*, 19, 1051, 2011.
18. Komboonchoo, S., Bechtold, T., Natural dyeing of wool and hair with indigo carmine (CI Natural Blue 2), a renewable resource based blue dye. *J. Clean. Prod.*, 17, 1487, 2009.

19. Gupta, D., Khare, S.K., Laha, A., Antimicrobial properties of natural dyes against Gram-negative bacteria. *Color. Technol.*, 120, 167, 2004.
20. Baliarsingh, S., Panda, A.K., Jena, J., Das, T., Das, N. B., Exploring sustainable technique on natural dye extraction from native plants for textile: identification of colourants, colourimetric analysis of dyed yarns and their antimicrobial evaluation. *J. Clean. Prod.*, 37, 257, 2012.
21. Mongkholrattanasit, R., Kryštůfek, J., Wiener, J., Dyeing and fastness properties of natural dyes extracted from eucalyptus leaves using padding techniques. *Fibers Polym.*, 11, 346, 2010.
22. Ali, S., Hussain, T., Nawaz, R., Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. *J. Clean. Prod.*, 17, 61, 2009.
23. Jothi, D., Extraction of natural dyes from African marigold flower (*Tagetes erecta* L.) for textile coloration. *Autex. Res. J.*, 8, 49, 2008.
24. Sinha, K., Chowdhury, S., Saha, P.D., Datta, S., Modeling of microwave-assisted extraction of natural dye from seeds of *Bixa orellana* (Annatto) using response surface methodology (RSM) and artificial neural network (ANN). *Ind. Crops Prod.*, 41, 165, 2013.
25. Sinha, K., Saha, P.D., Datta, S., Extraction of natural dye from petals of Flame of forest (*Butea monosperma*) flower: Process optimization using response surface methodology (RSM). *Dyes Pigm.*, 94, 212, 2012.
26. Kulkarni, S.S., Gokhale, A.V., Bodake, U.M., Pathade, G.R., Cotton dyeing with natural dye extracted from pomegranate (*Punica granatum*) peel. *Univers. J. Environ. Res. Technol.*, 1, 135, 2011.
27. Narayana Swamy, V., Gowda, K.N., Sudhakar, R., Natural dye from the bark of *Casuarina equisetifolia* for silk. *Int. J. Pharm. Bio. Sci.*, 4, 94, 2013.
28. Perumal, P.C., Sophia, D., Raj, C.A., Ragavendran, P., Starlin, T., Gopalakrishnan, V.K., In vitro antioxidant activities and HPTLC analysis of ethanolic extract of *Cayratia trifolia* (L.). *Asian Pac. J. Trop. Dis.*, 2, 952, 2012.
29. Sinha, K., Saha, P.D., Ramya, V., Datta, S., Improved extraction of natural blue dye from butterfly pea using microwave assisted methodology to reduce the effect of synthetic blue dye. *Int. J. Chem. Tech.*, 4, 57, 2012.
30. Janani, L., Hillary, L., Phillips, K., Mordanting methods for dyeing cotton fabrics with dye from *Albizia coriaria* plant species. *Int. J. Sci. Res. Pub.*, 4, 1, 2014.
31. Samanta, A.K., Agarwal, P., Datta, S., Studies on color interaction parameters and color fastness properties for dyeing of cotton fabrics with binary mixtures of jackfruit wood and other natural dyes. *J. Nat. Fiber.*, 6, 171, 2009
32. He-yuan, Q. I. U., Jie-man, C. H. E. N., Jing-ru, H. U., Microwave extraction and stability of brown pigment from *Camellia oleifera* shells. *Food Sci.*, 16, 43, 2009.
33. Swamy, V.N., Gowda, K.N., Sudhakar, R., Natural dye extracted from *Vitex negundo* as a potential alternative to synthetic dyes for dyeing of silk. *J. Inst. Eng. India Ser. E.*, 97, 31, 2016.

34. Ghouila, H., Haddar, W., Ticha, M.B., Baaka, N., Meksi, N., Mhenni, M. F., Jannet, H.B., *Rhus pentaphylla*bark as a new source of natural colorant for wool and silk fibers. *J. Tunisian Chem. Soc.,* 16, 95, 2014.
35. Bouzidi, A., Baaka, N., Salem, N., Mhenni, M.F., Mighri, Z., *Limoniastrum monopetalum* stems as a new source of natural colorant for dyeing wool fabrics. *Fibers Polym.*, 17, 1256, 2016.
36. Giacomini, F., Menegazzo, M.A.B., dos Santos, J.C.O., Arroyo, P.A., de Barros, M.A.S.D., Ecofriendly dyeing of silk with extract of yerba mate (*Ilex paraguariensis*). *Text. Res. J.*, 87, 829, 2017.
37. Wang, N., Chu, Y.L., Wang, J., Zhu, S.L., Study on extraction and toxic properties to drosophila melanogaster of red pigment from *Cinnamomum camphora* (L.). *Food Sci. Technol.*, 11, 81, 2009.
38. Onal, A., Eser, F., Akinci, I., Extraction of dyestuff from basil (*Ocimum basilium*) and investigation of dyeing properties of cotton and wool fabrics using (urea + ammonia + calcium oxalate) mixture. *J. New Results Sci.*, 2, 19, 2013.
39. Haddar, W., Elksibi, I., Meksi, N., Mhenni, M.F., Valorization of the leaves of fennel (*Foeniculum vulgare*) as natural dyes fixed on modified cotton: A dyeing process optimization based on a response surface methodology. *Ind. Crops Prod.*, 52, 588, 2014.
40. Vankar, P.S., Shanker, R., Dixit, S., Mahanta, D., Tiwari, S. C., Chemical characterisation of extract derived from *Daphne papyraceae* and sonicator dyeing of cotton, silk and wool with the extract. *Pigm. Resin. Technol.*, 38, 181, 2009.
41. Narayanaswamy, V., Ninge Gowda, K. N., Sudhakar, R., Dyeing and color fastness of natural dye from *Psidium guajuva* on silk. *J. Nat. Fiber.*, 10, 257, 2013.
42. Luo, P., Niu, H., Zheng, G., Bai, X., Zhang, M., Wang, W., From salmon pink to blue natural sensitizers for solar cells: *Canna indica* L., *Salvia splendens*, cowberry and *Solanum nigrum* L. *Spectrochim. Acta Mol. Biomol. Spectrosc.*, 74, 936, 2009
43. Sarkar, A. K., Seal, C. M., Color strength and colorfastness of flax fabrics dyed with natural colorants. *Cloth. Text. Res. J.*, 21, 162, 2003.
44. Merdan, H., Eray, F., Onal, A., Kavak, F., Extraction of total dyestuff from centaury (*Hypericum scabrum* L.) and dyeing of natural fibres under different conditions. *Asian J. Chem.*, 20, 608, 2008.
45. Arora, J., Agarwal, P., Gupta, G., Rainbow of natural dyes on textiles using plants extracts: Sustainable and eco-friendly processes. *Green Sustain. Chem.*, 7, 35, 2017.
46. Kumar, C.S., Dhinakaran, M., Extraction and application of natural dyes from orange peel and lemon peel on cotton fabrics. *Text. Res. J.*, 80, 2117, 2017.
47. Mariselvam, R., Ranjitsingh, A.J.A., Selvakumar, P.M., Krishnamoorthy, R., Alshatwi, A.A., Eco friendly natural dyes from *Syzygium cumini* (L) (Jambolan) fruit seed endosperm and to preparation of antimicrobial fabric and their washing properties. *Fibers Polym.*, 18, 460, 2017.

48. Islam, M., Hasan, K.F., Deb, H., Faisal, A.M.M., Xu, W., Improving the fastness properties of cotton fabric through the implementation of different mordanting agents dyed with natural dye extracted from marigold. *American J. Polym. Sci. Eng.*, 4, 1, 2016.
49. Patil, D.B., Patil, K.N., Gaikwad, P.V., Patil, P.J., Shewale, U.L., Bhamburdekar, S.B., Extraction of natural dye from rose flower for dyeing cotton fabrics. *Int. J. Innov. Res. Multidiscip. Field.*, 2, 135, 2016.
50. Singh, S., Gahlot, M., Process development for printing on silk fabric (mulberry) with dye extracted from wax mellow (*malvaviscus arboreus*) flowers. *Man-Made Text. India*, 51, 304, 2008.
51. Al-Alwani, M.A., Ludin, N.A., Mohamad, A.B., Kadhum, A.A.H., Baabbad, M.M., Sopian, K., Optimization of dye extraction from *Cordyline fruticosa* via response surface methodology to produce a natural sensitizer for dye-sensitized solar cells. *Results Phys.*, 6, 520, 2016.
52. Ebrahimi, I., Parvinzadeh Gashti, M., Extraction of juglone from *Pterocarya fraxinifolia* leaves for dyeing, anti-fungal finishing, and solar UV protection of wool. *Color Technol.*, 131, 451, 2015.
53. Rym, M., Farouk, M., Bechir, E.M., Dyeing properties of cationized and non-cationized cotton fabrics dyed with *Vitis vinifera* L. leaves extract. *J. Text. Inst.*, 107, 525, 2016.
54. Wibowo, R., Gunlazuardi, J., Natural dye sensitizer from cassava (*Manihot utilissima*) leaves extract and its adsorption onto TiO2 photo-anode. *Mater. Sci. Eng.*, 188, 1, 2017.
55. Chattopadhyay, S.N., Pan, N.C., Roy, A.K., Saxena, S., Khan, A., Development of natural dyed jute fabric with improved colour yield and UV protection characteristics. *J. Text. Inst.*, 104, 808, 2013.
56. Sukri, N.A., Uzir, A., A comparison of boiling and soxhlet extraction method in natural dyeing. *J. Mech. Manu.*, 1, 53, 2014.
57. Jha, C.K., Kumar, R., Venkat K.S., Devi, R.V., Extraction of natural dye from marigold flower (*Tagetes erecta* L.) and dyeing of fabric and yarns: A focus on colorimetric analysis and fastness properties. *Der. Pharm. Lett.*, 7, 185, 2015.
58. Zarkogianni, M., Mikropoulou, E., Varella, E., Tsatsaroni, E., Colour and fastness of natural dyes: revival of traditional dyeing techniques. *Color. Technol.*, 127, 18, 2011.
59. Shabbir, M., Islam, S.U., Bukhari, M.N., Rather, L.J., Khan, M.A., Mohammad, F., Application of *Terminalia chebula* natural dye on wool fiber—evaluation of color and fastness properties. *Text Cloth Sustain.*, 2, 1, 2017.
60. Ticha, M.B., Meksi, N., Attia, H.E., Haddar, W., Guesmi, A., Jannet, H.B., Mhenni, M.F., Ultrasonic extraction of *Parthenocissus quinquefolia* colorants: Extract identification by HPLC-MS analysis and cleaner application on the phytodyeing of natural fibres. *Dyes Pigm.*, 141, 103, 2017.
61. Adeel, S., Gulzar, T., Azeem, M., Saeed, M., Hanif, I., & Iqbal, N., Appraisal of marigold flower based lutein as natural colourant for textile dyeing under the influence of gamma radiations. *Radiat Phys Chem.*, 13, 35, 2017.

62. Chirila, L., Popescu, A., Stanculescu, I.R., Cutrubinis, M., Cerempei, A., Sandu, I., Gamma irradiation effects on natural dyeing performances of wool fabrics. *Rev. De. Chim*, 67, 2628, 2016.
63. Talib, N., Ahmad, M.R., Ismail, K., Ab Kadir, M.I., Comparison of supercritical fluid extraction and ultrasound-assisted extraction of natural dyes from a brown seaweed (*Sargassum spinosum*). *Int. J. Text. Sci.*, 5, 141, 2016.
64. Baaka, N., Haddar, W., Ticha, M., Amorim, M.T.P., Mhenni, M.F., Sustainability issues of ultrasonic wool dyeing with grape pomace colourant. *Nat. Prod. Res.,* 31, 1, 2017.
65. Ticha, M.B., Haddar, W., Meksi, N., Guesmi, A., Mhenni, M.F., Improving dyeability of modified cotton fabrics by the natural aqueous extract from red cabbage using ultrasonic energy. *Carbohydr. Polym.*, 154, 287, 2016.
66. Benli, H., Bahtiyari, M.İ., Combination of ozone and ultrasound in pretreatment of cotton fabrics prior to natural dyeing. *J. Clean. Prod.*, 89, 116, 2015.
67. Guesmi, A., Ladhari, N., Sakli, F., Sonicator dyeing of modified acrylic fabrics with indicaxanthin natural dye. *Ind. Crops Prod.*, 42, 63, 2013.
68. Hussaan, M., Iqbal, N., Adeel, S., Azeem, M., Javed, M.T., Raza, A., Microwave-assisted enhancement of milkweed (*Calotropis procera* L.) leaves as an eco-friendly source of natural colorants for textile. *Environ. Sci. Pollut. Res.*, 24, 5089, 2017.
69. Ali, N.F., El-Khatib, E.M., El-Mohamedy, R.S.S., Ramadan, M.A., Antimicrobial activity of silk fabrics dyed with saffron dye using microwave heating. *Int. J. Curr. Microbiol. App. Sci.*, 3, 140, 2014.
70. Dayioglu, H., Kut, D., Merdan, N., Canbolat, S., The effect of dyeing properties of fixing agent and plasma treatment on silk fabric dyed with natural dye extract obtained from *Sambucus ebulus* L. plant. *Procedia. Soc. Bav. Sci.*, 195, 1609, 2015.
71. Mosquera, D.M., Carrillo, M.P., Gutiérrez, R.H., Diaz, R.O., Hernández, M. S., Fernández-Trujillo, J.P., Microwave technology applied to natural ingredient extraction from Amazonian fruits. *Foods.*, 1, 1, 2013.
72. Grujic, D., Savic, A., Topalic-Trivunovic, L., Jevsnik, S., Rijavec, T., Gorjanc, M., The influence of plasma pretreatment on the structure and antimicrobial properties of knitted fabrics treated with herbal extracts. *Acc. J.,* 21, 30, 2015.
73. Baliarsingh, S., Behera, P.C., Jena, J., Das, T., Das, N.B., UV reflectance attributed direct correlation to colour strength and absorbance of natural dyed yarn with respect to mordant use and their potential antimicrobial efficacy. *J. Clean. Prod.*, 102, 485, 2015.
74. Kim, J.K., Jo, C., Hwang, H.J., Park, H. J., Kim, Y.J., & Byun, M.W., Color improvement by irradiation of *Curcuma aromatica* extract for industrial application. *Radiat. Phys. Chem.*, 75, 449, 2006.
75. Avinc, O., Celik, A., Gedik, G., Yavas, A., Natural dye extraction from waste barks of Turkish red pine (*Pinus brutia* Ten.) timber and eco-friendly natural dyeing of various textile fibers. *Fibers Polym.*,14, 866, 2013.

76. Asgarpanah, J., Ramezanloo, F., Chemistry, pharmacology and medicinal properties of *Peganum harmala* L. *African J. Pharm. Pharmacol.*, 6, 1573, 2012.
77. Bournine, L., Bensalem, S., Fatmi, S., Bedjou, F., Mathieu, V., Iguer-Ouada, M., Kiss, Robert Duez, P., Evaluation of the cytotoxic and cytostatic activities of alkaloid extracts from different parts of *Peganum harmala* L.(Zygophyllaceae). *Eur. J. Integr. Med.*, 9, 91, 2017.
78. Adeel, S., Zuber, M., Rehman, F., Zia, K. M., Radiation induced assessment of dye yielding plants as potential source of colourants for textile dyeing. Ph.D Theisis (Department of Applied Chemistry, Government Collage University Faisalabad, Pakistan). On the Process.
79. Gohari, A.R., Saeidnia, S., Mahmoodabadi, M.K., An overview on saffron, phytochemicals, and medicinal properties. *Pharmacogn. Rev.*, 7, 61, 2013.
80. Nerome, H., Ito, M., Machmudah, S., Kanda, H., Goto, M., Extraction of phytochemicals from saffron by supercritical carbon dioxide with water and methanol as entrainer. *J. Supercrit. Fluids.*,107, 377, 2016.
81. Mehrparvar, L., Safapour, S., Sadeghi-Kiakhani, M., Gharanjig, K., A cleaner and eco-benign process for wool dyeing with madder, *Rubia tinctorum* L., root natural dye. *Int. J. Environ. Sci. Technol.*, 13, 2569, 2016.
82. Ohama, P., Namwong, S., Kumpun, S., Pigment Extraction of Safflower, Dyeing Properties and Antimicrobial Study of Dyed Silk. *Int. J. Key Eng. Mater.*, 675, 19, 2016.
83. Adeel, S., Naseer, K, Javed, S., Saqib, M., Amin, N., Naz, S., Hussaan M., Microwave assisted improvement in dyeing behavior of chemical and bio-mordanted silk fabric using safflower (*Carthamus tinctorius* L.) extract. BS (H) Theisis.
84. Mandal, S., Patra, A., Samanta, A., Roy, S., Mandal, A., Mahapatra, T.D., Pradhan, S., Das, K., Nandi, D.K., Analysis of phytochemical profile of *Terminalia arjuna* bark extract with antioxidative and antimicrobial properties. *Asian Pac. J. Trop. Biomed.*, 3, 960, 2013.
85. Sinha, K., Aikat, K., Das, P., Datta, S., Dyeing of modified cotton fiber with natural *Terminalia arjuna* dye: Optimization of dyeing parameters using response surface methodology. *Environ. Prog. Sustain. Energy.*, 35, 719, 2016.
86. Adeel, S., Zuber, M., Rehman, F., Zia, K.M., Radiation induced assessment of dye yielding plants as potential source of colourants for textile dyeing. Ph.D Theisis (Department of Applied Chemistry, Government Collage University Faisalabad, Pakistan). On the Process.
87. Batool, F., Adeel, S., Azeem, M., Khan, A.A., Bhatti, I.A., Ghaffar, A., Iqbal, N., Gamma radiations induced improvement in dyeing properties and colorfastness of cotton fabrics dyed with chicken gizzard leaves extracts. *Radiat. Phys. Chem.*, 89, 33, 2013.
88. Khan, A.A., Iqbal, N., Adeel, S., Azeem, M., Batool, F., Bhatti, I.A., Extraction of natural dye from red calico leaves: gamma ray assisted improvements in colour strength and fastness properties. *Dyes Pigm.*, 103, 50, 2014.

89. Adeel, S., Azeem, M., Kamal, S., Rehman, F., Ghaffar, A., Habib, N., Iqbal, N., Arshad, I., Kamran, M., Shabir, A.U., Microwave assisted investigation of golden duranta (*Duranta repnes* L.) leaves as a natural colorant for surface oxidized cellulosic dye. *Oxid. Commun.*, 39, 3507, 2016.
90. Adeel, S., Gulzar, T., Azeem, M., Saeed, M., Hanif, I., Iqbal, N., Appraisal of marigold flower based lutein as natural colourant for textile dyeing under the influence of gamma radiations. *Radiat. Phys. Chem.*, 130, 35, 2017.
91. Rehman, F., Adeel, S., Hanif, R., Muneer, M., Zia, K. M., Zuber, M., Jamal, M. A., Khosa, M. K., Modulation of marigold based lutein dye and its dyeing behavior using UV radiation. *J. Nat. Fibers.,* 14, 1, 2017.
92. Hussaan, M., Iqbal, N., Adeel, S., Azeem, M., Javed, M.T., Raza, A., Microwave-assisted enhancement of milkweed (*Calotropis procera* L.) leaves as an eco-friendly source of natural colorants for textile. *Research Environ. Sci. Pollut. Res.*, 24, 5089, 2017.
93. Abalaka, M., Oyewole, O.A., Kolawole, A.R., Antibacterial activities of Azadirachta indica against some bacterial pathogens. *Adv. Life Sci.,* 2, 5, 2012.
94. Malviya, N., Mahajan, S., Phytochemical screening of bark of some important trees of college campus with special reference to tannin, glycoside and their medicinal properties. *Int. Res. J. Environ. Sci.,* 2, 13, 2013.
95. Adeel, S., Zuber, M., Rehman, F., Zia, K.M., Radiation induced assessment of dye yielding plants as potential source of colourants for textile dyeing. Ph.D Theisis (Department of Applied Chemistry, Government Collage University Faisalabad, Pakistan). On the Process.

9

A Review on Phytochemistry, Pharmacological and Coloring Potential of *Lawsonia Inermis*

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Abstract

Lawsonia inermis, locally known as henna, is one of the most popular and ancient plants. Various parts of the plant have been employed for traditional medicine, decoration, and cosmetic purposes around the world. Literature reveals the presence of large number phytochemicals in the whole plant such as phenolic compounds, terpenes, steroids, and alkaloids etc. Pharmacological studies indicated that the extract and isolated compounds from this species possess excel bioactivities such as antimicrobial, antifungal, anticancer, anthelmintic, antidiabetic, antioxidant, wound healing, and immunomodulatory etc. The chapter reviews the phytochemical, pharmacological and dyeing aspects of *L. inermis* plant.

Keywords: *Lawsonia inermis*, phytochemistry, pharmacology, dyeing, biological activity.

9.1 Introduction

Plants play a pivotal role in maintaining human health and improving the quality of human life for thousands of years and have served humans well, as valuable components of medicines, seasonings, beverages, cosmetics, and dyes. The Indian subcontinent is endowed with various plant species enriched with ethno-pharmacological properties, which have been extensively used in

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Indian systems of conventional as well as non-conventional system of medicine such as Siddha, Unani, Ayurveda, and Homoeopathy [1].

L. inermis; syn. *L. alba* Linn. is the sole species of the family *Lythraceae*, commonly known as henna or mehendi. Geographically, henna is distributed in Egypt, Arabic countries, Persian countries, India, Pakistan, China, Sudan, and Florida. It has the appearance of a much-branched and small shrub-like tree up-to 2–6 m in height, with spine-tipped branchlets. The leaves are described as smooth, opposite, sub-sessile, elliptical-shaped and broadly lanceolate, with depressed veins clearly visible on the dorsal view. At mature stage, the leaves of the plant are greenish brown in color with a characteristic odor as well as a bitter and astringent taste. Its flowers contain four sepals, a ~2 mm calyxtube, with white or red stamens present as pairs on the perimeter of the calyx tube, and obvate, crumbled petals. The ovary is erect and four-celled. The fruits are brown filled with ~40 angular seeds (Figure 9.1) [2, 3].

Henna is known as an important ancient dye, evidence being the Egyptian mummies found in the tombs that had their nails dyed with henna. Consequently, the relics from the excavation at Mohanjodaro and Harappa (Indus Valley Civilization), Ajanta Caves Painting and Mughal dyeing, printing and painting, show the use of natural dyes such as Madder, Indigo, and Henna. Henna leaves have been extensively used as a cosmetic for staining hands, palms, hairs, and other body parts during religious festivals and marriages etc. (Figure 9.1) [2–5]. Extensive phytochemical investigations by various researchers on *L. inermis* plant revealed

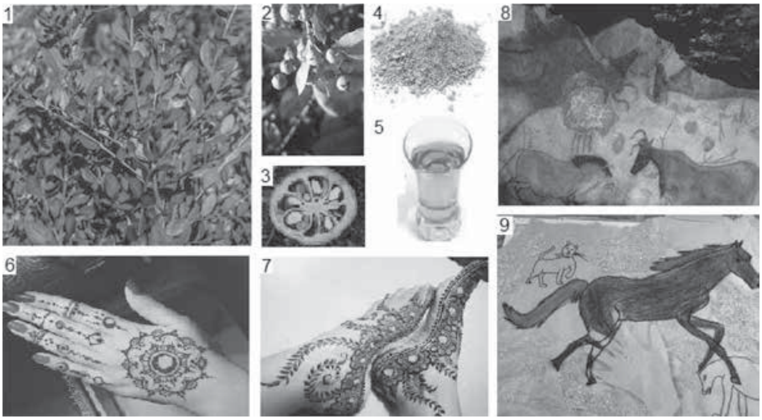


Figure 9.1 *Lawsonia inermis* plant (1), fruits (2), seed (3), powdered leaves (4), essential oil (5), body arts (6,7), and cave paintings (8,9).

that it contains a number of phytochemicals such as flavonoids, quinoids, naphthalene derivatives, coumarins, xanthones, terpenoids, alkaloids, and tannins, many of which show remarked bioactivities [2–4]. Lawsone, a naphthoquinone exhibits strong dyeing potential and can be used for natural as well as synthetic fibers [6]. This article covers extensively and systematically the depth and breadth of modern research involving *L. inermis* plant, organized into easily accessible and comparable information towards phytochemistry, ethno-pharmacology, and coloring potentiality.

9.2 Phytochemistry

More than 90 compounds have been isolated from whole *L. inermis* plant. The abundance of many biologically active compounds enabled its diversified value-added applications. The main classes are discussed herein.

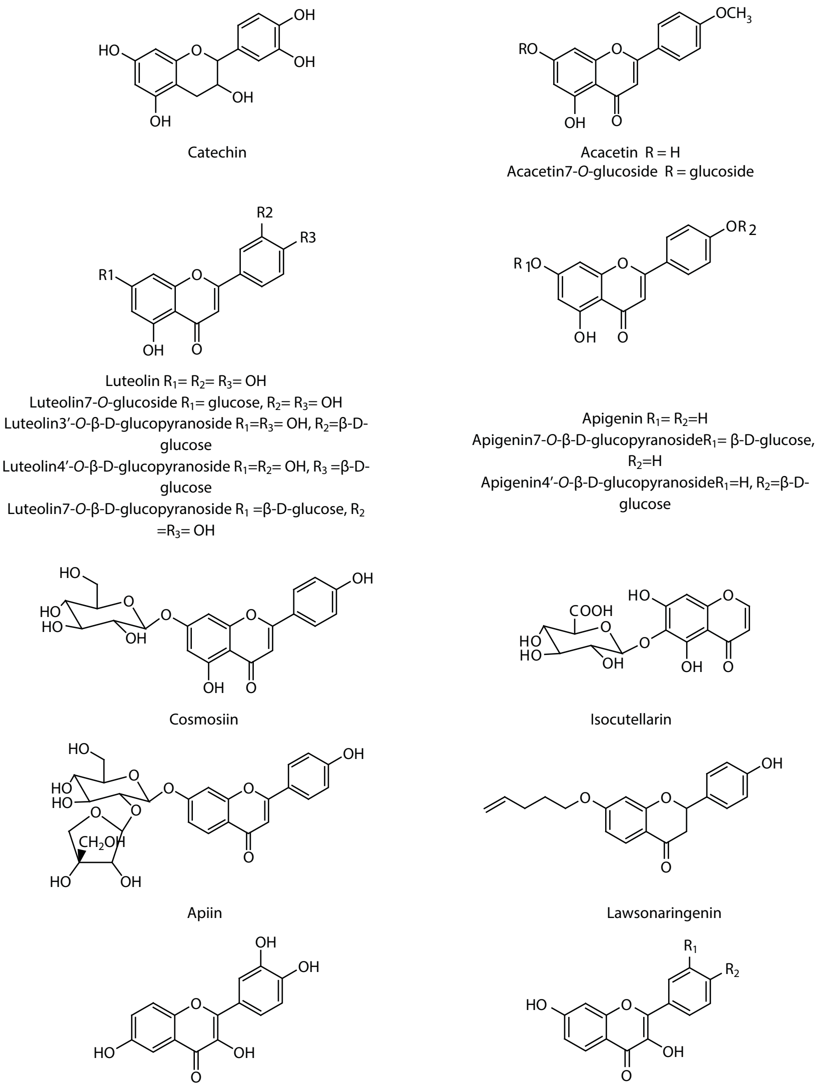
9.2.1 Phenolics

9.2.1.1 Flavonoids

Before the 1990s, some flavonoids such as acacetin, acacetin-7-*O*-glucoside, luteolin, luteolin-7-*O*-glucoside, apigenin-7-*O*-β-D-glucopyranoside, apigenin-4'-*O*-β-D-glucopyranoside, and luteolin-3'-*O*-β-D-glucopyranoside have been reported from the aerial parts of henna (Figure 9.2) [7, 8]. Later, Mikhaeil *et al.* reported apiin and cosmosiin [9]. Consequently, isoscutellarin, lawsochrysin, lawsochrysinin, lawsonaringenin, 3',4'-dimethoxyflavone, 7-hydroxyflavone, 3,3',4',7-tetrahydroxyflavanone and rhoifolin were described in leaves of the plant [4, 10]. Furthermore, Liou *et al.* reported the occurrence of apigenin, luteolin-4'-O-β-D-glucopyranoside, luteolin-7-*O*-rutinoside, diosmetin-7-*O*-rutinoside and luteolin-7-*O*-β-D-glucopyranoside in stems and leaves (Figure 9.2) [11].

9.2.1.2 Naphthoquinones

Naphthoquinones, abundantly reported in *L. inermis* are identified as lawsone, 2-hydroxy-1,4-naphthoquinone, isoplumbagin, 4-hydroxy-α-tetralone, 3α,4α-dihydroxy-α-tetralone, lawsonadeem and 3-amino-2-methoxycarbonyl-1,4-naphthoquinone (Figure 9.3) [2, 3, 11]. Lawsone, the chief coloring constituent, is particularly concentrated in the leaf petioles of the plant which attributed to excellent bioactive functionality [2].



Catechin

Acacetin R = H
Acacetin7-*O*-glucoside R = glucoside

Luteolin R_1= R_2= R_3= OH
Luteolin7-*O*-glucoside R_1= glucose, R_2= R_3= OH
Luteolin3′-*O*-β-D-glucopyranoside R_1=R_3= OH, R_2=β-D-glucose
Luteolin4′-*O*-β-D-glucopyranoside R_1=R_2= OH, R_3 =β-D-glucose
Luteolin7-*O*-β-D-glucopyranoside R_1 =β-D-glucose, R_2 =R_3= OH

Apigenin R_1= R_2=H
Apigenin7-*O*-β-D-glucopyranosideR$_1$= β-D-glucose, R_2=H
Apigenin4′-*O*-β-D-glucopyranosideR$_1$=H, R_2=β-D-glucose

Cosmosiin

Isocutellarin

Apiin

Lawsonaringenin

Figure 9.2 Structures of flavonoids.

9.2.1.3 Naphthalenes

In small amount, naphthalene derivatives are present in *L. inermis*. For example, lawsoniaside [12], 1,2,4-trihydroxynaphthalene-1-*O*-β-D- glucopyranoside, three methyl naphthalene carboxylates, lawsonaphthoate A-C [3, 11] are reported in the leaves and 1,2-Dihydroxy-4-*O*-glucosyloxynaphthalene isolated from aerial parts (Figure 9.4) [8].

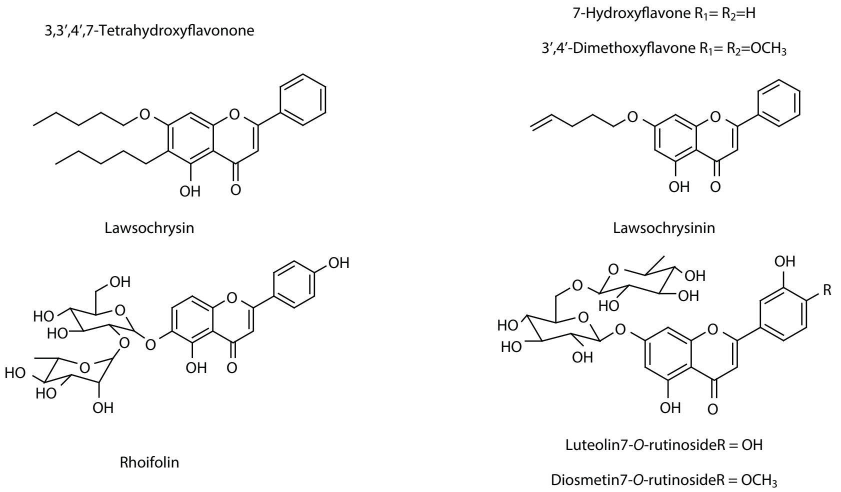


Figure 9.2 (*Continued*).

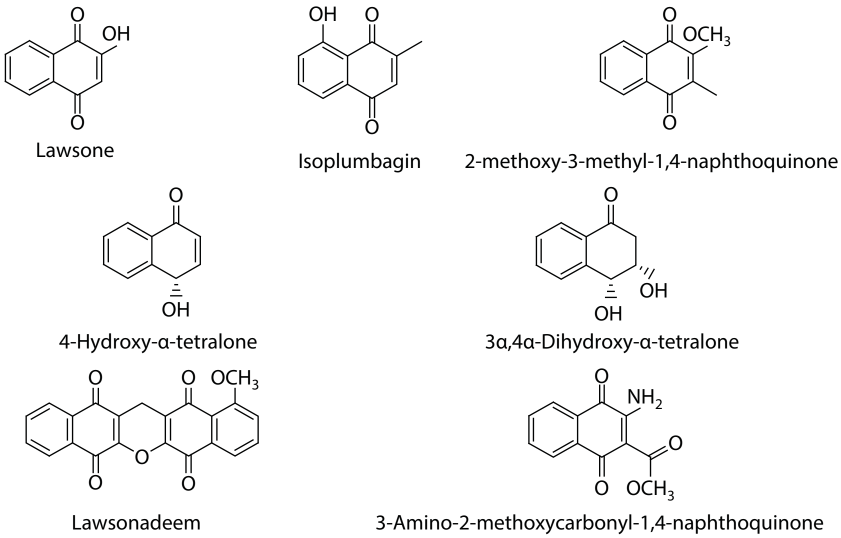
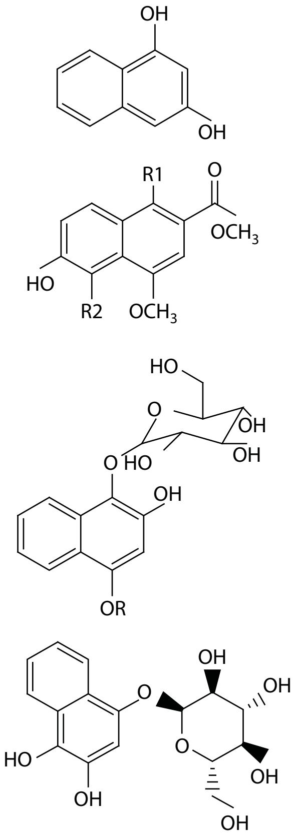


Figure 9.3 Structures of naphthoquinones.

9.2.1.4 Acetylenes

A few derivatives of acetylenes have been isolated in the leaves of this plant are, lawsochylin A-C shown in Figure 9.5 [3].



1,3-dihydroxynaphthalene

Lawsonaphthoate A R_1= OH, R_2= H

Lawsonaphthoate B R_1= OCH_3, R_2= H

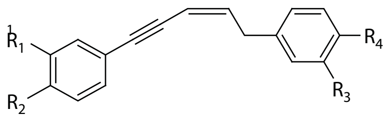
Lawsonaphthoate C R_1= OH, R_2= OCH_3

Lawsoniaside R = β-D-glucopyranoside

1,2,4-Trihydroxynaphthalene-1-*O*-β-D-glucopyranoside

1,2-Dihydroxy-4-*O*-glucosyloxynaphthalene

Figure 9.4 Structures of naphthalenes.



Lawsochylin A R_1= R_3= H, R_2= R_4= OH

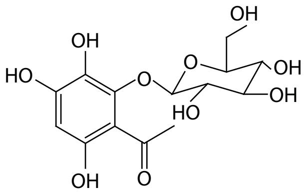
Lawsochylin B R_1= R_2= R_4= OH, R_3=H

Lawsochylin C R_1=H,R_2= R_4= OH, R_3= OCH_3

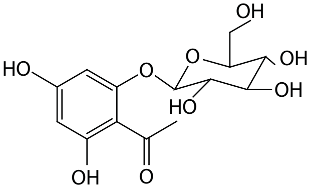
Figure 9.5 Structures of acetylenes.

9.2.1.5 Alkyl Phenones

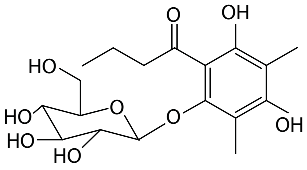
Alkyl phenones reported in the leaves of *L. inermis* are lalioside, lawsoniaside A and 2,4,6-trihydroxyacetophenone-2-*O*-β-D-glucopyranoside (Figure 9.6) [12, 13].



Lalioside

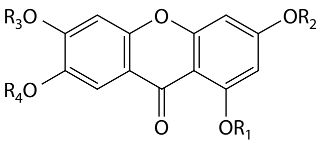


2,4,6-Trihydroxyacetophenone-2-*O*-β-D-glucopyranoside



Lawsoniaside A

Figure 9.6 Structures of alkyl phenones.



Laxanthone I R_1= R_2= H, R_3= R_4= CH_3

Laxanthone II R_1=H, R_2= R_3=$COCH_3$, R_4= CH_3

Laxanthone III R_1=H, R_2= R_4=CH_3,R_4= $COCH_3$

Figure 9.7 Structures of xanthones.

9.2.1.6 *Xanthones*

Figure 9.7 shows three xanthone compounds which have been isolated from aerial parts, namely, Laxanthone I, II & III [3, 9].

9.2.1.7 *Coumarins*

Coumarins (Figure 9.8) are also common constituents along with naphthoquinones. The presence of Lacoumarin was reported in the whole plant [14]. The leaves were found to be enriched with the occurrence of several coumarins such as fraxetin, scopoletin, esculetin, daphneside, dephnorin and agrimonolide-6-*O*-β-D-glucopyranoside [2, 3, 10].

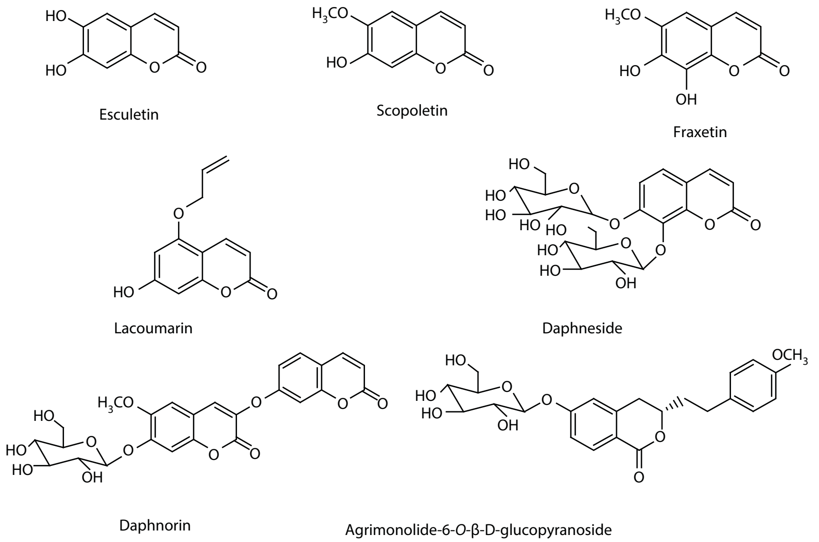


Figure 9.8 Structures of coumarins.

9.2.1.8 *Tannins*

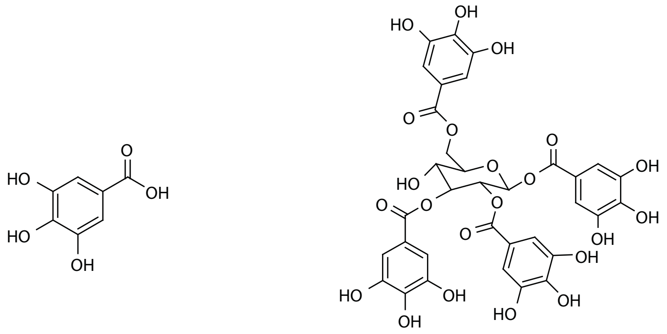
Tannins are found in a small amount. Figure 9.9 illustrates the tannin compounds, like gallic acid, tannic acid, 1,2,3,6-Tetra-*O*-gallolyl-β-D-glucose and 1,2,3,4,6-Penta-*O*-gallolyl-β-D-glucose isolated from the whole *L. inermis* plant [3, 9, 10].

9.2.1.9 *Lignans*

Some lignans have been reported in the leaves of *L. inermis*, for example, (+)-syringaresinol-*O*-β-D-glucopyr- anoside, (+)-syringaresinol-di-*O*-β-D-glucopyranoside and (+)-pinoresinol-di-*O*-β-D-glucopyranoside (Figure 9.10) [3, 10].

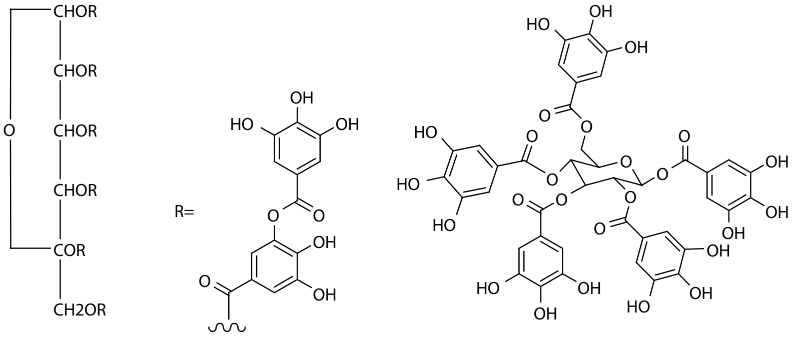
9.2.1.10 *Others*

Including the above described phenolic compounds, some other compounds also reported in various parts of the plant. Lawsonicin and *p*-coumaric acid were reported in aerial parts, while three 1,5-diphenylpent-3-en-1-ynederivatives: lawsochylin A–C; 4-hydroxy-benzaldehyde and dihydrodehydrodiconyferyl alcohol were isolated from the leaves (Figure 9.11) [3, 9–11].



Gallic acid

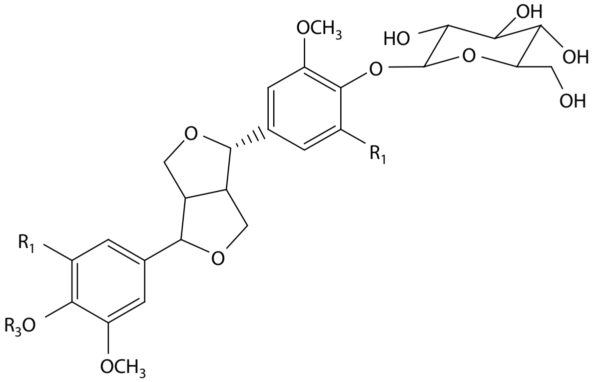
1,2,3,6-Tetra-*O*-gallolyl-β-D-glucose



Tannic acid

1,2,3,4,6-Penta-*O*-gallolyl-β-D-glucose

Figure 9.9 Structures of tannins.



(+)-Syringaresinol-*O*-β-D-glucopyranoside R_1= OCH_3, R_3= H

(+)-Syringaresinol-di-*O*-β-D-glucopyranoside R_1= OCH_3, R_2= ^{2}-D-glucopyranoside

(+)-Pinoresinol-di-*O*-β-D-glucopyranoside R_1= H, R_2= ^{2}-D-glucopyranoside

Figure 9.10 Structures of lignans.

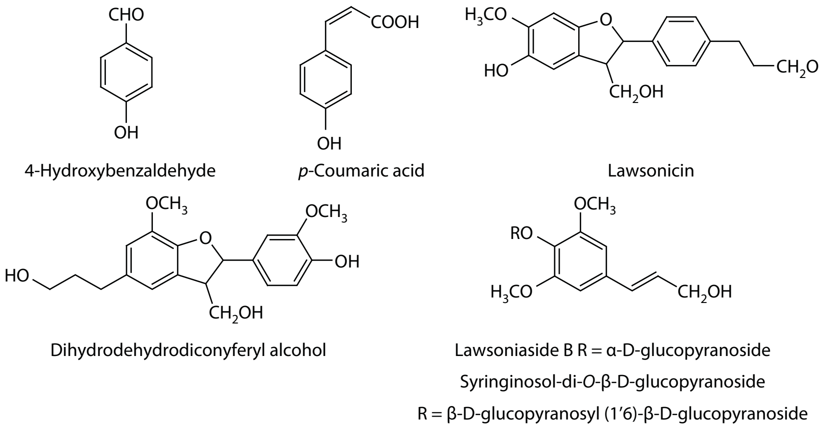


Figure 9.11 Structures of other phenolic compounds.

9.2.2 Terpenoids

A wide variety of terpenoids are present in this plant (Figure 9.12). The brown-orange essential oil obtained from flowers has a pleasant odor, mainly attributed to the presence of α and β-ionone isomers and their derivatives along with other alcohol and aldehyde derivatives. The fragrance was utilized in perfume industry in old era [2, 3, 16]. In addition, bisabolene, 1,8-cineole, α-pinene, phytol, and *p*-cymene were identified in the leaf essential oil [17, 18]. Many non-volatile terpenoids have been isolated and identified in the aerial parts, for example, lupeol, betulin, betulinic acid, vomifoliol, 9-Hydroxy-4-megastigmen-3-one, lawsowaseem, lawsoshamim, β-sitosterol, lawsonic acid, and lawsonin [2, 11, 19–21]. Seeds contain lawnermis acid and lawnermis acid methyl ester [22].

9.2.3 Steroids

Figure 9.13 depicts lawsaritol (24-β-ethylcholest-4-en-3-β-ol). It is the only single sterol isolated from the roots of *L. inermis* [23].

9.2.4 Alkaloids

Recently, two alkaloids namely, harmine and harmaline are firstly identified in the alcoholic dried mature seed extract by Jacob and Saral (24).

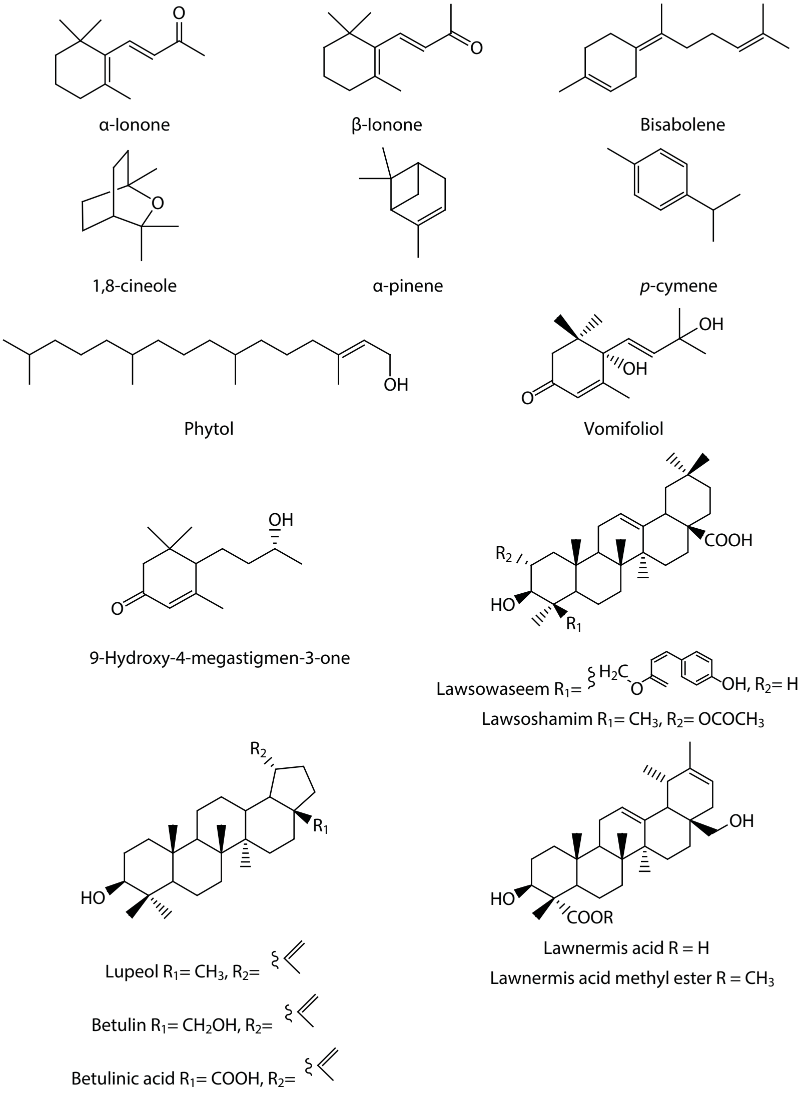
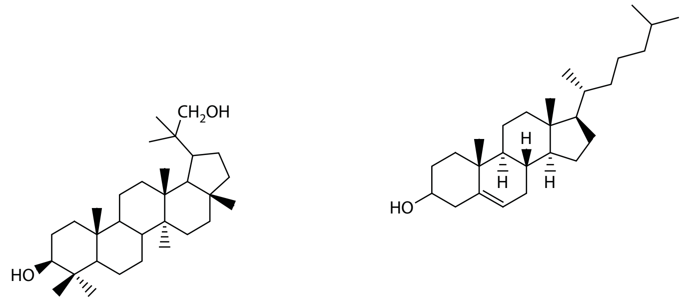


Figure 9.12 Structures of terpenoids.

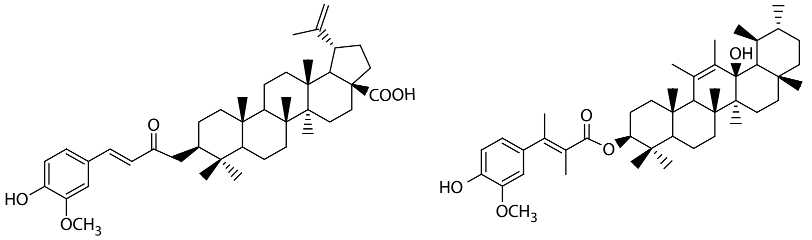
9.2.5 Miscellaneous Compounds

Figure 9.15 highlights other chemical compounds isolated from different parts of *L. inermis* plant. The aerial parts were reported to produce



(20S)-3β,30-Dihydroxylupane

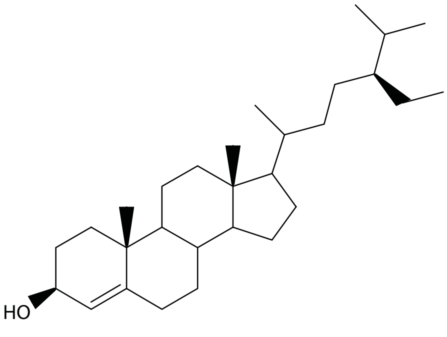
β-Sitosterol



Lawsonic acid

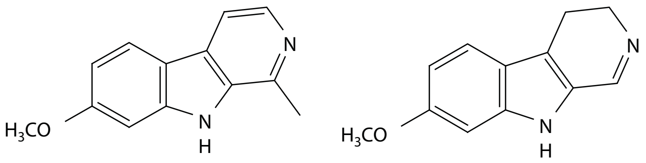
Lawsonin

Figure 9.12 (*Continued*).



Lawsaritol

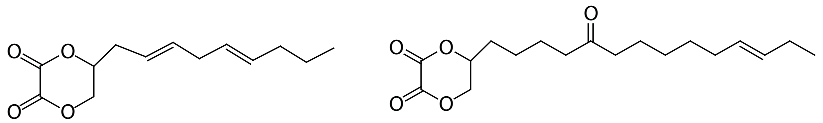
Figure 9.13 Structure of lawsaritol.



Harmine

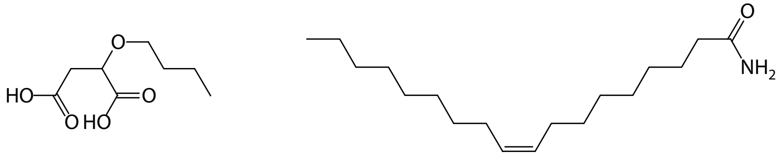
Harmaline

Figure 9.14 Structures of alkaloids.



5-[1'-(Docosa-2'E,5'E-dienyl)]-1,4-dioxin-2,3-dione

12-[2'-(1',4'-Dioxin-5',6'-dione)-8"E-undecenyl-dodecanate]



2-Butoxysuccinic acid

Oleamide

Figure 9.15 Structures of other miscellaneous compounds.

two dioxin derivatives, 5-[1'-(Docosa-2'E,5'E-dienyl)]-1,4-dioxin-2,3-dione and 12-[2'-(1',4'-Dioxin-5',6'-dione)-8"E-undecenyl-dodecanate] by Siddiqui *et al.*, [25]. Additionally, two open chained compounds, 2-butoxysuccinic acid and oleamide were also isolated from stems and leaves [11] of this plant.

9.3 Pharmacological Potential

The utilization of medicinal properties of plants has been successfully adopted since prehistoric times. Middle Eastern civilization developed the Greco-Arabic system of medicine (Unani system of medicine), which is practiced well in the Indian sub-continent. One such plant, *L. inermis* gains much attention of the researchers worldwide for its excellent pharmacological activities ranging from anti-inflammatory to anticancer activities. Widespread researches undertaken on pharmacological arrays on *L. inermis* plant demonstrated that lawsone exhibited pronounced effect corresponds to a number of activities. Active responses of the aerial plant extracts attributed to the presence of a number of phytoconstituents such as flavonoids, terpenoids, tannins etc. The functional pharmacological activities shown by this plant include, antimicrobial [2, 3, 26], antitumor [27], anthelmintic [28], antitrypanosomal [28], antileishmanial [28, 29], antidiabetic [30], antioxidant [9, 13, 31], hepatoprotective [32], wound healing [33], immunomodulatory [9, 34], anti-inflammatory, analgesic and antipyretic [9, 35], memory boosting [36], and anti-ulcer [37] activities. Along with the above pharmacological actions, leaf and bark extracts have been found to be effective towards the treatment of various ailments, including jaundice and enlargement of liver [38] and eczema [39].

9.4 Coloring Potential

Henna has been used to dye the skin and hair for many centuries. The traditional use of henna leaves powder is documented in the dyeing of hair and nails as well as traditional paintings on the skin and other body parts. Egyptian mummies have been found their fingers/ toe nails, finger tips, palms and soles of the feet with red, orange or yellow color dyed with henna dye. It was also used in ancient Egypt for coloring men's beards and mustaches, as well as for the manes and tails of the horses. Around 3200 BC Henna and Indigo were being mixed to dye hair black. Some Jews admired this custom during the 'Captivity in Egypt' in the 12th century BC, but its use was frowned upon by the Orthodox, who insisted that elegantly decorated female Egyptian marrying Jews must shave their heads, nails and thoroughly scrub their palms and soles. Its use for fragrance is referred to in the *Song of Solomon*; its scent is said to be like that of roses and it was still used in bouquets in Egypt since early of 20th century. Henna is used in Yemen, where old men are seen with reddened beards, which indicates that they have made the pilgrimage to Mecca [2, 3–6].

The chief coloring phytochemical in the leaves of *L. inermis* is identified as 2-Hydroxy naphthoquinone (Lawsone; Figure 9.3) which has been used as a famous natural dye since prehistoric times [40]. Industrial classification describes Lawsone as Natural Orange 6 and CI 75480. The inherent coloring and biological abilities of *L. inermis* leaves make it a spacious and considerable research option for scientific communities. Therefore, the application of *L. inermis* as a dye in the coloration of textiles is conducted for both natural as well as man-made textile fibers. Natural protein fibers such as wool and silk are very commonly used textile fibers suitable for dyeing with henna due to their substantivity towards lawsone molecule [41–43]. Among the natural fibers, vegetable fibers are the most popular apparel fiber obtained from the cell wall of plants and are cellulosic in composition. These fibers have been dyed with a wide range of mordanting agents with henna [44, 45]. Similarly, the application of *L. inermis* leaves as dye studied for the dyeing of synthetic fibers, for example, nylon and polyester (most important classes of synthetic textile fibers) [46]. Furthermore, Ali and Sayeed reported the coloring ability of lawsone for food applications [47]. Additionally, another application of henna dye was reported in paints [48] and in preoperative surgery as a durable skin marker [49].

Protective textiles find immense applications in day-to-day life and have been a growing need to develop active finishes for textile materials that can offer improved protection to the users from microbes (bacteria, mould or fungi), which cause numerous problems [50, 51]. Textile products have huge favorable surface conditions for microorganism growth (i.e., pathogenic or odor-generating bacteria and moulds), when in contact with the human body, the textile materials offer an ideal environment for growth, providing oxygen, water, and warmth, as well as nutrients from spillages and body exudates [52, 53]. To overcome the situation, several antimicrobial agents have been developed and utilized. Later, novel and eco-friendly substitutes have grown due to the environmental hazards and allergic responses of their synthetic counterparts [50–55].

Natural products derived from plants/animals have been known for a long time for dyeing as well as medicinal properties. Many of the plants used for dye extraction have been identified, exhibit potent medicinal properties and thus can be used with respect to antimicrobial agents [51, 56]. In an investigation, the dyeing and antimicrobial characteristics of chitosan treated wool fabrics using henna as a natural dye was described by Dev *et al.*, [51]. In this study, the results proved that the chitosan treated wool fabrics showed an increase in dye uptake of fabrics and treated fabrics were found to be antimicrobial against human pathogens, and the chitosan treatment enhances the antimicrobial characteristics of the henna dye. The fastness properties were found to be good against washing, light, and perspiration. In addition, more studies have been performed on the protective potentiality of henna dye. In a subsequent study, Yusuf *et al.* [57] described that mordanted wool yarn showed the increase in dye uptake resulting in high color strength and better fastness properties but considerable decrease in antimicrobial activity while a slight decrease in the case of antifungal activity was observed with the application of mordants. Fastness properties of henna dyed samples were found considerably good. A later study by the same group has showed that henna dye exhibits remarked anticandidal activity with sufficient fastness properties [58].

Due to the wide application of henna in hair coloration and body paints, numerous studies about potential health hazards have been performed. As a general result, the studies have demonstrated that henna is a natural product with low health risk potential. From an assessment of the genotoxicity of 2-hydroxy-1,4-naphthoquinone dye (Lawsone) ingredient of henna, Kirkland and Marzin suggested from their study on henna that it poses no genotoxic risk to the consumer [59, 60]. Therefore, it is indicated that the extract of leaves of henna can be applied on textile substrates to produce colored protective clothing and textiles with considerable antimicrobial functionalities.

9.5 Conclusion and Future Outlook

L. inermis, commonly known as henna has been traditionally used in Egypt, Arabic countries, Persian countries, India, Pakistan, China, Sudan etc. to decorate and to combat various infections concerning in different indigenous systems of medicine like Siddha, Ayurveda, and Unani and indirectly in the pharmaceutical preparations. Several phytochemicals are reported in this species, for example, phenolics, terpenoids, alkaloids, sterols, and other miscellaneous compounds. Pharmacological studies showed that the extract and isolated compounds from this species possess excel bioactivities such as antimicrobial, antifungal, anticancer, anthelmintic, antidiabetic, antioxidant, wound healing, immunomodulatory etc. Therefore, *L. inermis* has the potential in the development of several lead compounds, which can be suitable alternatives to modern synthetic drugs, with a wide pharmacological spectrum. The information summarized here is intended to serve as a reference tool to the researchers in the fields of ethnopharmacology and natural products chemistry with a green approach. More rigorous research on chemical constituents and their action mechanisms in exhibiting certain biological activities are further needed to understand the future research dimension of this plant.

References

1. Srinivasan, D., Nathan, S., Suresh, T., Perumalsamy, P.L., Antimicrobial activity of certain Indian medicinal plants used in folkloric medicine. *J. Ethnopharmacol.*, 74(3), 217–220, 2001.
2. Chaudhary, G., Goyal, S., Poonia, P., Lawsoniainermis Linnaeus: A phytopharmacological review. *Int. J. Pharm. Sci. Drug Res.*, 2(2), 91–98, 2010.
3. Semwal, R.B., Semwal, D.K., Combrinck, S., Cartwright-Jones, C., Viljoen, A., *Lawsonia inermis* L.(henna): Ethnobotanical, phytochemical and pharmacological aspects. *J. Ethnopharmacol.*, 155(1), 80–103, 2014.
4. Uddin, N., Siddiqui, B.S., Begum, S., Bhatti, H.A., Khan, A., Parveen, S., Choudhary, M.I., Bioactive flavonoids from the leaves of *Lawsonia alba* (Henna). *Phytochem. Lett.*, 4(4), 454–458, 2011.
5. Yusuf, M., Shabbir, M., Mohammad, F., Natural colorants: Historical, processing and sustainable prospects. *Nat. Prod. Bioprospect.*, 7(1), 123–145, 2017.
6. Bechtold, T., Natural colorants–quinoid, naphthoquinoid and anthraquinoid dyes, in: *Handbook of Natural Colorants*, T. Bechtold, and R. Mussak (Eds.), pp. 151–182, John Wiley & Sons Ltd., Chichester, UK, 2009.
7. Mahmoud, Z.F., Salam, N.A., Khafagy, S.M., Constituents of henna leaves (*Lawsonia inermis* L.) growing in Egypt. *Fitoterapia*, 51, 153–155, 1980.

8. Afzal, M., Al-Oriquat, G., Al-Hassan, J.M., Flavone glycosides from *Lawsoniainermis*. *Heterocycles*, 14, 1973–1976, 1980.
9. Mikhaeil, B.R., Badria, F.A., Maatooq, G.T., Amer, M.M.A. Antioxidant and immunomodulatory constituents of henna leaves. *Zeitschriftfür Naturforschung*, C59, 468–476, 2004.
10. Cuong, N.X., Nhiem, N.X., Thao, N.P., Nam, N.H., Dat, N.T., Anh, H.L.T., Van Kiem, P., Van Minh, C., Won, J.H., Chung, W.Y., Kim, Y.H., Inhibitors of osteoclastogenesis from *Lawsoniainermis* leaves. *Bioorg. Med. Chem. Lett.*, 20(16), 4782–4784, 2010.
11. Liou, J.R., El-Shazly, M., Du, Y.C., Tseng, C.N., Hwang, T.L., Chuang, Y.L., Hsu, Y.M., Hsieh, P.W., Wu, C.C., Chen, S.L., Hou, M.F., 1, 5-Diphenylpent-3-en-1-ynes and methyl naphthalene carboxylates from *Lawsoniainermis* and their anti-inflammatory activity. *Phytochem.*, 88, 67–73, 2013.
12. Takeda, Y., Fatope, M.O., New phenolic glucosides from *Lawsoniainermis*. *J. Nat. Prod.*, 51(4), 725–729, 1988.
13. Hsouna, A.B., Trigui, M., Culioli, G., Blache, Y., Jaoua, S., Antioxidant constituents from Lawsonia inermis leaves: Isolation, structure elucidation and antioxidative capacity. *Food Chem.*, 125(1), 193–200, 2011.
14. Bhardwaj, D.K., Murari, R., Seshadri, T.R. and Singh, R., Lacoumarin from *Lawsoniainermis*. *Phytochem.*, 15(11), 1789, 1976.
15. Ostovari, A., Hoseinieh, S.M., Peikari, M., Shadizadeh, S.R., Hashemi, S.J., Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α-d-Glucose and Tannic acid). *Corrosion Sci.*, 51(9), 1935–1949, 2009.
16. Prasad, G.B.R., Assessment of ethno-medicinal plants from Chamundi Hill, Mysore. *J. Med. Plants Res.*, 5(20), 5200–5202, 2011.
17. Ogunbinu, A.O., Ogunwande, I.A., Walker, T.M., Setzer, W.N., Study on the essential oil of *Lawsoniainermis* (L) *Lythraceae*. *J. Essential Oil Bearing Plants*, 10(3), 184–188, 2007.
18. Kidanemariam, T.K., Tesema, T.K., Asressu, K.H., Boru, A.D., Chemical investigation of *Lawsonia inermis* L. leaves from Afar region, Ethiopia. *Oriental J. Chem.*, 29(3), 1129–1134, 2013.
19. Siddiqui, B.S., Kardar, M.N., Khan, S., Two new triterpenoids from *Lawsonia alba*. *Zeitschriftfür Naturforschung*, B60, 37–40, 2005.
20. Siddiqui, B.S., Kardar, M.N., Triterpenoids from *Lawsonia alba*. *Phytochem.*, 58, 1195–1198, 2001.
21. Siddiqui, B.S., Kardar, M.N., Ali, S.T., Khan, S., Two new and a known compound from *Lawsonia inermis*. *Helvetica Chimica Acta*, 86(6), 2164–2169, 2003.
22. Handa, G., Kapil, A., Sharma, S., Singh, J., Lawnermis acid: A new anticomplementary triterpenoid from *Lawsoniainermis* seeds. *Indian J. Chem. Sect. B: Org. Chem. including Med. Chem.*, 36(3), 252–256, 1997.
23. Gupta, S., Ali, M., Alam, M.S., Niwa, M., Sakai, T., Isolation and Characterization of a Dihydroxysterol from *Lawsoniainermis*. *Nat. Prod. Lett.*, 4(3), 195–201, 1994.

24. Jacob, P.P., Saral, A.M., Two harmala alkaloids from *Lawsonia inermis* seeds. Chem. *Nat. Comp.*, 49(4), 780–780, 2013.
25. Siddiqui, B.S., Uddin, N., Begum, S., Two new dioxin derivatives from the aerial parts of *Lawsonia alba*. *Nat. Prod. Res.*, 23(18), 1740–1745, 2009.
26. Yusuf, M., Phytochemical analysis and antibacterial studies of *Lawsonia inermis* leaves extract. *J. Chem. Pharmaceut. Res.*, 8 (3), 571–575, 2016.
27. Raja, W., Agrawal, R.C., Ovais, M., Chemopreventive action of Lawsonia inermis leaf extract on DMBA-induced skin papilloma and B16F10 melanoma tumour. *Pharmacol. Online*, 2, 1243–1249, 2009.
28. Okpekon, T., Yolou, S., Gleye, C., Roblot, F., Loiseau, P., Bories, C., Grellier, P., Frappier, F., Laurens, A., Hocquemiller, R., Antiparasitic activities of medicinal plants used in Ivory Coast. *J. Ethnopharmacol.*, 90(1), 91–97, 2004.
29. Serakta, M., Djerrou, Z., Mansour-Djaalab, H., Kahlouche-Riachi, F., Hamimed, S., Trifa, W., Belkhiri, A., Edikra, N., Pacha, Y.H., Antileishmanial activity of some plants growing in Algeria: *Juglansregia, Lawsoniainermis* and *Salvia officinalis*. *Afr. J. Trad. Complement. Alternat. Med.*, 10(3), 427–430, 2013.
30. Chauhan, H.V., *In-vivo* antidiabetic, lipid lowering and antioxidant activities of methanolicextaract of *Lawsoniainermis* leaves. *Res. J. Pharmacy Technol.*, 4(5), 764–767, 2011.
31. Kumar, M., Kumar, S., Kaur, S., Identification of polyphenols in leaf extracts of Lawsonia inermis L. with antioxidant, antigenotoxic and antiproliferative potential. *Int. J. Green Pharmacy*, 8(1), 23–36, 2014.
32. Hossain, C.M., Maji, H.S., Chakraborty, P., Hepatoprotective activity of *Lawsoniainermis* Linn, warm aqueous extract in carbon tetrachloride induced hepatic injury in Wister rats. *Asian J. Pharm. Clinical Res.*, 4(3), 106–109, 2011.
33. Gupta, N., Jain, U.K., An update-prominent wound healing property of indigenous medicines. Res. *J. Pharmacy Technol.*, 4(2), 203–213, 2011.
34. Varghese, J., Immunostimulant activity of *Adhatodavasica, Lawsoniainermis, Alkannatinctoria*. *Indian Drugs*, 42, 345–352, 2005.
35. Alia, B.H., Bashir, A.K., Tanira, M.O.M., Anti-inflammatory, antipyretic, and analgesic effects of *Lawsonia inermis* L.(henna) in rats. *Pharmacol.*, 51(6), 356–363, 1995.
36. Iyer, M.R., Pal, S.C., Kasture, V.S., Kasture, S.B., Effect of Lawsonia inermis on memory and behaviour mediated *via* monoamine neurotransmitters. *Indian J. Pharmacol.*, 30(3), 181–185, 1998.
37. Goli, V., Macharla, S.P., Bhasker, K.V., Gowrishankar, N.L., Bhaskar, J., Dhanalakshmi, C., Antiulcer activity of leaf extract of Lawsonia inermis in albino rats. *Res. J. Pharmacy Technol.*, 4(9), 1436–1438, 2011.
38. http//:www.ayushveda.com/ayurveda-articles/livercare.htm (Accessed on 30/8/2017). Liver care: Useful herbs and Treatments.
39. Nawab, M., Mannan, A., Siddiqui, M., Evaluation of the clinical efficacy of Unani formulation on eczema. *Indian J. Trad. Knowledge*, 7(2), 341–344, 2008.

40. Raheel, M., History, Identification, and Characterization of Old World Fibers and Dyes, in: *Ancient Technologies and Archaeological Materials*, S.U. Wesseman and W.S. Williams (Eds.), pp.121–156, Gordan & Breach Publishers, The Netherlands, SA, 1994.
41. Mohammad, F., Yusuf, M., Shahid, M., Khan, S.A., Ibrahim Khan, M., Ali Khan, M., Dyeing of wool with the extract of henna leaves using mixed metal mordants. *Colourage*, 59(7), 51–57, 2012.
42. Yusuf, M., Mohammad, F. Natural Colorant from *Lawsonia inermis* Leaves: Reflectance Spectroscopy-Induced Optimal Conditions of Extraction and Dyeing, in: *Plant-Based Natural Products: Derivatives and Applications*, Shahid-ul-Islam (Ed.), pp. 89–101, Scrivener-John Wiley & Sons Publishing, Hoboken, NJ, USA, 2017.
43. Alam, M., Rahman, M., Haque, M., Extraction of henna leaf dye and its dyeing effects on textile fibre. *Bangladesh J. Sci. Ind. Res.* 42 (2), 217–222, 2007.
44. Iqbal, J., Bhatti, I.A., Adeel, S., Effect of UV radiation on dyeing of cotton fabric with extracts of henna leaves. *Indian J. Fibre Text. Res.*, 33, 157–162, 2008.
45. Ali, S., Hussain, T., Nawaz, R., Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. *J. Clean. Prod.*, 17(1), 61–66, 2009.
46. Badri, B.M., Burkinshaw, S.M., Dyeing of wool and nylon 6.6 with henna and lawsone. *Dyes Pigm.*, 22(1), 15–25, 1993.
47. Ali, R., Sayeed, S.A., Lawsone: phenolic of henna and its potential use in protein-rich foods and staining in Antinutrients and Phytochemicals in Food. *ACS Symposium Series, Vol. 662*, pp. 223–244, 1997.
48. Abidin, Z.H.Z., Taha, R.M., Puteh, R., Arof, A.K., Characteristics of paints prepared from lawsonia pigment and dammar from *Dipterocarpus grandifoleus*, in Materials Science Forum, Vol. 517, pp. 290–293, Trans Tech Publications, Switzerland, 2006.
49. Mehendale, V.G., Chaudhari, N.C., Shenoy, S.N., Mehendale, A.V., Henna as a durable preoperative skin marker. *World J. Surg.*, 35(2), 311–315, 2011.
50. Han, S., Yang, Y., Antimicrobial activity of wool fabric treated with curcumin. *Dyes Pigm.*, 64, 157–161, 2005.
51. Dev, V.R.G., Venugopal, J., Sudha, S., Deepika, G., Ramkrishna, S., Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. *Carbohydrate Polym.*, 75 (4), 646–650, 2009.
52. Khan, M.I., Ahmad, A., Khan, S.A., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., 2011. Assessment of antimicrobial activity of catechu and its dyed substrate. *J. Clean. Prod.*, 19(12), 1385–1394, 2009.
53. Velmurugan, P., Chae, J.C., Lakshmanaperumalasamy, P., Yun, B.S., Lee, K.J., Oh, B.T., Assessment of the dyeing properties of pigments from five fungi and anti-bacterial activity of dyed cotton fabric and leather. *Color. Technol.*, 125, 334–341, 2009.
54. Khan, S.A., Ahmad, A., Khan, M.I., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., Antimicrobial activity of wool yarn dyed with *Rheum emodi* L.(Indian Rhubarb). *Dyes Pigm.*, 95(2), 206–214, 2012.

55. Shahid, M., Ahmad, A., Yusuf, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Dyeing, fastness and antimicrobial properties of woolen yarns dyed with gallnut (QuercusinfectoriaOliv.) extract. *Dyes Pigm.*, 95(1), 53–61, 2012.
56. Shahid, M., Yusuf, M., Mohammad, F., Plant phenolics: A Review on Modern extraction techniques, in: *Recent Progress in Medicinal Plants: Vol. 41- Analytical and Processing Techniques*, J.N. Govil and M. Pathak, (Eds.), pp. 265–287, Studium Press LLC, Houston, USA, 2015.
57. Yusuf, M., Ahmad, A., Shahid, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsonia inermis*). *J. Clean. Prod.*, 27, 42–50, 2012.
58. Yusuf, M., Shahid, M., Khan, M.I., Khan, S.A., Khan, M.A., Mohammad, F., Dyeing studies with henna and madder: a research on effect of tin (II) chloride mordant. *J. Saudi Chem. Soc.*, 19(1), 64–72, 2015.
59. Kirkland, D., Marzin, D., An assessment of the genotoxicity of 2-hydroxy-1,4-naphthoquinone, the natural dye ingredient of henna. *Mut. Res: Genetic Toxicol. Environ. Mutagen.*, 537(2), 183–199, 2003.
60. Kirkland, D., Marzin, D., 2-Hydroxy-1,4-naphthoquinone, the natural dye of henna is non-genotoxic in the mouse bone marrow micronucleus test and does not produce oxidative DNA damage in Chinese hamster ovary cells. *Mut. Res: Genetic Toxicol. Environ. Mutagen.*, 560(1), 41–47, 2004.

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Sustainable Application of Natural Dyes in Cosmetic Industry

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Abstract

Dyeing the grey hairs or changing the hair color is a modern trend in cosmetics. A wide variety of synthetic hair colors have been developed and been used since decades. However, long term use of these synthetic hair dyes has caused harmful effects on the scalp and hairs. This damaging of the hairs by synthetic chemicals has raised the public concerns about their use. Therefore, people are more interested to use non-toxic and natural hair dyes as an alternate to synthetic dyes. Natural dyes are extracted from green resources without any chemical treatment and due to their eco-friendly nature these dyes have found a wide range of application in the textile and cosmetic industry, particularly in hair dyeing. Different herbs and plants impart different color intensity and have been used as approved coloring agents in cosmetics and fashion industry. Depending upon their chemistry, different methods have been reported for the extraction of natural dye and their applications. One of the most important advantages of natural dyes is: these are non-toxic, safe, healthy, eco-friendly, and economical. Therefore, they find a wide potential for their use in cosmetic industry. However, there is, still a strong need for the method developments, documentation and investigation of new plant species for their potential application in cosmetic industry.

Keywords: Natural dye, color, cosmetic application, sustainability, green resources

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10.1 Introduction

Natural dyes were the only source of colors available to humans until the first synthetic dye was discovered in 1956. As the name indicates, natural dyes are derived from natural resources like plant, animal, mineral, and microbes. The sources of natural colors and traditions of dyeing vary from region to region around the world. Recently, extensive research and development of synthetic dyes and their rapid industrialization has replaced most of the natural colors by synthetic ones. The advantages of synthetic dyes over the natural dyes are: their availability in a form that can be readily applied, simple process of application, the variety of colors, shades, and good fastness properties [1]. However, recent public awareness about environment has increased their interest in the use of natural dyes because: natural dyes are easily biodegradable and renewable, non-toxic, eco-friendly, and provide additional health benefits to the users [2, 3].

Natural pigments have a wide range of applications in various fields: in textile industry for dyeing the natural and synthetic fibers [4], in food industry for coloration of food products [5], in pharmaceuticals for making tablets coatings and for coloring the cosmetic products [6]. The market for natural colors in cosmetics continues to expand all over the world on account of the increased awareness among consumers of the side effects allied with prolonged use of some synthetic coloring compounds. Now the current trend towards healthy natural products, constituents in cosmetics is gaining popularity on account of their sustainability. Manufacturers are seeking natural coloring materials that offer additional multifunctional effects such as UV protection, anti-aging, antioxidant and antibacterial in foundations, lip care products, hair colorants, and other cosmetics [7]. Many natural colors that meet these requirements are evolved from plant source and find their traditional use in foods and cosmetics. Plant pigments such as anthocyanins and carotenoids have scientifically validated antioxidants with anti-inflammatory benefits [8]. Historically, plant pigments such as curcumin from turmeric, anthocyanins from beet, carotenoids from peppers and saffron, chlorophyll from green leaves, have also been used to color food and cosmetics. Extracts of these sources provide health benefits that go far elsewhere their coloring properties alone. Indo-Pak region has a rich legacy of products and rituals that have continued for thousands of years in natural pigments to use in various applied fields such as food, flavor, pharmaceuticals, and Ayurvedic medicines etc.

One of the most important fields of cosmetics is hair dyes. Due to the hazardous utilization and concerns of synthetic colorants, researchers have compelled the agencies to use eco-friendly colorants of natural origin.

Therefore, scientists are trying to discover new methods to isolate natural dyeing colorants which are not only harmonized with nature but also make the hair color shine with new appearance [9, 10]. This chapter discusses various aspects of natural dyes, their sources, and applications in cosmetic industry especially as hair coloring agent.

10.2 Classification of Natural Dyes

Natural dyes can be classified on the basis of their source of origins, structures, color, and method of application etc.

10.2.1 Sources of Origin

10.2.1.1 Plant Origin

Plants have been used potentially as a rich source of natural dyes since ancient times. Different plant parts such as leaves, flowers, bark, stems, fruits, roots etc., are used for the extraction of a variety of colors [11, 12]. Some plant may impart more than one color depending upon the part of the plant being used and its method of application. The shade of the color also depends on various factors such as temperature, plant age, the planting condition such as soil, and water conditions. Plant based natural dyes have great importance because of their natural abundance in form of raw biomass such as leaves, shells, rinds, barks, flowers, roots etc. They have a variety of applications in textile, pharmaceutical, cosmetic, and food industry. An increasing consumer's interest in natural dyes is because of environmental awareness in recent decade spread by many agencies based on their commercial availability. Some important plant based natural dyes showing brilliant colors reported in literature are described as follows.

Blue dyes: This dye is also known as "king of the natural dyes." The dye is mainly derived from "*Indigofera tinctoria*". The actual coloring component is a light yellow substance known as Indican (Figure 10.1),which is isolated from the leaves of the plant[13]. Different other plants have also been used as a source of indigo dye such as Woad, dyers Knotweed (*Polygonumtinctorium*), Pala Indigo (*Wrightiatinctoria*).

Red dyes: This is one of the long chains of natural colors which are isolated from plants. Madder yields red color natural dye which is extracted from various species of the plant *Rubia*. The family is also known as "Queen of the natural dyes." The main active coloring constituent of the European Madder *Rubia tinctorum* is "alizarin" as shown in Figure 10.2 is mainly

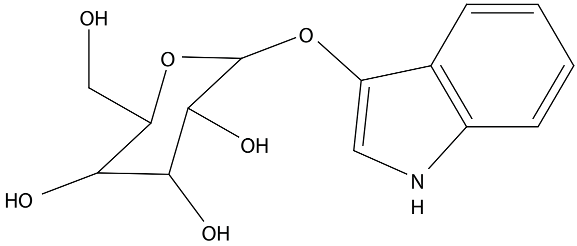


Figure 10.1 Indican.

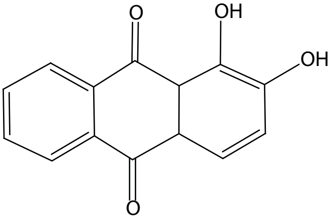


Figure 10.2 Alizarin.

isolated from the roots in addition to other parts of the plant[14]. The coloring components of Indian red dye "*Rubia cordifolia*" are a mixture of munjistin and purpurin. It is mordant type of dye and generally produces bright color complexes with metal ions. Different shades are produced depending upon the nature of the mordant used for dyeing [15].

The red dye is also derived from Brazil wood and the same is also obtained from the wood of "*Caesalpina sappan*" in India, Malaysia, and Philippines. The color of the dye can be darkened depending upon the conditions of extraction. If used in combination with other dyes, different other shades like orange and maroon color can also be obtained. Safflower florets have been used for extracting bright cherry red color dye. There are mainly two dye producing components in this plant: a water soluble yellow present in abundance (26–36 %) and a water insoluble component known as carthamin (0.3–0.6 %) as shown in Figure 10.3. [16].

Yellow Dyes: Yellow dye is another long chain of natural colorants. The yellow dye derived from rhizomes of turmeric (*Curcuma longa*) is chemically curcumin (Figure 10.4), belonging to the class Diaroyl methane. It is used to give yellow color to fibers like silk, cool, cotton, and hair [17].

Saffron is also a well known yellow dye obtained from stigmas of the plant *Crocus sativus*. The coloring pigment is crocin (Figure 10.5) which is a carotenoid, impart rich golden yellow color to the wool, silk, and cotton [18].

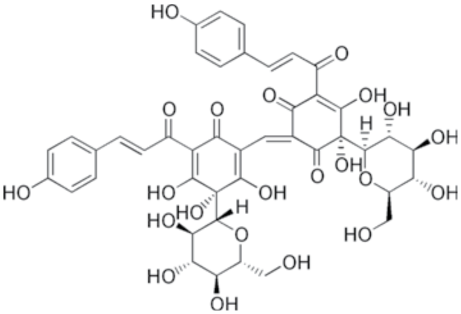


Figure 10.3 Carthamin.

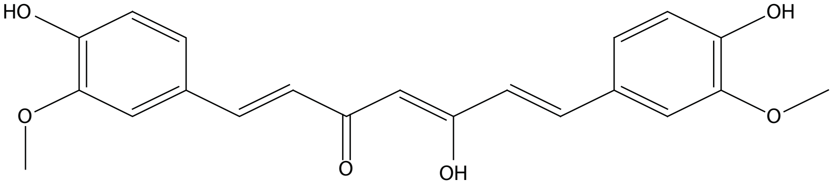


Figure 10.4 Curcumin.

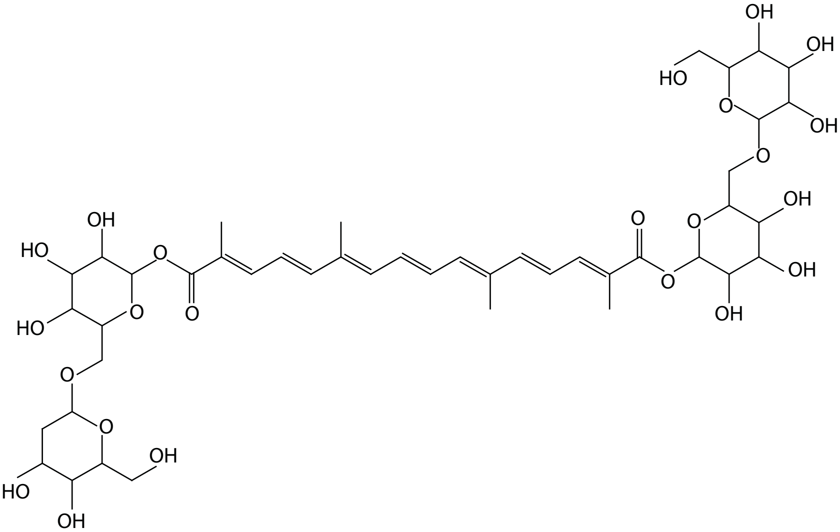


Figure 10.5 Crocin.

Annatto (*Bixaorellana*) belonging to the family *Bixaceae* is also known for the yellow orange dye. The main coloring pigments are carotenoid i.e., bixin (Figure 10.6) and norbixin, present in the reddish waxy coating of the seeds. It is used for dyeing the wool, cotton, and silk and also for dyeing the foods and cosmetics.

Berberine another yellow natural colorant is isolated from the plant Barberry (*Berberis aristata*). It is an active alkaloid constituent of the dye that exhibit good washing and average light fastness and can directly be used for silk, cotton and wool [19]. The rinds of the fruit pomegranate *(Punicagranatum*) are used as source of yellow dye shades. It yields pelletierine, called tannate of pelletierine to impart yellow color.The dye gives good fastness properties to wool, silk, and cotton [20]. *Buteamonosperma* tree produces bright yellow to brown and orange colors with suitable amordant. The dye obtained from this plant can color all natural types of fibers. Dried fruits from *Mallotus phillipensis* yield a red orange dye powder that can impart golden yellow and bright oarange yellow color onto cotton, silk, and wool [21]. Shells of onion can also be used to yield yeallow color dye. The main constituent of the dye is flavonoid, which gives bright colors to wool anda silk [22]. Rhizomes and roots of herb *Rheum emodi* also yield yellow dye mainly due to active component emodin (Figure 10.7)

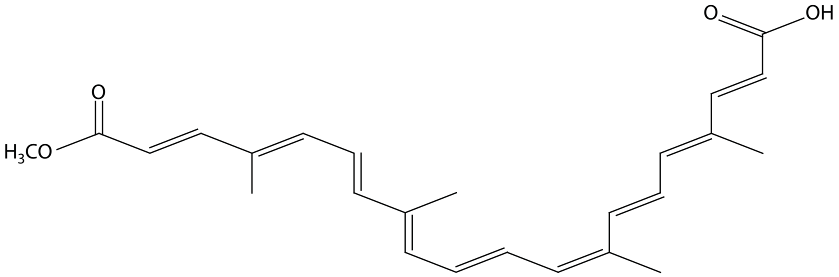


Figure 10.6 Bixin.

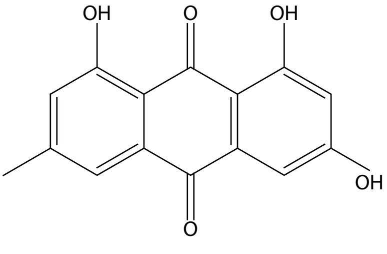


Figure 10.7 Emodin.

for coloring wool, silk, and cotton. Different species of *Rheum,* also known as Rhubarb grow wildly in the temperate and subtropical regions of Asian countries e.g., Kashmir, India, Pakistan, China, and Turkey. The plant extracts in alkaline conditions yield yellow, brown, and grey shades in the presence of mordant which shows good fastness [23].

10.2.1.2 Animal Origin

Natural dyes from animal source were mainly used in ancient times. Most of these dyes provided red color. One of the oldest dyes is Tyrian purple from sea mollucs, *Murex* that imparts deep violet color dye. It is very expensive as one gram of dye is obtained from thousands of Mollucs. Cochineal, a red color dye from insects *Dactylopius coccus* is also very expensive. The main colorant in the insect is carminic acid (Figure 10.8). It has been used since ancient times to dye animal fibers. Both *Murex* and cochineal have anthraquinone type [24].

10.2.1.3 Mineral Origin

Some mineral pigments are found in nature such as red ocher, cinnabar, yellow ocher, azurite (Figure 10.9 a, b, c, d) malachite, gypsum, raw sienna, charcoal black etc. are mineral used for coloration purpose. They are mainly used in paintings [25, 26].

10.2.1.4 Microbial Origin

Some bacterial species such as *Bacillus, Brevibacterium, Achromobacter, Rhodococcus*etc produce pigments as secondary metabolites. A detail of pigment producing microorganisms has been provided in the review [27, 28, 29]. Dyes obtained from microbial source have advantage as microbes can grow under controlled environment on economical substrate.

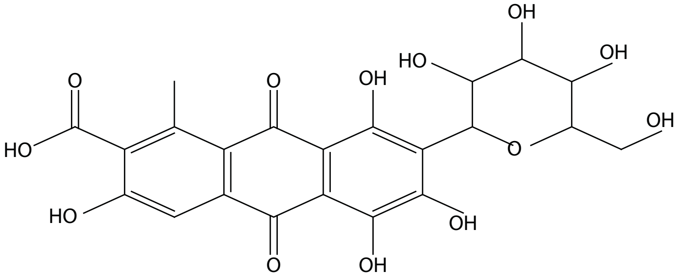
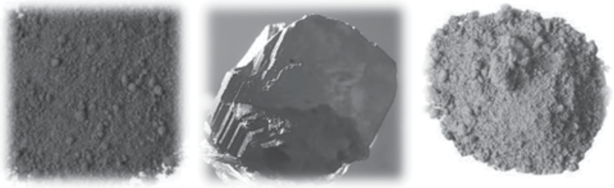


Figure 10.8 Carminic acid.



(**a**) Red Ocher (**b**) Cinnabar (**c**) Yellow ocher

(**d**) Azurite

Figure 10.9 Mineral pigments.

10.3 Application of Natural Dyes in Cosmetics

Cosmetics include products that are intended to be sprayed, rubbed or sprinkled and applied to the body parts for their cleansing, beautifying, and attractive appearance. In general, cosmetic include all those products which are used to enhance and beautify the appearance of the human body. A variety of products are included in this category i.e., skin care products including creams and lotions, perfumes, foundation creams, nail polishes, eye and facial make up, lipsticks, hair care products, baby skin care products, colored contact lenses and body butters etc. [30].

The trend to use natural dyes from various sources in the world of cosmetic, fashion, and style has been increased in the recent decades. Although synthetic colors have many advantages but the serious drawback has caused the people to rush towards natural dyes. The development of biodegradable green natural cosmetics has additional benefits, in the making and stabilizing the cosmetics that they have pharmacological properties such as anti-inflammatory, anti-biotic, anti-microbial activities etc. [31].

10.3.1 Natural Lip Cosmetics

To color the lips is an ancient practice of beauty enhancing in females. Different shades of colors have been used for this purpose and hundreds of shades of lipsticks are available in the market to satisfy the women demand. In recent years, the chemicals used in the lipsticks are under scrutiny since the ingredients are eaten away or accidently swallowed by users in the body. Coal tar is the main source of ingredient used to synthesize synthetic dyes and can cause nausea, allergy, dermatitis, and drying of the lips [32]. Moreover, the dyes used in the lipsticks and lip balm may cause several harmful effects. Lipsticks are usually composed of waxes such as beeswax, ozokerite and candelilla, oils such as mineral oils, cocoa butter, lanolin, olive oil, and petrolatum. Organic and inorganic pigments are used to get the required shade of the lipsticks. In order to incorporate the natural colors and pigments in the cosmetics like lipsticks, different efforts have been made by the researchers [33]. *Bixa orellena that* produces coloring pigment, the bixin, which is extracted from the seed coat of the fruit, gives red colors to the cosmetic products [34]. Formulations of the lip jelly have been successfully made using the red colors of this plant. The coloring chemicals extracted from the pigments of *Beta vulgaris* taproots are also used for coloration of lipsticks and balms. Along with their use to produce natural color lipsticks, beetroots provide an excellent source of certain minerals and folate. They contain red color pigment called betaines which also have the great medicinal importance [35]. Natural dyes from *Ixora coccinea* L., commonly known as Jungle geranium have been used in the field of textile and cosmetics. Using different types of mordant while dyeing with *I. coccinea* dye yield different type of colors such as pink, lilac, and grey shades are obtained. Such color shades of *I. conninea* are used in the formulation of lip balm and has been evaluated for its stability, smoothness, and spreadability [36].

10.3.2 Natural Hair Dyes

Hair being important part of the body plays an important role in the general appearance of the body. The color and physical appearance of hair can be changed easily without any difficult procedure. Since ancient times, different types of herbal dyes have been used to change the appearance of hair color. To dye the graying hair is one of the oldest cosmetic applications to give the hair a glamorous and charming look, used by ancient culture in different countries. Egyptians, Persians, Chinese, and Hindu literature show the application of hair dyes in their culture. In early days, hair dyes were obtained from metallic compounds, plant extracts, and dried plants or by mixing plants and different metallic compounds. Before the invention of synthetic dye, different plant extracts and herbal preparations such as mullein, birch bark, turmeric, and saffron were used for hair dyeing [37, 38]. Indigo, which is generally known for textile dyeing can be used as mixture with henna to give light brown to black color shades to hair fibers. Extract of the chamomile flower acts as hair bleaching agent and still it is used now a days. Different parts of the trees as bark, leaves, and nut shells may be used for dyeing hairs. Brazilian wood tree yield brown color dyes used for dyeing hair. Dyes are also produced from the walnut and mulberry tree leaves or nut and also from the galls which is a specie of the oak trees. These plant based dyes can be mixed with metals such as iron, aluminium, and copper to give long lasting or rich dye shades [39].

Different plant extracts were used as hair dye in Europe and Asia before the discovery of modern synthetic hair dye. Indigo, which is also known as fabric dye can be combined with the henna extract to prepare brown to black shades of hair dyes [40]. Henna extract acts as an outstanding conditioning agent in cosmetics. It is also used in hair care formulations such as shampoos and conditioners for centuries. Lawsone, an active coloring agent in henna, is a colorless molecule, however, when exposed to light or air, it is converted into a compound which has color characteristics. Different shades of the color can also be produced if the henna leave extract is mixed with other herbs such as rhubarb, chamomile and calendula. Thus, without any adverse effects on hairs, it can be used to cover the graying hair and may give a long lasting hair color [41].

With the invention of the synthetic hair dyes and other efficient hair products, the industry of hair cosmetics has gained increasing importance. Dyes give fancy appearance to hair by bleaching and coloring [42]. So it is necessary to get the complete knowledge about the chemistry of hair dye, its method of application and possible side effects on hair and body health before its application.

The most commonly used cosmetics to cover the graying hair or used for changing the hair color are the hair dyes. According to the source of origin, hair dyes are classified as:

1. Natural hair dyes: Being non-toxic in nature, sustainable, eco-friendly colorant, they work for short time [37].
2. Mineral or metallic hair dye includes salts of lead and silver. They require daily use to sustain their working and to retain hair color. These dyes are potentially toxic but remained permanent [26].
3. Synthetic hair dyes are the most popular form of hair dyes and are classified according to their degree of permanency[42] as follows:
    i. Temporary hair dyes: These dyes stay on hair for short period of time and do not incorporate into the hair

structure. They have high molecular weight and stay on the surface of the hair.

ii. Semi-permanent hair dyes: These colorants have low molecular weight but do not penetrate deep into the hair. Such type of dye colors the hair for some weeks.

iii. Permanent hair dyes: These are type of dyes that have low molecular weight and penetrate the hair deeply. Such type of dyes colors the hair permanently.

10.4 Methods of Application as Hair Colorant

Coloration of hair is one of the ways to change the individual appearance and is as old as the history of dyes. Most of the men and women in the modern societies change their hair colors, where almost 75% of the American women change their hair color, and in Europe, 5–10 % men and almost 60% of the women dye their hairs [43, 44]. With increasing population, the market of hair dyeing has been increasing rapidly. Depending upon the type and conditions of dyeing, hair colorants are distinguished with regard to their performance as temporary, semi-permanent, and permanent hair dyes. For example with reference to the number of shampoo wash, a hair dye can sustain, a semi-permanent hair dye last for 6–12 shampoo washes while permanent hair dye don't wash out[40].

With regard to the application of natural dyes to the hairs, the colorant is classified according to their source and chemical nature. It is important to understand the structure of human hair before we explain the mechanism of its dyeing with natural colors. The outermost layer of a human hair which is exposed to the environment is called cuticle. This layer forms a roof tile like outer structure, which must be opened up in order for the colorant to access the inner layer cortex. In human hairs, the cortex mainly consists of ortho-cortical cells and is known as ortho-cortex. Chemically hair is composed of the fibrous insoluble protein known as keratin, which also forms the basis of other structures such as wool, nails, feather, and horns. Important amino acids that take part in the composition of keratin are leucine, arginine, glutamine, and serine. The color of the hairs is because of the pigment known as melanin, which is deposited in the stem of the hair[45]. The apparent color of these granular pigments is due to light scattering effect. The mechanism and behavior of dyeing the human hair is very similar to that of the wool fiber because of their similar physical and chemical structure. However, strategies to dye the human hair are completely different from that of wool fiber because hairs are dyed on the scalp. Different aspects that have to be considered for dyeing the human hair are complex and certain requirement are taken into account such as: safety and health risk related to particular dye, stability and quality of dye and their practical applications. There are three binding mechanisms: van der Waals forces, hydrogen bonding, and metal complex forming, which are involved for the binding of natural dye molecules to the hair fibers[46]. Because of mild dyeing conditions (low temperature, pH, and time) used for hair dyeing, only the smaller size dye molecules can penetrate inside the hair fiber. In case of henna, the leaves powder is formed into a paste in acidic condition using orange or lemon juice and rested for some hours. The lawson molecules are small enough to penetrate and diffuse into hair. There is no mordant or fixative required in this case[47].

10.5 Natural Dyes as Hair Colorant

There are various plants that are used for hair coloration, but following plants are commonly used for hair coloration based on their sustainability and availability.

10.5.1 Henna (*Lawsonia Inermis* Linn)

Henna (*Lawsonia inermis* L.), is cultivated in North Africa, India, Middle East, and other Asian countries on commercial scale. It is very popular in Indo-Pak as mehndi and used in social and cultural festivals, marriage ceremony etc. *Lawsonia inermis* belongs to the family *Lythraceae* consisting of about 500 species and is widely spread out in the tropical and temperate regions[48]. Plant leaves yield an orange-red pigment known as naptho-quinone dye also called lawsone (Figure 10.10) [49]. Henna leaves have 1-4% lawsone content, depending on climate and soil conditions. The lower dye content leaves are harvested, roughly powdered and sifted, and sold to the hair dye industry. This pigment is prepared in the form of paste from dried powdered leaves of the henna and traditionally and culturally used as cosmetic product in hair dyeing. It can also be incorporated in other

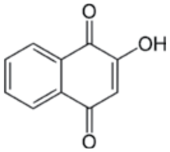


Figure 10.10 Lawsone.

cosmetic products. Henna is one of the important dyeing agents used in the cosmetics. Usually fresh and dried leaves of the *Lawsonia inermis* plant are used as source of orange color dye. It is used in Ayurvedic medicine in the treatment of skin ailments, burns, wounds [50]. Lawsone is widely used in cosmetology for its dyeing properties, uses as hair and nail color and in the traditional decoration of the soles of the feet and the palms of the hands[51]. Except few natural dyes used as hair color such as henna or walnut, no single natural dye gives the right color.

The phytochemical studies of the *Lawsonia inermis* have explored hundreds of secondary metabolites present in henna, which have diverse chemistry. *L. inermis* contains different constituents such as flavonoids, alkaloids, naphthalene derivatives, naphthoquinones, triterpenoids, xanthones, tannins, saponins, quinoids, coumarins, carbohydrates, organic acids,phenolics, and phenolic glycosides [49].

Henna has a wide range of applications in different fields of life mainly in textile, cosmetic, pharmaceutical, and also used as ornamental purposes. According to phytochemical analysis, henna exhibit a variety of biological activities such as anti-bacterial, anti-fungal, anti-parasitic, hepatoprotective, anthelmintic, anti-inflammatory, immune modulatory, virucidal, anti-bacterial, anti-cancer, analgesic, anti-oxidant, and allelopathy[52]. Blending of henna paste in oil increases the ornamental action of henna. A combination of henna leaves and indigo has been used for making natural hair color. However, a mixture of natural colorant with the synthetic coloring agents has been used in the market as semi synthetic hair color, which contains henna, hibiscus, amla, bhrinraj, methi, and paraphenylenediamine (PPD) that has been marketed as Indica herbal hair color.

Henna has been used to color an orange red or rust shade to keratin in skin, nails, and hairs as shown in designs below (Figure 10.12). Now a day,

Figure 10.11 *Lawsonia inermis.*

Figure 10.12 Design and color or *Lawsonia inermis leaves paste.*

temporary tattoos are also produced as mixture of aromatic compound, PPD and natural henna to create a black color henna that stains the skin color black very rapidly. Temporary tattoos from henna are getting very popular globally and look very fascinating because henna has a low allergic reactions and smoothening effects on skin[40].

Henna leaves have also been extensively used for centuries for coloration of nails, hands, hair, and textile in the Middle East, the Far East, and Northern Africa. Along with the treatment of headache, jaundice, skin aproblems, amebiasis, enlargement of the spleen, ulcer, cough, leukoderma, hepatopathy, ophthalmic conditions, falling of hairs, and jaundice, roots of this plant act as abortifacientand are also useful in leprosy, amenorrhea, dysmenorrhea, diuretic, and premature graying of hairs[53]. Henna is known to have a cooling effect on the body and its paste is useful to treat fever and antibacterial for gram positive bacterial and antitumor effect in rats. Plant extract is also used as stimulator in hair growth and treating the dandruff. The molecule lawsone possess natural affinity to interact with the hair protein and thus, it has been used to enhance the hair growth apart from curing the nature [51].

10.5.2 Indigo (*Indigoferatinctoria*)

Indigofera is a larger genus with about 750 species of flowering plants belonging to the family *Fabaceae*. They are widely distributed throughout the tropical and subtropical regions. The plant is generally native to Asia and some parts of Africa; however, it can be cultivated throughout the world. Now a day, synthetic indigo dye is common but natural dye from *I.tinctoria* is also available in the market. Indigo dye is mostly obtained from leaves of the plant *I. tinctorial* where along with Indican (Figure 10.13), various other pigments such as galactose and mannose,

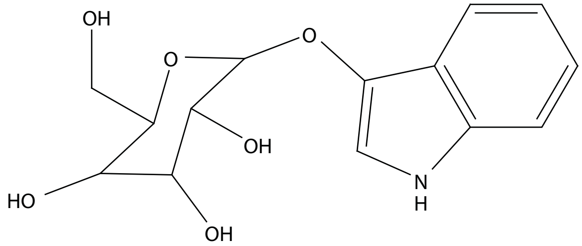


Figure 10.13 Indican.

glycoside, indigotin, flavonoids, terpinoids, alkaloids, indiruben, rotenoidetc. are also found [54].

The indigo dyes are one of the oldest dyes used for textile dyeing and printing. The leaves and roots of the plant are used for medicine purposes to treat abdominal disorders and many types of toxicities. It has been used as cover crop in rice and coffee plants, as green fertilizer for maize, sugar care and cotton crops contrasting that some members of the genus have poisonous nature. In the past, painters used the indigo dye for blue watercolor shades and in some areas it is still used as dye plant. It has been used as hair colorant in combination with other dyes (henna) as well. It has also been used as coloring agent for washing liquids, soap bars, and personal care products [55]. It has also been used as folk medicine and juice of the plant leaves was used as prophylactic against hydrophobia and to treat epilepsy, bronchitis, nervous disorders, bronchitis and as ointment for sores, ulcers, and roots are used for urinary problem and hepatitis. *Indigofera tinctoria* has been used to dye the hair black or brown or for covering the graying hair and can also be used in combination with henna to obtain different shades of brown (light to dark brown). In addition to its anti-fungal and anti-bacterial properties, it is used as cleansing agent and restores the pH of the scalp along with promoting the hair growth, giving them soft, shiny, and healthy appearance. For obtaining best results, the indigo dye must be used immediately after making into paste because the dye does not retain its shade if it is prepared in advance [56].

10.5.3 Shoe Flower (*Hibiscus Rosa-sinensis* L.)

Hibiscus rosa-sinensis L. (Figure 10.14) also known as shoe flower is an important member of the family *Malvaceae*. The plant is native to East Asian countries and is national to Malaysia. The phytochemistry of *Hibiscus*

Figure 10.14 *Hibiscus rosa-sinensis* L.

rosa-sinensis reveals several important phytochemicals i.e., vitamins, thiamine, Anthocyanins& flavonoids, cyanidin-3,5-diglucoside,riboflavin, niacin, riboflavin, tannin, phenol, alkaloids, saponins, ascorbic acid, cyanidin chloride, glycosides, flavonoids, and carotenes. It is also used for ornamental purposes in the world. Plant has many important uses such as for skin and hair care cosmetics, control of diabetes and also used in cancer prevention [57].

The plant has many important applications. It is used as shoe shiner in different parts of Indo-Pak. It is also used as an indicator for pH because the flower colour turns dark pink or magenta in the acid and green in the basic solution. The plant has many medical uses in the Chinese medicines and its extract absorb UV radiations and also act as anti-solar agent. Like other plants, Shoe flower has application as hair dye to cover grey hair to natural black color. The mixture which is composed of *Lawsonia inermis*, *Hibiscus rosa-sinenis*, *Murraya koenigii*, *Emblicao fficinalis*, *Azadirachta indica*, *Trigonella foenum* along with *Aloe vera* gel is used to obtain the hair dye [58]. In many countries, the dye is used for coloring hairs, beard, eye brows, foods, and liquors. The flower yields dark purplish or magenta dye. A pigment anthocyanin called cyanidin-di-glucosideis also reported in the flowers to act as a colorant for foods, fruits, and cooked vegetables. The flower preparations are used in hair care formulations. *H. rosa-sinensis*is used to treat respiratory problems, fever, and women health problems. In skin care, it is used to soften and soothe the skin and internally to treat the digestive problems. The aqueous and alcoholic extracts are used as anti-infective, prophylactic again skin diseases, antidandruff, and anti-allergic conditions. Petroleum ether extracts of the flowers and leaves posses hair growth activity and has potential application as hair growth accelerator both *in vivo* and *in vitro* [58]. Both the leaves and flowers of *H. rosa-sinensis* are used as a source of reddish Hibiscus dye, which is now becoming very popular as hair dye all over the world.

Figure 10.15 *Phyllanthus emblica.*

10.5.4 Amla (*Emblica Officinalis* Linn)

Phyllanthus emblica syn Emblica officinalis belongs to family *Euphorbiaceae* and also known as amla (Figure 10.15). It is one of the oldest plants that are used for various purposes. The plant is distributed in the subtropical and tropical regions of India, Indonesia and China. Various investigations have revealed that amla has anti-viral properties along with its anti-bacterial and antifungal activities. It is very nutritious and dietary source of vitamin C, amino acids, proteins, amino acids, ascorbic acids hundred folds higher than that of apple. Fruit also contains glutamic acid, proline, lysine, alanine, aspartic acid, and minerals [59]. *P. emblica* is an important part of food industry and is used in candies, pickles, jellies, sauces, and powders. It is used as cardiac tonic, diuretic, liver tonic, diuretic, antipyretic, anti-inflammatory, laxative, restorative, stomachic, and digestive medicine. The fruit contain a variety of phenolic compounds and possess therapeutic actions such as antimutagenic, antitumour, anticarcinogenesis etc.

The ripen fruit is used extensively as laxative in different countries and is used as preserved form in sugar. *Phyllanthus emblica* shows poweful hepato protective actions against carbon tetrachloride induced damage to kidneys. Plant has important applications in cosmetics and promotes hair growth and prevents graying of hairs [60]. Amla seed oil is used all over the world and it is an important ingredient of herbal shampoos [61]. It is also used in dyeing industry and also in firework. Plant is used as hair tonic in traditional recipes for hair growth and hair dye. The dried fruit is boiled with coconut oil. The prepared darkish oil is very excellent in preventing graying of hairs. Water rich in amla extract obtained by soaking amla in water overnight is used for hair washing to nourish the hairs [62].

10.5.5 Beet (*Beta Vulgaris*)

Beet (*Beta Vulgaris)* is a plant in the *Chenopodiaceae* family. It is best known in its frequently cultivated varieties, the best known of which is probably the red or purple root vegetable known as the beetroot or garden beet. Beet is responsible for a good source of anthocyanins, natural antioxidants that contribute to its deep red color, a natural source of vitamins and minerals. The color of red/purple beet root is due to a variety of betalain pigments (Figure 10.16), unlike most other red plants, such as red cabbage, which contain anthocyanin pigments.

Beet extract is often used for a nice red color in cosmetics and other cosmetic products. This extract is used as a hair color and bleaching, facial moisturizer/treatments, anti-aging, acne treatment, toners, astringents, masks, shampoo, exfoliate/scrubs, moisturizers, lip balm [36].

10.6 Advantages/Merits

There is an increasing trend in the application of natural dyes in the field of textile, pharmaceutical, food, and cosmetic industry because of their advantages over synthetic dyes. Since natural dyes are coming from renewable, natural resources, they do not add any harmful effects to the environment, which make them more attractive for consumers. Because of their biodegradable nature, disposing off the natural dyes does not cause any environmental pollution. Natural dyes are non-toxic and can be confidently used in the cosmetic products, pharmaceuticals, and foods.[63]. They have not shown any considerable allergic actions if used in the skin care products. If used in lipsticks, these natural colors are safer than synthetic pigments. In order to attain a soft or smoothening effect, natural

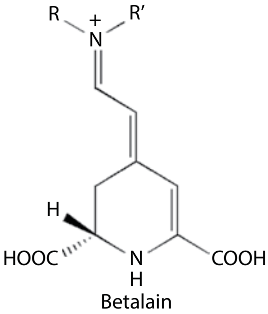


Figure 10.16 Betalain.

dyes are very good choice. Moreover, the natural dyes provide additional health benefits and offer more health safety [64]. For example, in addition to their coloring properties, natural dyes and pigments offer antimicrobial, anticancer, anti-inflammatory, analgesic etc. effects to the consumer [65, 66]. In the field of cosmetic, the applications of natural colors have encouraged the development of natural cosmetic products. The natural ingredients in cosmetics have additional pharmaceutical benefits along with their cosmetic properties and they have been approved as being useful for human medicines.

10.7 Disadvantages/Demerits

There are certain factors which limit the application of natural dyes. Using natural dyes is more expensive because a large amount is needed in order to color a fabric with natural dye as compared to synthetic dye. The quality of dyeing in some cases is not that consistent and colors fades quickly. Another issue is the availability of the natural dyes because sometimes it varies from season to season, place, and specie of the plant in order to get the required color of natural dye. Production of natural dyes requires a large area of land in order to meet their increasing demand with the population.

10.8 Conclusion

The sustainable products in hair dyeing and the world of cosmetics are gaining popularity due to stringent environmental regulations imposed by many agencies to use synthetic products. Owing to their harmful effects, the fashion industry is now moving towards the natural dyed products. Hair Dyeing is a big business in the world of fashion because to look different, the people dye their hairs with natural and synthetic colorants. But to revive the traditional culture, natural colorants are now being welcomed in hair dyeing, cosmetics, food flavors, pharmaceuticals. New plants are being introduced and new methods are being employed to get maximum yield required for hair dyeing and cosmetic use. To meet the demand of consumers, modern tools such as radiation technologies have been implemented to make the process cost, time, and energy effective but also the industry of fashion more sustainable and green. The chapter is a little try to give the knowledge of people around the globe who are involved in fashion industry about applied use of natural colorants. Hence, there is a dire need to spread knowledge about sustainable hair dyeing and to find new sources of natural plant derived dyes for extraction of colorants though eco-friendly heating sources.

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References

1. Li, D., Sun, G., Coloration of textiles with self-dispersible carbon black nanoparticles. *Dyes aaPigm.*, 72, 144, 2007.aa
2. Han, S.,Yang, Y.,Antimicrobial activity of wool fabric treated with curcumin. *Dyes Pigm.*, 64157, 2005.
3. Hill, D. J.,Is there any future for natural dyes. *Rev. Prog. Col.*, 2718, 1997.
4. Verma, N., Gupta, N.P., Parthsarthy, S.,Eco-friendly dyeing of wool. *Indian Text. J.*, 10882, 1998.
5. Hendry, G.A.F., Houghton, J.D.,*Natural Food Colorants,* Springer Science & Business Media, 1, 1996.
6. Dweck, A.C., Natural ingredients for colouring and styling. *Int. J. Cosmet. Sci.*, 24, 287, 2002.
7. Patil, N.N.,Datar, A.G., Applications of natural dye from *Ixoracoccinea L.* in the field of textiles and cosmetics. *Color Technol.*, 132, 98, 2016.
8. Deepak M.K.,Surendra S.K., Mahabaleshwar V.H., Hanhong B., Significance of antioxidant potential of plants and its relevance to therapeutic applications. *Int. J. Biol. Sci.,* 11, 982, 2015.
9. Guerra-Tapia, A.,Gonzalez-Guerra, E., Hair cosmetics: Dyes. *Actas Dermo-Sifiliograficas.*, 105, 833, 2014.
10. John, F.C., An historical review of the use of dye precursors in the formulation of commercial oxidation hair dyes. *Dyes Pigm.*, 41, 127, 1999.
11. Aburjai, T., Natsheh, F.M., Plants used in Cosmetics. *Phytother. Res.,*17, 987, 2003.
12. Baliarsingh, S., Panda, A.K., Jena, J., Das, J.T., Das, N.B., Exploring sustainable technique on natural dye extraction from native plants for textile: identification of colorants, colorimetric analysis of dyed yarns, and their antimicrobial evaluation.*J. Clean. Prod.*, 37, 257, 2012.

13. Nittaya, C., Sorasak, L., Suree, P., Pigment extraction techniques from the leaves of *Indigoferatinctoria* Linn and*Baphicacanthuscusia*Brem andchemical structure analysis of their major components. *CMU. J.*, 1, 149, 2002.
14. Ester, S.B., Ferreira, Alison, N., Hulme, Hamish, M., Anita, Q., The natural constituents of historical textile dyes. *Che. Soc. Rev.*, 6, 329, 2014.
15. Margareta, S.F., The chemistry of plant and animal dyes. *J. Chem. Educ.,* 58, 301, 1981.
16. Zehra, E., Resurgence of safflower (*Carthamustinctorius L.)* utilization: A global view. *Eur. J. Agron.*, 4, 83, 2005.
17. Gulrajani, M.L., Gupta, D.B., Agarwal, V., Jain, M., Some studies on natural yellow dyes, part 1: C.I. Natural Yellow 3 (turmeric). *Indian Text. J.,* 102, 50, 1992.
18. Siva, R., Status of natural dyes and dye-yielding plants in India.*Curr. Sci.,* 92, 916, 2007.
19. Gulrajani, M.L., Deepti, G., Maulik. S.R., Studies on dyeing with natural dyes: Part II—Dyeing of berberine on acrylic fibre. *Indian J. Fiber Text. Res.*, 24, 223, 1999.
20. Kulkarni, S. S., Gokhale, A.V., Bodake, U.M., Pathade, G.R., Cotton Dyeing with Natural Dye Extracted from Pomegranate (*Punicagranatum*) Peel. *Univers. J. Environ. Res. Technol.*, 1, 135, 2011.
21. Vankar, P.S., Chemistry of natural dyes. *Reson.*, 5, 73, 2000.
22. Fazal-Ur-Rehman, Shahid, A., Muhammad, S., Bhatti, A.I., Faiza, N., Nasim, A., Zulifqar, A., Dyeing of γ-irradiated cotton with natural flavonoid dye extracted from irradiated onion shells (*Allium cepa*) powder. *Radiat. Phy. Chem.,* 92, 71, 2013.
23. Shafat, A.K., Aijaz, A., Mohd, I.K., Mohd. Y., Mohammad, S., Nikhat, M., Faqeer, M., Antimicrobial activity of wool yarn dyed with *Rheum emodi L.* (Indian Rhubarb). *Dyes Pigm.*, 95, 206, 2012.
24. Cardon, Dominique, Natural dyes: Sources, tradition, technology and science, Archetype, 978–1–904982–00–5, 2007.
25. Diez, G.M., Vinagre, A.T., Mineral dyes. InPavlov I–Southeast–a Window into the Gravettian Lifestyles. 167, 2005.
26. Vankar, P.S., *Handbook on natural dyes for industrial applications.* Niir Project Consultancy Services, 4, 2016.
27. Dufosse, L., Microbial production of food grade pigments. *Food Technol. Biotechnol.*, 44, 313, 2006.
28. Kamla, M., Jayanti, T., Sneh, G., Microbial pigments: A review. *Int. J. Microb. Resour. Technol.*, 1, 361, 2012.
29. Ariedea, M.B., Candidao, T.M., Jacomea, A.L.M., Velascoa, M.V.R., de-Carvalhob, J.C.M., Babya, A.R., Cosmetic attributes of algae – A review. *Algal. Res.,* 25, 483, 2017.
30. Daughton, C.G., Ternes, T.A., Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health. Perspect.,* 107, 907, 1999.

31. Ani, B., Gabriella, C., Fabio, A., New trends in cosmetics: by-products of plant origin and their potential use as cosmetic active ingredients. *Cosmet.*, 2, 82, 2015.
32. Sani, A., Gaya, M.B., Abubakar, F.A., Determination of some heavy metals in selected cosmetic products sold in kano metropolis, Nigeria. *Toxicol. Rep.*,3, 866, 2016.
33. León, M., Surumay, Y.,Marquina-Chidsey, G., Arias, D., Development of a cosmetic product using a natural dye extracted from Jambolan fruit *Syzygiumcumini* (L). Skeels. *Rev. FacIng.,* 3, 131, 2015.
34. Wurts, M.L., Torreblanca, R.A., Analysis of the seed *Bixaorellana*, L. (annatto) and the waste generated in the extraction of its pigments. *Arch. Latinoam. Nutr.,* 33, 606, 1983.
35. Marwa, M.D., Sami, G.A., Sofian, S.M., Abdulmottaleb, E.Z., Asma, A.H.S., Abdurazag, A.A., Salah, B.M., Use of *Beta vulgaris* as natural coloring agent for foods and cosmetics in Libya. *J. Chem. Pharm. Res.,* 5, 340, 2013.
36. Patil, N.N., Ajit, G.D., Applications of natural dye from *Ixoracoccinea* L. in the field of textiles and cosmetics. *Color. Technol.,* 132, 98, 2016.
37. Bechtold, T., *Natural colorants in hair dyeing: handbook of natural colorants,* John Wiley & Sons, Ltd. 339, 2009.
38. Dweck, A.C., Comprehensive focus on natural dyes. *Color Cosmet.*, 57, 2009.
39. Boga, C., Delpivo, C., Ballarin, B.,Morigi, M., Galli, S., Micheletti, G., Tozzi, S., Investigation on the dyeing power of some organic natural compounds for a green approach to hair dyeing. *Dyes Pigm.,*97, 9, 2013.
40. Dweck, A.C., Natural ingredients for colouring and styling. *Int. J. Cosmet. Sci.,* 24, 287, 2002.
41. Hu, Y.L., Luo, J.Y., Zhao, H.Z., Zhang, S.S., Yang, S.H., Yang, M.H., Application of natural plant pigment in hair dyes. *J. Chinese Materia. Medica.* 41, 3226, 2016.
42. Madnani, N., Khan, K., Hair cosmetics. *Indian J. Dermatol. VenereolLeprol.*, 79, 654, 2013.
43. http://science.howstuffworks.com/hair-coloring.htm
44. http://ec.europa.eu/enterprise/cosmetics/html/som_hairdyes.htm
45. Anderson, J.S., The chemistry of hair colorant. *J. Soc. Dyers Color.*, 116, 193, 2000.
46. Akram, M., Wolf, W., Granulation of powdered direct hair dyes. German Patent 4233874, 19940414, Priority DE 1992–4233874, 1992–21008, 1992.
47. Lenz, U., Natural dyestuffs in hair cosmetics, a forum Farberplanzens, Dornburg Germany, Fachagentur, NachwachsendeRohstoffe. Guelzow Germany, 145, 1997.
48. Jones, S.B., Luchainger, A.B., *Plant Systematic*, Mc Gram Hill Book Company, New York, London,1979.
49. Chaudhary, G., Goyal, S., Poonia, P.,*Lawsonia inermis* Linnaeus: A Phytopharmacological Review. *J. Pharm. Sci. Drug. Res.*, 2, 91, 2010.
50. Cartwright-Jones, C., Developing Guidelines on Henna: A Geographical Approach, Essay for Master degree, Kent State University, Kent Ohio, www.hennapage.com, August 2006.

51. Cartwright-Jones, C., Henna for Hair. How-to Henna,TapDancingLizard™ LLC, Stow, Ohio, 2006.
52. Yusuf, M. Ahmad, A., Shahid, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsonia inermis*). *J. Clean. Prod.*, 27, 42, 2012.
53. Afzal, M., Al-Oriquat, Al-Hussan, J.M., Mohammed, N., Flavone glycosides from *Lawsonia inermis*. *Heterocycl.*, 14, 1973, 1980.
54. Chanayath, N., Lhieochaiphant, S., Phutrakul, S., Pigment extraction techniques from the leaves of *Indigoferatinctoria Linn.*and *Baphicac anthuscusia Brem*. and chemical structure analysis of their major components. *CMU J.*, 1, 149, 2002.
55. Bechtold, T., Mussak, R., Handbook of natural colorant, pp. 343, John Wiley and Sons Ltd, 2009.
56. Kumar, J. K., Sinha, A.K., Resurgence of natural colourants: a holistic view. *Nat. Prod. Res.*, 18, 59, 2004.
57. Bhaskar, A., Nithya, V., Vidhya, V.G., Phytochemical screening and *in vitro* antioxidant activities of theethanolic extract of Hibiscus *Rosasinensis* L. *Annals Biol. Res.*, 2, 653, 2011.
58. Uttara, J., Swapnali, B., Mohini, U., Formulation and preliminary evaluation of natural hair colorant.*Int. J. Pharm. Bio. Sci.*, 1, 1, 2010.
59. Zhang, Y., Tanaka, T., Iwamoto, Y., Yang, C., Kouno, I.,Phyllaemblic acid, a novel highly oxygenated norbisabolane from the roots of Phyllanthusemblica. TetrahedronLett., 41, 1781, 2000.
60. Gupta, A., Malviya, R., Singh, T.P., Sharma, P.K., Indian medicinal plants used in hair care cosmetics: A short review. Pharmacogn. J., 2, 361, 2010.
61. Dhale, D.A., Mogle, U.P.,Phytochemical screening, and antibacterial activity of Phyllanthusemblica(L.), Sci. Res. Rep., 1, 138, 2011.
62. Krishnamoorthy, J.R., Ranganathan, S., Gokul S.S., Ranjith, M.S.,Dano: A herbal solution for dandruff. Afr. J. Biotechnol., 5, 960, 2006.
63. Adeel, S., Kiran, S., Ayesha, T., Fazal-Ur-Rehman, Gulzar, T., and Rafi, S., Zuber, *Radiation pre-treatment: A potential Novel Technology to Improve Fastness Properties of Plant Derived Natural Dyes*. Wiley-Scrivener Publishing LLC USA, pp 65–87, 2017.
64. Adeel, S., Rafi, S., Salman, M., Fazal-ur-Rehman and Abrar, S., Potential Resurgence of Natural Dyes in Applied Fields. Wiley-Scrivener Publishing LLC USA. pp 1–26, 2017.
65. Adeel, S., Fazal-ur-Rehman, Rafi, S., Kamran, M., Zuber, M., Bhatti, I.A., Akhtar, N., *Current innovations in synthetic dyes and dyeing*. Studium Press LLC Press USA. 2018
66. Adeel, S., Zuber, M., Rehman, F., and Zia, K. M., Microwave-assisted extraction and dyeing of chemical and bio-mordanted cotton fabric using harmal seeds as a source of natural dye. *Environ. Sci. Pollut. Res.* 2018. https://doi.org/10.1007/s11356–018-1301–2

11

Application of Natural Dyes to Cotton and Jute Textiles: Science and Technology and Environmental Issues

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Abstract

Growing consciousness for eco-friendliness of textile products has caused more interest to the consumers for using natural dyes particularly for natural fibers like cotton, silk, and jute etc. including their organic counterpart. Productions of synthetic dyes are dependent on petrochemical source and some of the synthetic dyes contain toxic/carcinogenic amines, and are not eco-friendly. Contrary to this, most of the natural dyes with few exceptions are based on vegetable/animal origin and are renewable, bio-degradable, energy-efficient, and eco-friendly. Natural dyes can produce uncommon and soothing shades, and in some cases the shades are enhanced with age during use. They are usually non-toxic/ non-carcinogen and non-allergic. However, the common drawbacks of natural dyes are its difficult reproducibility, shade limitation, non-uniform shade, poor to moderate fastness, and non-availability of standard application methods. For producing eco-friendly dyed textiles, natural dyes are being preferred in Japan, UK, and USA. Hence, lot of studies have been reported recently for exploring the different aspects of natural dyeing of textiles, but most of the studies are related to simple application of different mordant and different types of natural dyes on different textile materials and their color yield and color fastness. Very few studies are related to its scientific and technological aspects including scientific optimization of dyeing process variables, study of mechanism of dye-mordant-fiber fixation, role of different mordanting assistants/additives, role of any chemical pre-treatments/modifications on dyeing, analysis of dyeing rate, dyeing kinetics, and use of binary or ternary

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mixture of nature dyes to obtain compound shades (to overcome shade limitations) and analysis of their compatibility etc. However, for understanding this gap, some studies on scientific and technological aspects have been carried out from this laboratory on application of single as well as different mixture of natural dyes like Tesu, Manjistha, catechu, Red sandal wood, Jackfruit wood, Sappan wood, Marigold, Manjistha and Babool as natural dyes both on cotton and jute. A brief summary on some of such work with important observation and conclusions are also mentioned for information to all concern. Special attempt has been made in these studies to understand technological feasibility of natural dyeing of cellulosic and ligno-cellulosic (cotton and jute) textiles for industrial exploitation for both small scale and large scale jute or textile industry by field trial at two mills.

Keywords: Natural dye, mordant, dyeing, jute, cotton

11.1 Introduction

Dyeing is a process of imparting color to textiles and other substrates, the coloring matter plays a significant role. Coloring matters can be broadly classified into two categories: (a) Natural, and (b) Synthetic. Natural dyes are the coloring matters derived from the natural sources [1–5]. It may be vegetable or animal matter in their origin. However, there are exceptions where the dyestuffs are of mineral origin. The Society of Dyers & Colorists color index (3rd edition) defines natural coloring matters as the natural dyes and pigments comprise of all the colors obtained from animal and vegetable matter with no or very little chemical treatments [1–4]. They are mainly mordant dyes [3], but they also include some vat, few disperse/ solvent dyes, some pigment color, a few direct, basic and acid dyes with or without mordanting ability.

The production of synthetic chemicals involves many chemical reactions requiring high energy. Moreover, there are many undesirable by-products generated during the reactions [6–8]. These toxic or environment un-friendly by-products have to be discharged in the rivers, ponds or into the atmosphere. These drawbacks of the synthetic dyes have prompted the researchers to look for alternatives of eco-friendly products and technologies using natural dyes for dyeing. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process like dyeing with natural dyes, which has thus become a necessity [8].

The major problem of natural dyes encountered is their availability due to difficulty in collection, and standardization of the methods of application. The question of availability, cost and poor color fastness properties are major negative factors [8] to reckon with. Very few studies are related to its scientific and technological aspects including scientific optimization of dyeing process variables, study of mechanism of dye-mordant-fiber fixation, role of different mordanting assistants/additives, role of any chemical pre-treatments/modifications on dyeing, analysis of dyeing rate, dyeing kinetics, and use of binary or ternary mixture of nature dyes to obtain compound shades (to overcome shade limitations) and analysis of their compatibility etc. Hence, there are needs of precise scientific and technological knowledge and development of systematic scientific methods of dyeing textiles with natural dyes vis-à-vis study of the color developed in variety of shades and color fastness performances of natural dyed textiles. For overcoming shade limitation, natural coloring also need to be compounded using mixture of natural dyes, which are compatible to each other for binary and ternary mixtures. Requirement of an easy method for compatibility rating between different pair of natural dyes is also a priority need of this sector.

The use of natural dyes on painting/textiles/leathers and furs has been known since ancient history [9]. Artisans and cottage level village dyers have been using this technique for a long time, even before its scientific basis has been known. Worldwide growing consciousness for use of eco-friendly products in daily life has generated increasing interest of consumers towards the use of textiles of natural fibers dyed with natural eco-friendly dyes. However, all natural dyes may not be necessarily eco-friendly and eco-friendliness of natural dyes must be always tested/verified before use.

Most natural dyes are non-substantive which means that they have little coloring power within themselves, and require the aid of mordant and sometimes with some mordanting assistants or additives for absorption and fixation of such dyes on the textile materials. These mordant and additives to be used in natural dyeing of textiles need to be eco-friendly as well.

In recent years, there has been an interest manifested towards natural dyes by both the consumers and producers of textile. The reason being manifold that includes ecological concern, bio-degradability, bio-compatibility of natural dyes with the environment etc. Other associated advantages include expected non-toxicity [8–10] and anti-allergen [8] properties of natural dyes. Before study of Science and Technological Aspects of Natural dyeing to Cotton and Jute, it is essential to test and characterise the purified natural dye to understand and predict its dyeing behaviour/performance after its extraction at optimised conditions of extraction, which for some of the selective natural dyes are discussed below.

11.2 Extraction of Color Solution from the Sources of Natural Dyes

Dried petals or barks or chopped woods or roots of selected natural dyes were initially crushed to powder form using a locally made mechanical vibrator cum grinder machine and then it was subjected to aqueous extraction under optimized conditions as shown below:

All the above aqueous extracts of corresponding natural dyes were double filtered in fine muslin and the filtrates were further concentrated by evaporation, employing additional heating in water bath to a desired concentration level to obtain 40% aqueous dye-extract (on the basis of weight of solid source material for each dye) or to obtain semi-solid dry mass of the each natural dye for subsequent purification.

11.3 Purification of Selected Natural Dyes

For characterization purposes, the concentrated aqueous extracts of the selected natural dyes were filtered and the filtrates were evaporated to a nearly semisolid dry mass under water bath as said above. The said semisolid dry mass of the dye extract was then put in a cage of the wrapped Whatman (42) filter paper and further subjected to extraction in Soxhlet apparatus using 1:1 ethyl alcohol/benzene mixture for 10 cycles for 2 h at 70 °C. The alcohol- benzene extract of the color component was finally subjected to evaporation in a water bath at 50 °C to get a semi-dry mass of the pure color component. Finally, this semi-dry mass of the color component was washed with acetone followed by washing with methyl alcohol followed by final drying in air to obtain the dry powder of the pure color component for each dye.

Table 11.1 Conditions of Extraction of Natural dye from source materials.

Natural dyes	MLR	Temperature, °C	Time, min
Red Sandal Wood	1:20	80	90
Jackfruit wood	1:10	100	30
Marigold	1:20	80	45
Manjistha	1:20	90	45
Babool	1:20	100	120
Sappan Wood	1:20	100	120

11.4 Testing and Characterization of Purified Natural Dyes Before its Application to Textiles

11.4.1 UV-VIS Spectral Analysis of Aqueous Extracted Solution of Natural Dyes

1% aqueous solution of each purified individual dye powder was separately prepared and was subjected to wavelength scan in a microprocessor attached Hitachi-U-2000 UV-UIS absorbance spectrophotometer for 190–1100 nm range to understand its predominant wavelength of color/shade to be produced and presence or absence of specific peaks in UV region, to understand its UV-absorbing nature of the dye (higher the no. of peaks or peak height in UV region indicate preferably higher UV absorbance accelerating fading under UV-light/sun-light).

Absorbance peaks of UV-VIS spectrum of dilute aqueous solution of each individual purified natural dye has been shown in Table 11.2 for all the six natural dyes (MG, BL, JFW, SW, RSW, and MJ). Most of the natural dyes show dominating UV-absorbance character either at 242–250 nm and/or at 370–380 nm, which is found to be much predominating at 242–250 nm zone in case of Babool and Marigold, while Manjistha has no such preferential UV-absorbance peak at 242–370 nm zone, except a sharp peak at 380 nm, which is more related to absorbance of quinone group in anthraquinone type of structure present in main color components of Manjistha. Besides these peaks in main UV-regions (190–370 nm), the other characteristics peaks of UV-VIS spectra of corresponding natural dye solution in the visible region (380–700 nm) are the peaks for predominating hue of the main color component of the corresponding dye. In some cases (as in MJ, RSW, Babool etc), there are more than one or multiple peaks in the visible region, which indicate the presence of more than one color components (in respective natural dye extracts) closely differing in predominating hues. The followings are the observed characteristic UV-VIS absorbance peaks of the corresponding UV-VIS spectra of 1% aqueous solution of individual purified natural dyes, as given in Table 11.2 and corresponding UV-Vis Spectra of (a) to (f) are given in Figure 11.1.

11.4.2 FTIR Spectral Analysis

The purified dye powder of individual natural dye was further washed in distilled water followed by further washing in 100% acetone before final drying and was subjected to FTIR Spectroscopy study in a double beam FTIR spectrophotometer (ModelJSM-4200-JASCOFTIR spectrophotometer) using KBr disc technique.

Table 11.2 UV-VIS absorbance peaks at different wavelength for purified selective natural dyes.

Name of the purified natural dyes	Major UV-VIS peaks observed at different wave length (nm)
(a) Marigold (MG)	250, 598
(b) Babool (BL)	242, 372, 550, 602
(c) Jackfruit Wood (JFW)	250, 540
(d) SappanWood (SW)	242, 373, 610
(e) Red Sandal Wood (RSW)	250, 370, 540, 602
(f) Manjistha (MJ)	380, 540, 610

IR- spectrum for each of purified natural dye powder has been shown in spectra (a) to (e) in Figure 11.2 and spectra (d) to (f) in Figure 11.3. The characteristics FTIR bands/peaks for each of purified natural dyes observed have been marked with corresponding wave number (cm^{-1}) for each spectra in both the Figure 11.2 and Figure 11.3 as well as these are also tabulated separately in Table 11.3 mentioning position of FTIR absorption band, type and made of vibrations, nature and appearance of bands/peaks along with description of responsible bonds and associated chemical functionality for each purified color components of the said natural dyes. The matter presented in Table 11.3 are self-explanatory showing and confirming the type of chemical functionality and bonds present in the main color components of each of the individual purified dyes. The known chemical structures of the main color components of each of these dyes have been reported in earlier literature. The FTIR bands of each purified natural dye are found to be much in tune with the earlier reported chemical structures of main color components of the individual natural dyes.

11.4.3 Analysis of DSC-Thermo Grams

The purified dye powder for individual natural dye was further washed in distilled water followed by further washing in 100% acetone before final drying and was then subjected to DSC-study by usual method using Shimadzu differential scanning calorimeter (Model-DSC-50) under flowing nitrogen (flow rate 50 cm^3/min) at a heating rate of 10 °C/min with 2 mg sample over a temperature range of ambient (30 °C) to 500 °C.

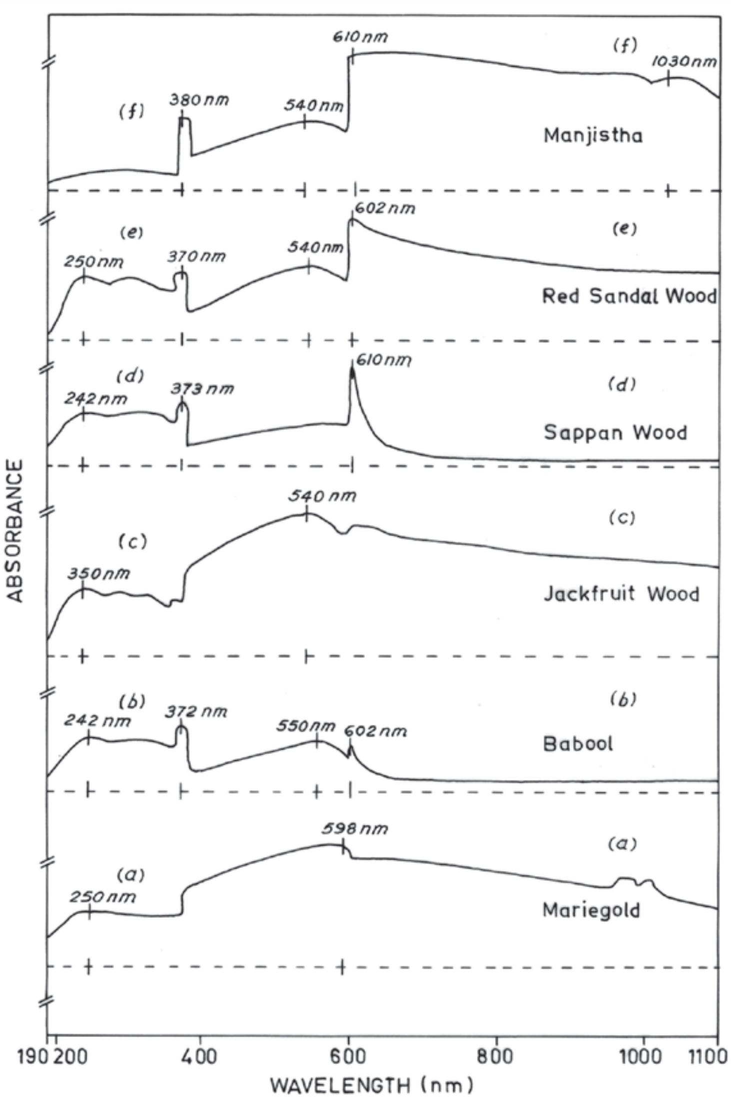

Figure 11.1 UV-VIS spectra of aqueous extract of color component of selective natural dyes.

Differential Scanning Calorimetry (DSC) thermo grams for each of the purified natural dye powder have been shown in Figure 11.4, showing endothermic and exothermic peaks at different temperature zones for heating the same from ambient (30 °C) to 500 °C temperature range at the heating rate of 10 °C/ min under flow of nitrogen (flow rate 50 cm^3/min). In

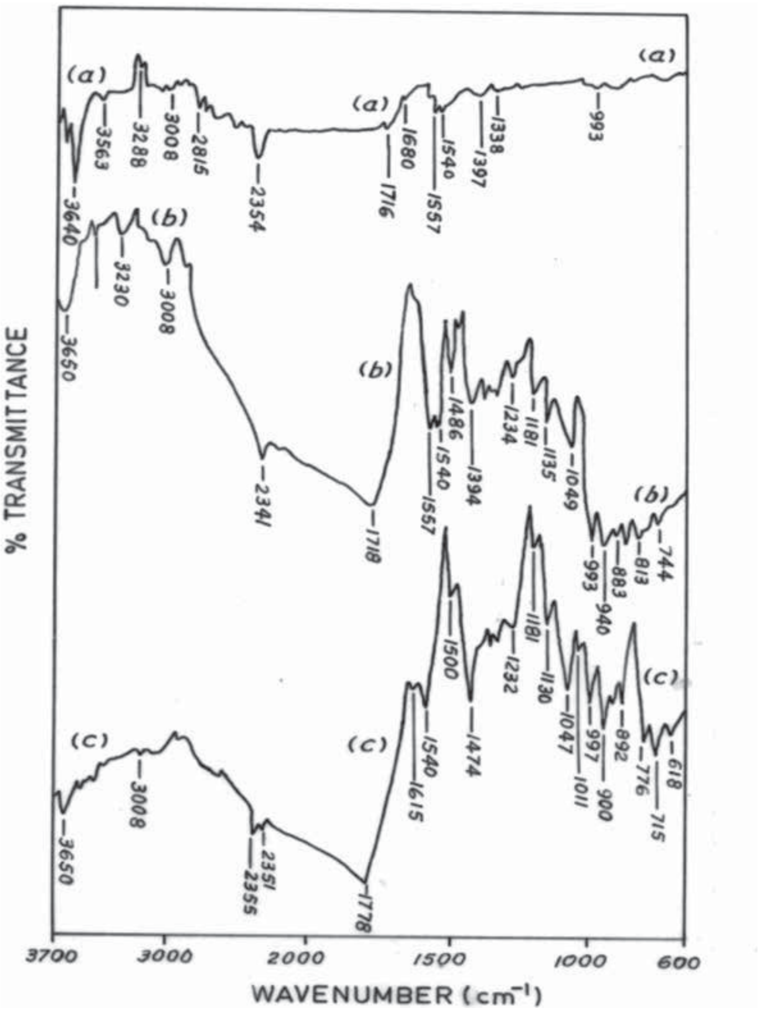

Figure 11.2 FTIR spectra of purified natural dyes (a) Red Sandal Wood (b) Jackfruit Wood and (c) Manjistha.

each case, the thermal transition temperatures are marked and mentioned in each thermo grams (a) to (f) in Figure 11.4 and as well as also tabulated in Table 11.4 mentioning the range/maximum peak for thermal transition temperatures (°C), nature and appearance of DSC peaks and probable reasons of the observed thermal transitions. The matters presented in Table 11.4 are self-explanatory and indicate the reasons of characteristics of exothermic and endothermic DSC-peaks of each thermo grams for each individual purified natural dye.

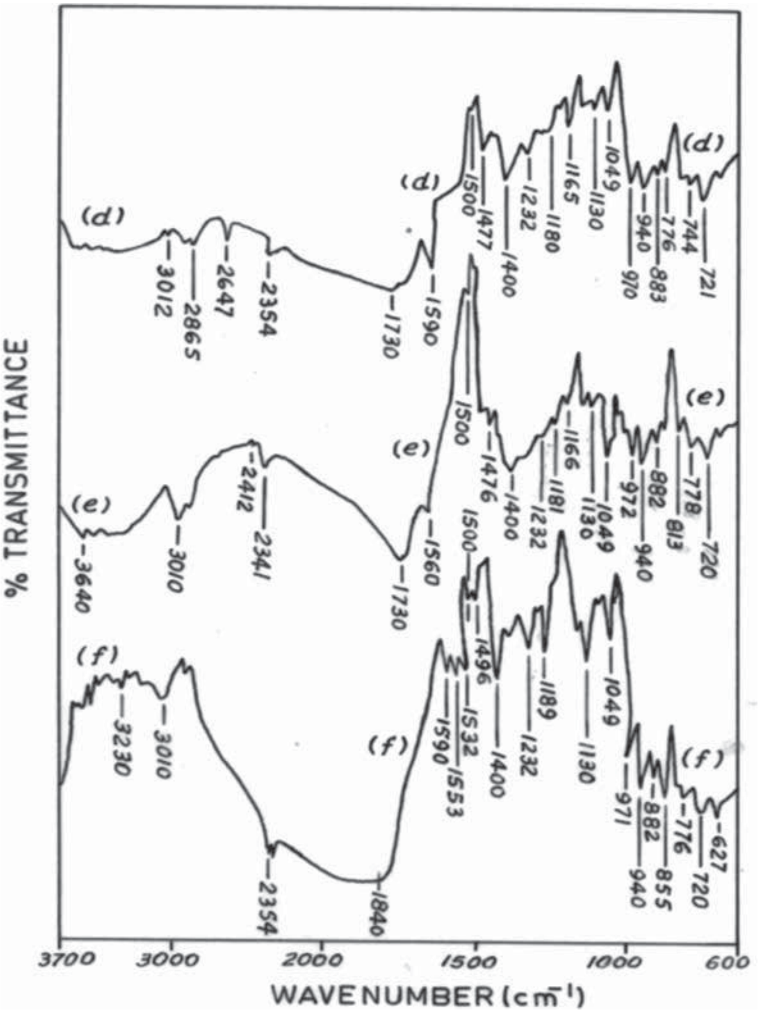

Figure 11.3 FTIR spectra of purified natural dyes (d) Marigold (e) Babool and (f) Sappan Wood.

11.5 Mechanism of Complex Formation Amongst Dye-Mordant and Fiber for Fixation of Natural Dyes on Different Fibers

In case of mordant able natural dyes, different textile fibers are mordanted with selective metallic salts which have a tendency to form coordinated complex with dye molecule on combining with natural dye forming a

Table 11.3 Spectroscopic data table for FTIR bands/peaks of selective purified natural dyes.

Position of absorption band, wave number in cm^{-1}	Nature and appearance of bands/ peaks	Bond and its mode of vibration with associated functional groups responsible [48, 49]
(a). For red sandal wood (RSW)		
993	Small	–C–H deformation in benzene ring
1338–1397	Doublet	–C–O–H bending in Primary and secondary alcohol
1540–1557	Small and doublet	–C=C stretching in non-conjugated –C=C
1680	Small	–C=C stretching in Non-conjugated –C=C
1716	Small	–C=O Quinone to aromitic ring or –C=O stretching in ring ketone in Aromatic ester and 6C ring ketone
2354	Weak but intense	–C–H stretching in Benzene ring
2815	Small	–C–H stretching in $–O–CH_3$ or methylol ether group
3008	Small	–C–H stretching in aromatic ring
3288	Small	–O–H stretching in bonded hydrogen (by H–bonds)
3563–3650	Small	–O–H stretching in Free –OH of phenolic structure
(b). For Jackfruit Wood (JFW)		
744–883	Multiplet	–C–H out of plane deformation in Benzene ring
940	Weak but intense	–C–O stretching vibration in higher cyclic ether linkages (as present for jackfruit wood)
993	Weak but intense	–C–H deformation in benzene ring

(*Continued*)

Table 11.3 Cont.

Position of absorption band, wave number in cm^{-1}	**Nature and appearance of bands/ peaks**	**Bond and its mode of vibration with associated functional groups responsible [48, 49]**
1049	Medium	–C–O stretching in primary or secondary alcohol
1135–1234	Multiplet and sharp	–C–O stretching and –OH in plane deformation in phenol
1394	Small	–C–H bending in Methyl ketone or methyl groups
1486	Sharp but small	–C=C stretching in aromatic ring
1540–1557	Small doublet	–C=C stretching in aromatic ring
1718	Small	–C=O stretching of Quinone to aromatic ring or –C=O stretching of ring ketone in aromatic ester and 6C ring ketone
2341	Small but sharp	–C–H stretching in benzene ring
3008	Small	–C–H stretching in aromatic ring
3230	Medium intense	Hydrogen bond –OH stretching in Phenolic structure
3563–3650	Weak but intense	–OH stretching in free –OH phenolic structure
(c). For Manjistha (MJ)		
618–900	Multiplet	–C–H out of plane deformation in benzene ring
997	Sharp	–C–H deformation in benzene ring
1011–1047	Medium	–C–O stretching in Primary or secondary alcohol
1130–1232	Very strong	–C–O stretching and –OH in plane deformation in Phenol
1474	Small	–C=C stretching in aromatic ring
1500–1540	Sharp	–C=C stretching in aromatic ring

(*Continued*)

Table 11.3 Cont

Position of absorption band, wave number in cm^{-1}	**Nature and appearance of bands/ peaks**	**Bond and its mode of vibration with associated functional groups responsible [48, 49]**
1615	Small	–C=O stretching in aromatic ring
1718	Broad	–C=O stretching in ring Quinone to aromitic ring or –C=O stretching in ring ketone in aromatic ester and 6C, ring ketone
2355–2351	Doublet	–C–H stretching in –O–CH_3 or methylol ether group
3008	Small	–C–H stretching in aromatic ring
3653–3650	Small	–O–H stretching in free –OH in phenolic structure
(d). For Marigold (MG)		
720	Small but intense	–C–H bending in poly methylene (as present in xanthophyl esters present in MG)
744–883	Multiplet and sharp	–C–H out of plane deformation in benzene ring
940	Tiny	–C–O stretching vibration in higher cyclic ether linkages
970	Small and sharp	–C–H deformation in aromatic ring
1049	Sharp and intense	–C–O stretching in primary or secondary alcohol
1130–1232	Multiplet	–O–H in plane deformation in Phenols
1390–1477	Sharp	–C=C stretching in aromatic ring
1590	Sharp and intense	–C=C stretching in aromatic ring
1730	Small	–C=C stretching and –C=O stretching in non-conjugated, –C=C

(*Continued*)

Table 11.3 Cont.

Position of absorption band, wave number in cm^{-1}	**Nature and appearance of bands/ peaks**	**Bond and its mode of vibration with associated functional groups responsible [48, 49]**
2354	Small	–C–H stretching in $–O–CH_3$ or methyl ether
2647		
3022–3012	Doublet	–C–H stretching in aromatic ring
(e) For Babool (BL)		
720	Small but intense	–C–H bending in poly methylene (as present in xanthophyl esters present in MG)
778–882	Sharp multiplets	–C–H out of plane deformation in benzene ring
940	Sharp	–C–O stretching vibration in higher cyclic ether linkages
972	Small and sharp	–C–H deformation in aromatic ring
1049	Sharp and intense	––C–O stretching in primary or secondary alcohol
1130–1232	Sharp multiplets	–OH in plane deformation in phenols
1400–1500	Multiplet	–C=C stretching in aromatic ring
1590	Tiny	–C=C stretching in aromatic ring
1730	Small	–C=C stretching in non-conjugated
2354–2312	Doublet	–C-H stretching in benzene ring
3640	Small	Free –OH in Phenol
(f). Sappan Wood (SW)		
627	Small	–C–H out of plane deformation in benzene ring
720	Small	–C–H bending in $(CH_2)_n$ i.epolymethylene

(*Continued*)

Table 11.3 Cont.

Position of absorption band, wave number in cm^{-1}	**Nature and appearance of bands/peaks**	**Bond and its mode of vibration with associated functional groups responsible [48, 49]**
776–882	Sharp multiplets	–C–H out of plane deformation in benzene ring
940	Sharp	–C–O stretching vibration in higher cyclic ether linkages
971	Sharp	–C–H deformation in aromatic ring structure
1049	Sharp	–C–O stretching in primary or secondary alcohol
1130–1232	Sharp multiplets	–OH in plane deformation phenols
1400–1500	Multiplet	–C=C stretching in aromatic ring
1532–1590	Multiplet	–C=C stretching in aromatic ring
1840	Very small	
2354	Broad trough	–C–H stretching in benzene ring
3010	Small	–C–H stretching in aromatic ring
3230	Small	Hydrogen bonded –OH stretching in phenol

coordinated complex with certain functional groups present in the dye, bound by co-ordinated/covalent bonds or hydrogen bonds and other interactional forces as shown below in Figure 11.5.

11.6 Technological Aspects of Natural Dyeing to Cotton and Jute: Effect of Different Mordants

11.6.1 Optimization of Mordanting and Dyeing Variables

Bleached jute and cotton fabrics were pre-mordanted using myrobolan as 1st mordant and then aluminium sulphate as 2nd mordant applied in sequence as per the following conditions of treatment given in Table 11.5.

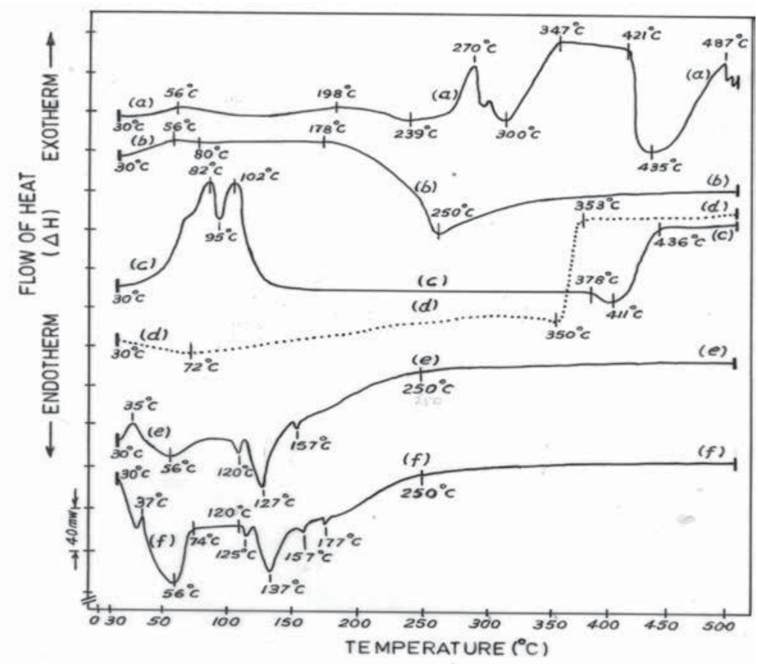

Figure 11.4 DSC Thermo grams of purified natural dyes (a) Babool (b) Jackfruit Wood (c) Red Sandal Wood (d) Sappan Wood € Marigold and (F) Manjistha.

Unless otherwise mentioned, selectively double pre-mordanted bleached jute and cotton fabric samples were dyed using purified dye powder in fixed concentration (1% owf) for each dye obtained from 40% aqueous dye extract of selected dyes based on the weight of solid dye source material. The dyeing was carried out either at optimized condition of dyeing derived from the present study and also varying dyeing process variables like temperature 80–100 °C, MLR 1:10 to 1:50 for time of Dyeing 30–90 min, pH 5–12 and adding 10–30 gpl sodium chloride as additive for study of process variables.

11.6.2 Effect of Selective Single and Double Mordanting on Jute and Cotton Fabrics for Natural Dyeing

As a initial part of the study of the present work, bleached jute and cotton fabrics have been mordanted using different single and double mordants and the resultant changes in mechanical properties (breaking tenacity, breaking extension, and bending length) and surface color strength (K/S value) and total color differences (dE) of the mordanted fabrics have been assessed and shown in Table 11.6 for single mordanting and in Table 11.7

Table 11.4 DSC- Thermal transition temperatures of extracted and purified natural dyes used.

Sample identity or name of compound dyes	Thermal transition temperatures, °C	Nature and appearance of DSC-peaks	Probable reasons of the observed thermal transitions
(a) Babool (BL)			
	56	Small wide hump (Exothermic)	Combined effects of breaking of H-bonds and moisture evaporation
	178	Broader crest (Exothermic)	Decomposition of other minor constituents
	239	Broader trough (Endothermic)	Decomposition of some other minor constituents
	279	Sharp peak (Exothermic)	Thermal decomposition of gallic acid
	300	Deep trough (Endothermic)	Decomposition of epicatechin
	347 to 421	Flat -plateau region (Exothermic)	No effects
	435	Deep trough (Endothermic)	Thermal decomposition of catechin
	487	Small sharp peak (Exothermic)	Thermal decomposition of theoflavones or other minor constituents present
(b) Jackfruit wood (JFW)			
	56	Small hump (Exothermic)	Combined effects of breaking of H-bonds and moisture evaporation

	80–178	Flat plateau region	No effects
	250	Wide trough (Endothermic)	Thermal decomposition of Morol
(c) Red sandal wood (RSW)			
	82	Sharp peak (Exothermic)	Breaking of strong H-bonds of deoxysantalin
	95	Sharp trough (Endothermic)	Thermal decomposition of deoxysantalin
	102	Sharp peak (Exothermic)	Breaking of more strong H-bonds of santalin-(A & B)
	129–378	Flat plateau region (Endothermic)	No effects
	411	Small trough (Endothermic)	Thermal decomposition of santalin-(A & B)
	436–500	Flat plateau region (Exothermic)	No effects
(d) Sappan wood (SW)			
	72	Small transition (Endothermic)	Moisture evaporation
	350	Small trough with sharp transition (Endothermic)	Thermal decomposition of Brazeline
	353–500	Flat plateau region (Exothermic)	No effects

(*Continued*)

Table 11.4 Cont.

Sample identity or name of compound dyes	Thermal transition temperatures, °C	Nature and appearance of DSC-peaks	Probable reasons of the observed thermal transitions
(e) Marigold (MG)			
	35	Tiny peak (Exothermic)	Breaking of H-bonds
	56	Medium trough (Endothermic)	Moisture evaporation[7]
	120	Small trough (Endothermic)	Thermal decomposition of Xanthophyl ester
	127	Sharp trough (Endothermic)	Thermal decomposition of Quectrol (flavanol)[7]
	157	Tiny trough (Endothermic)	Decomposition of other minor constituents
	250–500	Flat plateau region (Exothermic)	No effects
(f) Manjistha (MJ)			
	37	Tiny peak (Exothermic)	Breaking of H-bonds
	56	Deep trough (Endothermic)	Moisture evaporation
	74–120	Flat plateau region (Exothermic)	No effects
	125	Small and Sharp trough (Endothermic)	Thermal decomposition of purpuroxanthin

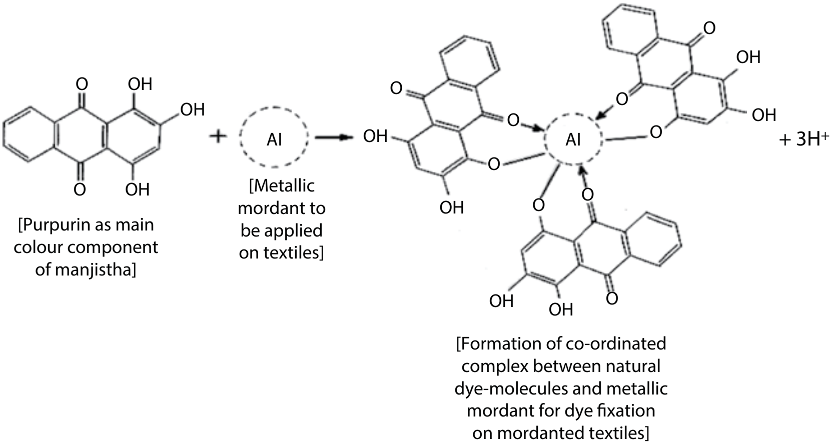

Figure 11.5 Mechanism of fixation of natural dyes through mordants.

Table 11.5 Mordanting conditions for sequential double mordanting jute and cotton fabric.

Treatment conditions	**Preparation and mordanting conditions for applying 1st and 2nd mordants**	
	1st mordant (Myrobolan)	***2nd mordant [$Al_2(SO_4)_3$]***
% Application	20% owf (Optimum)	20% owf (Optimum)
Material to liquor ratio (MLR)	1:20	1:20
Temperature	80 °C	80 °C
Time	30 min	30 min
After-treatment	Finally dried without washing, to make it ready for second mordanting	Finally dried in air without washing to make it ready for subsequent dyeing

for sequential double mordanting. It can be observed from the data in Table 11.6 and Table 11.7 that when bleached jute and cotton fabrics are mordanted singly with stannous chloride alone or double mordanted with harda and stannous chloride applied in sequence, there is a considerable loss of fabric strength. While, bleached jute and cotton fabrics when mordanted with aluminium sulphate and harda shows less loss in strength as

Table 11.6 Tensile properties, bending length, surface color strength and color differences of jute and cotton fabrics treated with selective single mordants (without dyeing).

Mordanting	**Warp way tenacity (cN / tex)**		**Warp way breaking elongation (%)**		**Warp way breaking elongation (%)**		**Selective color strength and color difference**			
							Jute		**Cotton**	
	(Jute)	**(Cotton)**	**(Jute)**	**(Cotton)**	**(Jute)**	**(Cotton)**	**K/S Value at λ_{max}**	**dE**	**K/S Value at λ_{max}**	**dE**
Control bleached fabric	6.09	5.41	3.47	5.36	4.2	2.1	0.80	–	0.01	–
5% myrobolan	5.56	5.21	5.60	5.25	4.1	2.1	1.40	0.50	0.07	7.10
10% myrobolan	4.89	5.03	5.73	5.19	4.2	2.1	1.57	0.54	0.15	8.27
15% myrobolan	3.71	4.48	5.88	5.14	4.3	2.2	1.74	0.64	0.25	9.36
20% myrobolan	3.50	4.78	5.97	5.08	4.4	2.2	1.96	0.73	0.36	10.49
5% $Al_2(SO_4)_3$	5.96	4.89	4.27	1.51	4.3	2.1	0.96	0.74	0.01	1.05
10% $Al_2(SO_4)_3$	5.85	4.67	4.31	1.63	4.4	2.1	1.05	0.87	0.03	1.27
15% $Al_2(SO_4)_3$	5.27	4.51	4.45	1.89	4.5	2.1	1.10	0.99	0.04	1.41
20% $Al_2(SO_4)_3$	4.88	4.26	4.47	1.97	4.6	2.2	1.20	1.10	0.07	1.50
30% $Al_2(SO_4)_3$	4.37	4.01	4.51	2.09	4.6	2.2	1.33	1.89	0.08	1.78
40% $Al_2(SO_4)_3$	4.07	3.97	4.61	2.19	4.7	2.3	1.34	1.94	0.09	2.01

5% $FeSO_4$	5.77	5.01	4.32	3.51	4.4	2.1	3.79	4.21	0.03	19.54
10% $FeSO_4$	5.06	4.99	4.64	3.69	4.4	2.3	4.63	4.87	0.04	20.05
15% $FeSO_4$	4.89	4.80	4.72	3.99	4.5	2.3	4.79	5.19	0.05	20.87
20% $FeSO_4$	4.45	4.72	4.84	4.09	4.5	2.4	5.03	5.97	0.06	21.02
30% $FeSO_4$	4.12	4.63	4.95	4.47	4.7	2.4	6.12	6.21	0.08	22.01
40% $FeSO_4$	3.99	4.54	5.01	4.97	4.8	2.5	6.54	6.84	0.09	23.33
5% $KAl(S0_4)_2$	3.47	4.01	4.79	3.98	4.0	2.1	0.95	1.01	0.02	5.31
10% $KAl(S0_4)_2$	3.30	4.12	4.91	4.12	4.0	2.2	0.99	1.37	0.02	5.51
15% $KAl(S0_4)_2$	3.12	4.27	5.01	4.23	4.0	2.3	1.10	1.64	0.03	8.61
20% $KAl(S0_4)_2$	3.00	4.34	5.11	4.57	4.1	2.5	1.15	1.77	0.04	8.88
5% $SnCl_2$	3.54	4.89	4.54	3.20	4.2	2.1	0.97	1.79	0.01	3.67
10% $SnCl_2$	3.32	4.27	4.71	3.89	4.2	2.3	1.01	1.89	0.01	3.78
15% $SnCl_2$	3.11	3.84	4.87	4.65	4.3	2.3	1.07	2.14	0.02	5.54
20% $SnCl_2$	2.98	3.21	5.09	4.98	4.3	2.5	1.12	2.29	0.02	5.93
5%EDTA	4.51	4.03	4.01	4.02	3.8	2.1	0.89	1.01	0.02	4.51
10%EDTA	4.32	4.35	4.15	4.34	3.8	2.1	0.89	1.07	0.03	5.41
15%EDTA	4.12	4.71	4.32	4.65	3.8	2.2	0.90	1.15	0.04	6.47
20%EDTA	4.04	4.98	4.57	4.70	4.0	2.2	0.91	1.19	0.04	7.43

Table 11.7 Tensile properties, bending length, color strength and color differences of jute and cotton fabrics treated with selective double mordants (without dyeing).

Mordanting	**Warp way tenacity (cN / tex)**		**Warp way breaking elongation (%)**		**Warp way bending length (cm)**		**Surface color strength and color difference**			
							Jute		**Cotton**	
	(Jute)	**(Cotton)**	**(Jute)**	**(Cotton)**	**(Jute)**	**(Cotton)**	**K/S Value at λ_{max}**	**dE**	**K/S Value at λ_{max}**	**dE**
Control bleached fabric	6.09	5.41	3.47	5.36	4.2	2.1	0.80	–	0.01	–
5% myrobolan +5% $Al_2(SO_4)_3$	5.02	5.15	5.57	5.76	4.1	2.2	1.61	2.54	0.13	9.87
10% myrobolan +10% $Al_2(SO_4)_3$	4.62	4.79	5.57	6.56	4.1	2.2	2.23	2.87	0.27	10.04
15% myrobolan + 15% $Al_2(SO_4)_3$	4.31	4.05	5.56	7.89	4.1	2.3	2.41	2.99	0.37	11.27
20% myrobolan + 20% $Al_2(SO_4)_3$	3.94	3.40	5.58	8.57	4.1	2.4	2.64	3.55	0.57	11.55
30% myrobolan + 30% $Al_2(SO_4)_3$	3.16	3.27	5.67	8.60	4.2	2.4	2.88	3.87	0.60	11.97
40% myrobolan + 40% $Al_2(SO_4)_3$	2.73	3.15	5.80	8.87	4.3	2.5	2.87	4.27	0.78	12.07

5% myrobolan + 5%$FeSO_4$	4.01	5.18	5.09	5.18	4.2	2.2	4.63	5.97	1.05	12.97
10% myrobolan + 10%$FeSO_4$	3.75	4.99	5.18	5.54	4.2	2.2	4.90	6.87	1.45	13.04
15% myrobolan + 15%$FeSO_4$	3.29	4.13	5.69	5.65	4.6	2.4	8.86	7.21	1.58	13.29
20% myrobolan + 20%$FeSO_4$	2.70	4.08	4.10	5.98	4.5	2.6	8.67	8.47	1.72	14.28
30% myrobolan + 30%$FeSO_4$	2.36	3.98	4.55	6.51	4.5	2.6	8.94	8.97	2.20	15.47
40% myrobolan + 40%$FeSO_4$	1.79	3.74	4.80	6.91	4.6	2.7	8.97	9.54	2.47	16.97
5% myrobolan + 5% $KAl(S0_4)_2$	3.59	4.50	5.39	4.31	4.1	2.3	0.99	3.27	0.45	6.54
10% myrobolan + 10% $KAl(S0_4)_2$	3.30	4.26	5.50	4.55	4.3	2.4	1.70	3.48	0.50	8.69
15% myrobolan + 15% $KAl(S0_4)_2$	3.84	4.06	5.64	4.75	4.3	2.6	2.24	3.89	0.56	9.87
20% myrobolan + 20% $KAl(S0_4)_2$	2.71	3.89	5.79	4.92	4.5	2.8	2.60	4.34	0.64	10.61

(*Continued*)

Table 11.7 Cont.

Mordanting	Warp way tenacity (cN / tex)		Warp way breaking elongation (%)		Warp way bending length (cm)		Surface color strength and color difference			
							Jute		Cotton	
	(Jute)	(Cotton)	(Jute)	(Cotton)	(Jute)	(Cotton)	K/S Value at λ_{max}	dE	K/S Value at λ_{max}	dE
10% myrobolan + 10% $SnCl_2$	3.20	4.08	4.01	5.04	4.4	2.4	1.54	3.43	0.03	7.01
15% myrobolan + 15% $SnCl_2$	3.04	3.32	4.39	4.86	4.6	2.6	1.89	3.54	0.04	7.21
20% myrobolan + 20% $SnCl_2$	2.79	3.02	4.69	4.48	4.8	2.8	1.98	3.63	0.06	7.39
5% myrobolan + 5% EDTA	5.27	4.71	5.61	6.98	4.2	2.1	0.94	2.01	0.02	5.77
10% myrobolan + 10% EDTA	4.80	4.44	5.97	7.65	4.2	2.2	1.10	2.09	0.03	5.87
15% myrobolan + 15% EDTA	4.52	4.21	6.21	8.54	4.3	2.3	1.15	2.21	0.04	6.01
20% myrobolan + 20% EDTA	4.30	4.03	6.41	9.77	4.3	2.3	1.50	2.34	0.05	6.11

compared to when it is double mordanted with stannous chloride and harda. It is interesting to note that harda being also a natural light yellow mordantable dye, it shows a steady increase in K/S value as well as show gradually increased color difference values with application increased percentage of harda on both bleached jute and cotton fabrics. In between jute and cotton, the increase in color difference is much higher for cotton than that observed for jute.

Among all the mordants used, the increase in K/S value and color differences are found to be highest for application of $FeSO_4$ as mordant, due to the inherent color of $FeSO_4$ salt as it is a salt of transition metal, that too is more predominate on cotton than on jute and shows an increasing trend with increase in percentage application of $FeSO_4$ on both the types of fabrics. The increase in color difference values after single mordanting (without dyeing) with selective mordants on both jute and cotton fabrics are in the following order-

For cotton: $FeSO_4$ >> Harda (Myrobolan) > $KAl(SO_4)_2$ > EDTA > $SnCl_2$ > $Al_2(SO_4)_3$

For jute: $FeSO_4$ >> $SnCl_2$ > EDTA > $KAl(SO_4)_2$ > $Al_2(SO_4)_3$ > Harda(myrobolan)

While, in case of double mordanting (without dyeing) with selected double mordanting systems, the increase in color difference values are in the following order-

For cotton:

Harda + $FeSO_4$ >> Harda + $Al_2(SO_4)_3$ > Harda + $KAl(SO_4)_2$ > Harda+$SnCl_2$ > Harda + EDTA

For jute:

Harda + $FeSO_4$ >> Harda + $KAl(SO_4)_2$ > Harda+$SnCl_2$ >> Harda + $Al_2(SO_4)_3$ > Harda + EDTA

This increase in K/S value and color difference value to a different extent after selective mordanting, may be due to changes in scattering for chemical interactions between the fibers and harda or salts used as mordant and additional sulphate or ferrous sulphate either singly or double mordanted with harda and aluminium sulphate or with harda and ferrous sulphate applied in sequence, they show much lower loss in fabric strength than that is observed for use of stannous chloride either in single mordanting and double mordanting. In general, on treatment with all the selective mordants, there is some loss in warp way fabric tenacity along with some increase in warp way breaking elongation of bleached jute and cotton fabrics, irrespective of the percentage of application of the corresponding mordants. However, with increase in application percentage of myrobolan or other chemical mordants singly and also in case of double mordanting with harda as first mordant and any one chemical mordants (like aluminium sulphate, ferrous sulphate, potassium aluminium sulphate, stannous chloride and EDTA) as second mordant, the strength loss increases noticeably. The strength loss is found to be minimum for use of EDTA as mordant on both jute and cotton fabrics, irrespective of its percentage of application and irrespective of its application either singly or in case of double mordanting with harda and EDTA applied in sequence on both bleached jute and cotton fabrics. The different degree of loss in fabric strength and associated low increase in breaking extension owing to mordanting treatment may be viewed as an effect of limited acidic degradation and disorientation caused in the polymeric chains of the fiber substrate by the tannic acid component of myrobolan and acid generated in aqueous solution of most of the other chemical mordants used except EDTA. For mordanting with $FeSO_4$ and $Al_2(SO_4)_3$ singly, the bending length value is found to increase and for mordanting with EDTA singly the same is found to reduce to a small extent and it remains almost unaltered in all other cases including the cases of double mordanting.

This increase in K/S value and colour difference value to a different extent after selective mordanting, may be due to changes in scattering for chemical interactions between the fibers and harda or salts used as mordant and additional inherent color input from the corresponding mordants. In case of double mordanting, in case of complimentary or opposite colour interactions, the dE values reduce (as in the case for Harda plus $FeSO_4$ double mordanting on bluish-white cotton) and in case of supportive and additive color interaction the dE value increases (in case of Harda + $FeSO_4$ double mordanting on creamish-yellow jute). Bleached jute and cotton fabrics differently mordanted with varying concentration of mordants have been subsequently dyed with varying concentrations of extracted dye liquor from jackfruit wood (JFW) following a prefixed normal dyeing condition as described earlier in item 3.2.8. All the dyed fabric samples have been subjected to assessment of its surface color strength (K/S value), brightness index and total color difference (dE) and color fastness behavior to washing, rubbing and exposure to light and the corresponding results are shown in Table 11.8 (for single mordanted fabric) and Table 11.9 (for double mordanted fabrics) for both jute and cotton fabrics.

Table 11.8 Brightness index, surface color strength and color differences at different and color fastness of dyed jute and cotton fabrics using jackfruit wood extract after single mordanting with selective mordants.

Mordant conc. %	Fabric	Dye* conc. (JFW) %	Shade obtained	Surface color strength and color difference		B.I	Color fastness to				
				K/S value at lmax	dE		Wash		Light	Rubbing	
							LOD	ST		Dry	Wet
20%myrobolan + 20% $Al_2(SO_4)_3$	J	nil	–	2.54	3.55	23.56	–	–	–	–	–
20%myrobolan + 20% $Al_2(SO_4)_3$ + JFW	J	20%	Greenish yellow	3.35	5.65	19.77	4	5	3	5	5
20%myrobolan + 20% $Al_2(SO_4)_3$	C	nil	–	0.08	11.5	49.71	–	–	–	–	–
20%myrobolan + 20% $Al_2(SO_4)_3$ + JFW	C	20%	Light green	0.55	7.45	49.66	5	4–5	3	5	4–5
20% myrobolan + 20%$FeSO_4$	J	nil	–	8.67	8.41	5.38	–	–	–	–	–
20% myrobolan + $FeSO_4$ +JFW	J	20%	Blackish brown	12.21	35.2	3.79	3	5	3	4–5	3–4

(*Continued*)

Table 11.8 Cont.

				Surface color strength and color difference		B.I	Color fastness to				
							Wash		Light	Rubbing	
Mordant conc. %	**Fabric**	**Dye* conc. (JFW) %**	**Shade obtained**	**K/S value at lmax**	**dE**		**LOD**	**ST**		**Dry**	**Wet**
20% myrobolan + 20% $KAl(SO_4)_2$	J	nil	–	2.6	4.34	24.17	–	–	–	–	–
20% myrobolan + 20% $KAl(SO_4)_2$ + 20% JFW	J	20%	Greenish brown	3.37	5.76	19.94	4	5	3	5	5
20% myrobolan + 20% $KAl(SO_4)_2$	C	nil	–	0.1	10.6	48.7	–	–	–	–	–
20% myrobolan + 20% $KAl(SO_4)_2$ + 20% JFW	C	20%	Light yellow	1.05	7.72	36.2	5	4–5	3	5	4–5
20% myrobolan + 20% $SnCl_2$	J	nil	–	2.51	3.63	25.57	–	–	–	–	–
20% $SnCl_2$ + 20% myrobolan + JFW	J	20%	Light ocher yellow	3.13	5.93	22.29	5	4–5	1	4–5	4–5

20% myrobolan + 20% $SnCl_2$	C	nil	–	0.06	7.39	58.88	–	–	–	–	–
20% SnCl2 + 20% myrobolan + JFW	C	20%	Light yellow	0.55	10.3	50.62	5	4–5	3	5	4–5
20% myrobolan + 20% EDTA	J	nil	–	1.5	2.34	27.71	–	–	–	–	–
20% EDTA + 20% myrobolan + JFW	J	20%	Cream	1.36	0.33	29.11	4	5	2	5	5
20% myrobolan + 20% EDTA	C	nil	–	0.05	6.11	65.65	–	–	–	–	–
20% EDTA + 20% myrobolan + JFW	C	20%	Cream	0.18	8.47	62.61	5	4–5	3	5	4–5

J = jute, C = cotton, JFW = Jackfruit wood color extract, BI = Brightness Index (ISO-2470).

*Exact % of color component in the natural source in unknown and hence, to control shade %, the dye conc. % is expressed on the basis of % of dry solid jackfruit wood taken for aqueous extraction of color.

Table 11.9 Brightness index, surface color strength and color differences and color fastness of dyed jute and cotton fabrics using jackfruit wood extract after sequential double mordanting with selective mordants.

Mordant conc. %	Fabric	Dye* conc. (JFW) %	Shade obtained	Surface color strength and color difference		B.I	Color fastness to				
				K/S value at λ_{max}	dE		Wash		Light	Rubbing	
							LOD	ST		Dry	Wet
20%myrobolan + 20 % $Al_2(SO_4)_3$	J	nil	–	2.54	3.55	23.56	–	–	–	–	–
20%myrobolan + 20 % $Al_2(SO_4)_3$ + JFW	J	20%	Greenish yellow	3.35	5.65	19.77	4	5	3	5	5
20%myrobolan + 20 % $Al_2(SO_4)_3$	C	nil	–	0.08	11.5	49.71	–	–	–	–	–
20%myrobolan + 20 % $Al_2(SO_4)_3$ + JFW	C	20%	Light green	0.55	7.45	49.66	5	4–5	3	5	4–5
20% myrobolan + 20 %$FeSO_4$	J	nil	–	8.67	8.41	5.38	–	–	–	–	–
20% myrobolan + $FeSO_4$ +JFW	J	20%	Blackish brown	12.21	35.2	3.79	3	5	3	4–5	3–4

20 % myrobolan + 20 % $KAl(S0_4)_2$	J	nil	–	2.60	4.34	24.17	–	–	–	–	–
20% myrobolan + 20% $KAl(S0_4)_2$ + 20 % JFW	J	20%	Greenish brown	3.37	5.76	19.94	4	5	3	5	5
20 % myrobolan + 20 % $KAl(S0_4)_2$	C	nil	–	0.10	10.6	48.70	–	–	–	–	–
20% myrobolan + 20% $KAl(S0_4)_2$ + 20 % JFW	C	20%	Light yellow	1.05	7.72	36.20	5	4–5	3	5	4–5
20 % myrobolan + 20 % $SnCl_2$	J	nil	–	2.51	3.63	25.57	–	–	–	–	–
20% $SnCl_2$ + 20% myrobolan + JFW	J	20%	Light ocher yellow	3.13	5.93	22.29	5	4–5	1	4–5	4–5
20 % myrobolan + 20 % $SnCl_2$	C	nil	–	0.06	7.39	58.88	–	–	–	–	–
20% $SnCl_2$ + 20% myrobolan + JFW	C	20%	Light yellow	0.55	10.3	50.62	5	4–5	3	5	4–5
20 % myrobolan + 20 % EDTA	J	nil	–	1.50	2.34	27.71	–	–	–	–	–
20% EDTA + 20% myrobolan + JFW	J	20%	Cream	1.36	0.33	29.11	4	5	2	5	5

(Continued)

Table 11.9 Cont.

Mordant conc. %	Fabric	Dye* conc. (JFW) %	Shade obtained	Surface color strength and color difference		B.I	Color fastness to				
				K/S value at l_{max}	dE		Wash		Light	Rubbing	
							LOD	ST		Dry	Wet
20 % myrobolan + 20 % EDTA	C	nil	–	0.05	6.11	65.65	–	–	–	–	–
20% EDTA + 20% myrobolan + JFW	C	20%	Cream	0.18	8.47	62.61	5	4–5	3	5	4–5

DE = Color difference, BI = Brightness Index, LOD = loss of Depth of Shade, ST = Staining on cotton, JFW = Jackfruit wood color extract.

*Exact % of color component in the natural source in unknown and hence, to control shade %, percentage of dry solid jackfruit wood taken for extraction of color is considered as the basis for dye concentration.

Relevant data in Table 11.8 and Table 11.9 for differently pre-dominated jute and cotton fabrics indicate that among differently mordanted bleached jute subsequently dyed with 20% aqueous extract of JFW in each case, the sequential double mordanting with 20% myrobolan and 20% ferrous sulphate on bleached jute fabric render the fabric relatively higher K/S value (around 12.21, Table 11.9) than those shown by other mordanting at comparable dose level. Use of 20% harda and aluminium sulphate mordanting technique followed by further dyeing with comparable dose of JFW color (20% JFW), the K/S value obtained on bleached jute fabric is around 3.35 (Table 11.9) and is considered as next good performer. In all the cases of dyeing with different percentage of aqueous extract of JFW using different mordants, the brightness index values are found to be reduced to a noticeable extent from the corresponding value obtained after respective mordanting, (Table 11.8 and Table 11.9). When the jute fabric is double mordanted with myrobolan and ferrous sulphate in sequence, it can be observed that there is a decrease in the brightness index with increase in K/S value. Hence, considering the dyeing results, the sequential mordanting system using 20% myrobolan as 1st mordant and 20% aluminium sulphate as 2nd mordant, as well as 20% myrobolan as 1st mordant and 20% ferrous sulphate as 2nd mordant applied in sequence before dyeing are found to be more prospective, rendering a higher degree of increase in surface color strength and these two systems of mordanting have been chosen for further study of dyeing process variables for both jute and cotton fabrics. However, the use of ferrous sulphate in any case always renders both jute and cotton fabrics a deep brownish/grey color owing to the inherent color of this transition metal salt anchored to the corresponding fibers, besides the improvement in K/S value due to the natural dye component. The different color/shade developed by different combinations of selective fiber-mordant-natural-dye systems are shown in Plate 1 and Plate 2 for this part of the work which reveals the variation in shades for use of different mordant system on bleached jute and cotton fabrics.

11.6.3 Effect of Dyeing Process Variables for Optimizing the Dyeing Conditions

Relevant data given in Table 11.10 and the plots shown in Figure 11.6(a–g) indirectly or directly show the effects of the dyeing process variables such as dyeing time, dyeing temperature, material-to-liquor ratio (MLR), pH (concentration of acid/ alkali added), concentrations of mordants, concentrations of dye extracted from natural dye (on the basis of % of solid JFW) and concentrations of common salt respectively on the surface color

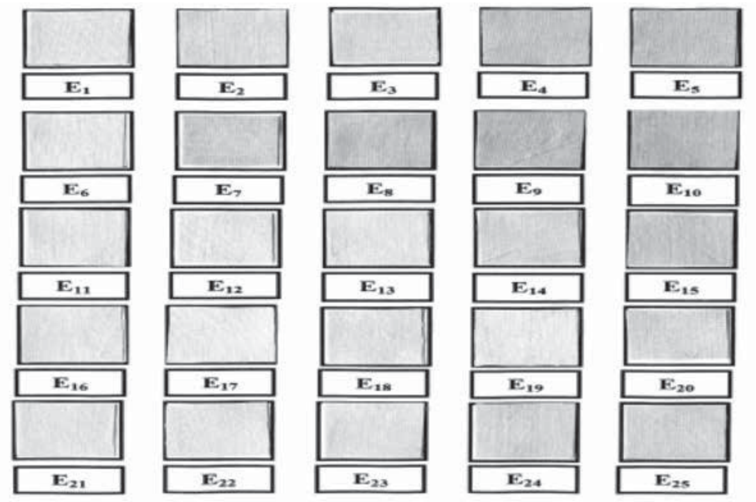

Plate-1 Natural dyed Cotton Fabrics with Mixture of Natural dyes.

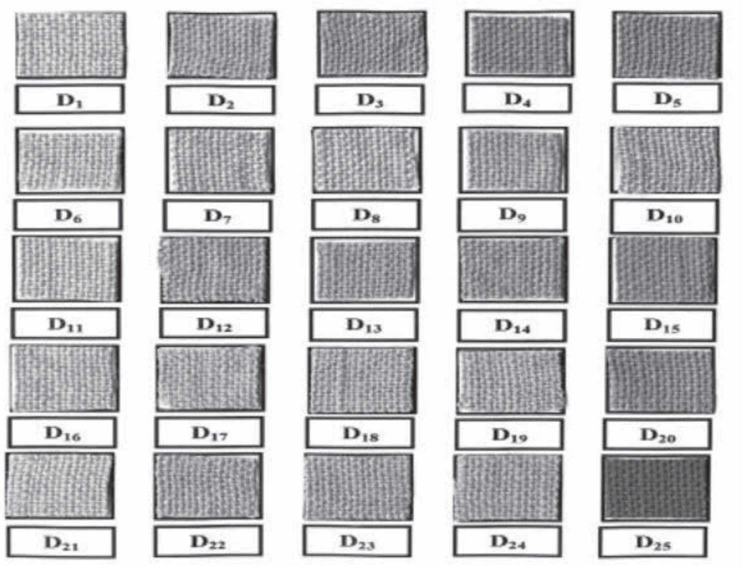

Plate-2 Natural dyed Jute Fabrics with Mixture of Natural dyes.

strength (K/S values) for dyeing of bleached jute and cotton fabrics with JFW extract after differently mordanting. The selective fiber-mordanting systems used for the study of dyeing process variables are: (a) double pre-mordanting with 20% harda (as 1st mordant) and 20% aluminium sulphate

Table 11.10 Data showing the surface color strength of the process variables for bleached jute and cotton fabrics dyed with jackfruit wood and double pre-mordanted with harda and $Al_2(SO_4)_3$ and harda and $FeSO_4$.

Variable dyeing parameters time (Min)	**Surface color strength (K/S values at l_{max})**			
	For harda + (Al_2SO_4)		**For harda + ($FeSO_4$)**	
	For jute	**For cotton**	**For jute**	**For cotton**
15	2.21	0.54	10.75	2.11
30	3.44	0.77	11.62	3.52
60	3.67	0.66	11.65	4.11
90	3.69	0.84	12.72	4.26
120	3.61	0.75	11.83	3.62
Temperature (°C)				
50	3.65	0.77	8.59	2.52
60	3.66	0.76	9.51	2.74
70	3.72	0.79	11.14	2.82
80	3.33	0.64	12.24	3.40
90	3.28	0.66	12.45	3.54
100	3.34	0.63	12.84	3.31
SALT (g/l)				
5	3.37	0.78	11.34	3.33
10	3.24	0.74	11.44	3.19
15	3.20	0.66	11.86	3.52
20	3.16	0.79	12.08	3.27
Mordant conc. (%)				
10	3.26	0.55	8.63	1.71
20	3.83	0.76	12.21	3.41
30	3.93	0.70	15.08	3.99
40	4.16	0.81	14.66	4.33

(*Continued*)

Table 11.10 Cont.

Variable dyeing parameters time (Min)	Surface color strength (K/S values at l_{max})			
	For harda + (Al_2SO_4)		For harda + ($FeSO_4$)	
	For jute	For cotton	For jute	For cotton
20	3.33	0.81	11.98	3.71
30	3.94	0.84	11.98	4.04
40	4.14	1.01	12.86	4.42
PH				
3	3.05	0.65	10.54	4.04
4	3.78	0.75	11.67	4.36
5	3.55	0.64	11.82	3.75
6	3.33	0.57	11.92	3.85
8	2.98	0.63	10.85	3.78
9	3.14	0.62	11.53	3.62
10	3.29	0.80	13.10	3.88
11	3.99	0.61	13.06	4.22
12	3.78	0.59	12.50	4.05
MLR				
1:10	2.91	0.59	9.81	2.5
1:20	3.60	0.65	10.52	3.3
1:30	3.82	0.66	13.01	3.5
1:40	3.71	0.63	11.25	3.4
1:50	3.51	0.58	11.10	3.0

(as second mordant) on jute; (b) double pre-mordanting with 20% harda (as 1st mordant) and then 20% ferrous sulphate (as 2nd mordant) on jute; (a′) double pre-mordanting with 20% harda (as 1st mordant) and 20% aluminiumsulphate (as 2nd mordant) on cotton and (b′) double pre-mordanting with 20% harda (as 1st mordant) and 20% ferrous sulphate (as 2nd mordant) on cotton.

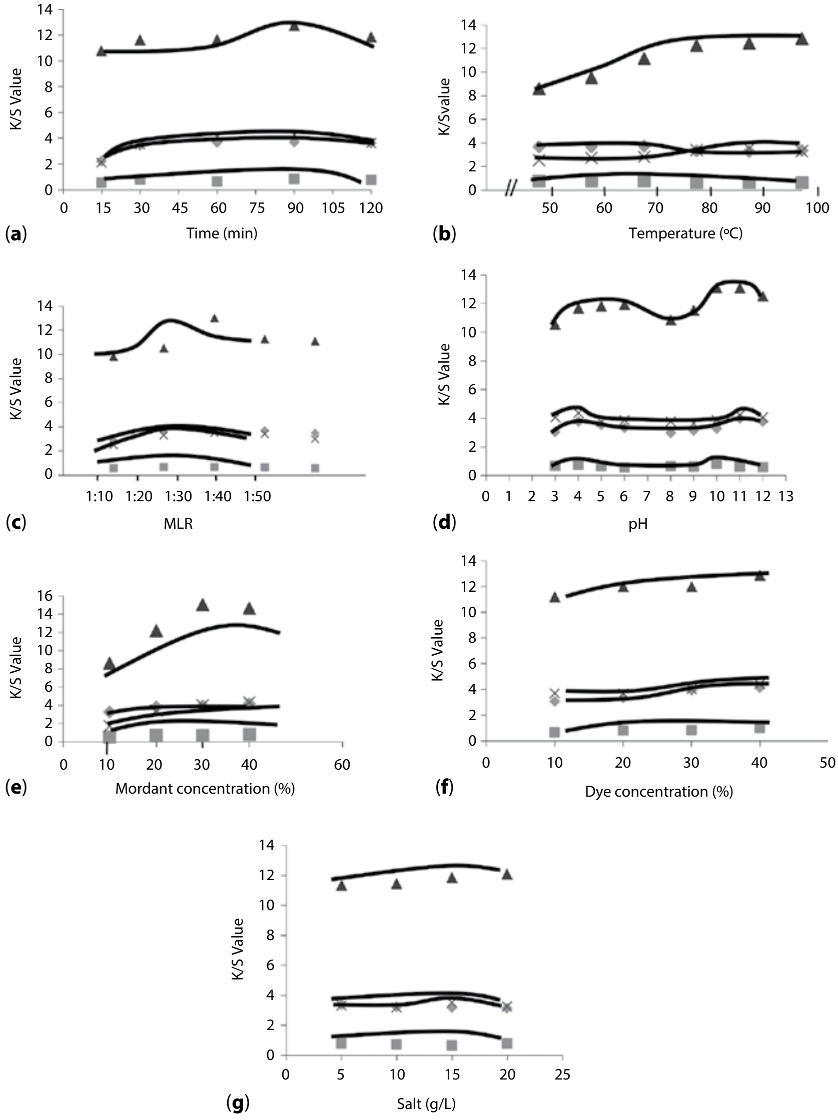

Figure 11.6 (a-g): Effects of dyeing process variables on color strength of jute and cotton fabrics dyed with jackfruit wood extract after double pre-mordanting with harda and aluminium sulphate and harda and ferrous sulphate.
Diamond: Jute—Harda + $Al_2(SO_4)_3$
Triangle: Jute—Harda + $FeSO_4$
Square: Cotton—Harda + $Al_2(SO_4)_3$
Cross: Cotton—Harda + $FeSO_4$

Relevant data given in Table 11.10 and plots shown in Figure 11.6 (a), indicate that all other variables remaining prefixed and unaltered, with increase in time of dyeing (15–120 minutes), K/S Value (surface color strength) slowly increases up to 90 minutes and then either levels off or slowly decreases after 90 minutes for all the combinations of fiber-mordanting systems (a), (b), (a′), and (b′). Among these mordanting systems, the increase in surface color strength is much higher for fiber- mordanting system (b) For other fiber-mordanting systems (a), (a′), and (b′), the effect of increase in dyeing time is much subdued, however showing the optimum dyeing time at 90 min. Rate of dyeing for fiber-mordanting system (b), however, is found to be sharp for 60–90 minutes period of dyeing. This higher rate of dyeing above 60 min and up to 90 min in case of fiber-mordanting system (b) may be due to possible reduction in activation energy required for absorption and fixation of dyes on fiber surface by jute-hemicellu-COO$^-$…Fe-ion complex formation, which is not possible in cotton.

Keeping other dyeing variables constant, with increase in dyeing temperatures (50–100 °C), the data shown in Table 11.10 and plots shown in Figure 11.6 (b), show that the surface color strength increases measurably for increase in dyeing temperature from 50–80 °C for double fiber-mordanting systems (b) and (b′) and then almost levels off. However, the rate of dyeing and rate of increase of K/S value are found to be much higher for fiber-mordanting system (b) than fiber-mordanting system (b′). While in case of fiber-mordanting system (a) and (a′), K/S value increases slowly at the temperature range of 50–70 °C and then drops down. Increase in time or temperature of dyeing inevitably supplies more energy usually facilitating higher rate of dye sorption for all the fiber-mordanting systems in general up to a certain limit of the dyeing temperature, before desorption starts. However, in case of application of ferrous sulphate as 2nd mordant on initially harda mordanted jute substrate, the effect is much predominant and higher than those obtained by other mordanting systems applied on both jute and cotton substrate, due to possible jute-hemicellu-COO$^-$…. Fe-ioncomplexing in case of fiber-mordanting system (b), as stated earlier.

For variation of MLR from 1:10 to 1:50, Table 11.10 and Figure 11.6 (c), initially the K/S value sharply increases up to MLR of 1:30 and then it gradually drops down for further increase of MLR for both the fiber-mordanting systems (b) and (b′); while the effect is much subdued and marginal in cases of fiber-mordanting systems (a) and (a′). However, for all these fiber-mordants systems, the optimum MLR is found to be 1:30.

Data in Table 11.10 and plots in Figure 11.6 (d), interestingly show varying degrees of crests and troughs in the trends of K/S value for variation of pH values between 3–12 for the said dyeing. However, for fiber-mordanting system (b) applying harda and ferrous sulphate in sequence on bleached jute fabric shows two relatively broader crests and one trough showing higher K/S value at pH 5.0 as well as at pH 11.0, where, among these two pH values, the highest K/S value being obtained at pH 11.0. For other fiber-mordanting systems (a), (a′), and (b′), the K/S values are found to be much lower than that obtained for fiber-mordanting system (b). But all the three other fiber-mordanting systems (a), (a′), and (b′) show corresponding maximum K/S value either at pH-4.0 or at pH-11.0 and these corresponding K/S values either at pH-4.0 and pH-11.0 for respective fiber-mordanting systems are also much closer. However, considering the surface color strength as well as color fastness behavior (corresponding results given in Table 11.11) together, pH-11.0 may be taken as optimum for all the fiber-mordanting systems studied in this part, as the color fastness properties are found to be relatively better at pH-11.0 than that obtained at pH 4.0–5.0, as shown in Table 11.11.

Data in Table 11.10 and plots in Figure 11.6 (e) show a slow increase in K/S value with increase in mordant concentrations up to 20% dose of mordants before showing the leveling off trend for fiber-mordanting systems (a) and (a′); while there is increase in K/S value for increase of mordant concentration up to 30% dosage for fiber-mordanting system (b′) before leveling off. The increase in K/S value is much sharper and predominant in case of fiber-mordanting system (b) upto 30% mordant concentration, above which it marginally drops down. Thus, for all the fiber-mordanting systems studied, the optimum mordant apparently concentration may be considered to be around 20–30%. However, there is noticeable loss in tensile strength after mordanting bleached jute and cotton fabrics with more than 20% dosages of the said mordants. Hence, use of more than 20% fiber-mordant concentration for mordant systems (a), (a′), and (b′) is not recommended. But despite some strength loss, use of 30% mordant concentration may be allowed for obtaining much higher K/S value for fiber-mordanting system (b), as the increase in K/S value for this double mordanted jute fabrics using 30% Harda and 30% $FeSO_{4,}$ is found to be exceptionally higher. So, for fiber-mordanting system (b), the optimum concentration of mordant should be within 20–30%.

Data in Table 11.10 and plots in Figure 11.6 (f) show slow increase in K/S values with increase in concentrations of extracted dye liquor from JFW up to 30% (on the basis of % solid JFW), above which it almost levels off reaching almost the saturation level. However, the K/S value obtained is always found to be much higher for fiber-mordanting system (b) than that obtained for other fiber-mordanting systems (a), (a′), and (b′). The higher dye uptake in case of fiber-mordanting system (b) in almost all the case study of the

Table 11.11 Effects of pH of the dye liquor on color fastness properties for jute and cotton fabrics for two different mordanting systems for dyeing with Jackfruit wood colorants.

Pre-mordanting treatment	pH of dye liquor	Color fastness to									
		Washing				Light		Rubbing			
		Jute		Cotton		Jute	Cotton	Jute		Cotton	
		LOD	ST	LOD	ST			Dry	Wet	Dry	Wet
20% myrobolan + 20% $Al_2(SO_4)_3$											
	3.0	5	4	4	5	2	3	3–4	3	4	3–4
	4.0	5	4	4	5	3	3	3–4	3	4	3–4
	5.0	4	4–5	4	5	3	3	3–4	3	4	3–4
	6.0	4	4–5	5	5	3	3	3–4	3	4	3–4
	8.0	4	4–5	5	5	4	4	4	3–4	4–5	4
	9.0	5	4	4	5	4	4	4	3–4	4–5	4
	10.0	4	5	4	5	4	4	4	3–4	4–5	4
	11.0	4	4–5	4	4–5	4	4	4	3–4	4–5	4
	12.0	4	4–5	4	5	4	5	4	3–4	4–5	4

	5.0	3	5	1	4–5	1	1	4	3–4	3–4	3
	6.0	3	4–5	1	4–5	1	1	4	3–4	3–4	3
	8.0	3	4–5	1	4–5	2	2	4	3–4	4	3–4
	9.0	4	4–5	1	4–5	2	2	4	3–4	4	3–4
	10.0	4	5	1	4–5	2	2	4	3–4	4	3–4
	11.0	4	4–5	1	4	2	2	4	3–4	4	3–4
	12.0	4	4–5	1	4	2	2	4	3–4	4	3–4

LOD = loss of Depth of Shade, ST = Staining on cotton.

dyeing process variables indicate and confirm that there is more attraction/substantivity of color component of JFW towards such mordanted jute causing jute-hemicellu-COO$^-$….Fe-ion complex formation.

Data in Table 11.10 and plots in Figure 11.6 (g) indicate that the optimum concentration of common salt for all the fiber-mordanting systems (a), (b), (a′), and (b′) is 15 gpl, as the K/S values are found to be maximum for use of this concentration of salt in the dye bath in all the cases. However, the observed much lower K/S value in cases of fiber-mordanting systems (a) and (a′) applying harda and aluminium sulphate in sequence on both bleached jute and cotton substrate is due to suppression of the action of harda by blocking it functional coordinating groups by aluminium metal ion [from $Al_2(SO_4)_3$] to a certain degree. Observed highest K/S value in case of fiber-mordanting system (b) applying harda and $FeSO_4$ in sequence on bleached jute substrate, the synergistic intensification of color yield is assumed to be due to higher absorption and fixation of the dye from JFW extract by the complex formed between the Fe-salts and the –COO$^-$ group of jute hemi-cellulose facilitating higher color strength, which is not possible in cotton due to absence of –COO$^-$ group. The observed slow increase in K/S value in cotton treated with same mordants is only due to the additive color yield for the additional incorporation of the inherent color of $FeSO_4$ itself. The addition of an electrolyte (common salt) to the dyeing liquor in the dye bath in case of dyeing with a mordant able anionic dye like JFW extract expectedly increase the exhaustion of the dye on the cellulosic or ligno-cellulosic fibers. They dissociate completely in the aqueous dye liquor at different temperature of dyeing and increase the force of repulsion between the dye molecules and water so that the dye molecule are more attracted to the cellulosic or ligno-cellulosic fibers. But higher amount of salt/electrolyte above a certain limit causes retardation effect in the dye adsorption.

11.7 Study of Dyeing Kinetics for Dyeing Jack Fruit Wood on Cotton and Jute Fabrics

11.7.1 Rate of Dyeing

The dye exhaustion curves indicating the rate of dyeing (Dye exhausted to the fiber determined by UV-absorbance spectrophotometry on jute and cotton respectively vs. dyeing time (i.e., D_f vs. t_d) for bleached jute and cotton fabrics dyed with aqueous extract of JFW using above said four double pre-mordanting systems (a) and (a′) on jute and cotton respectively applying

20% harda and 20% $Al_2(SO_4)_3$ applied in sequence and pre-mordanting systems (b) and (b′) on jute and cotton respectively applying 20% harda and 20% $FeSO_4$ in sequence followed by subsequent dyeing under optimized conditions of dyeing is shown in Table 11.12 and corresponding plots in Figure 11.7. It is observed from Figure 11.7 that with increase in dyeing time, the dye uptake (D_f) increases steadily up to 90 min dyeing time and then almost levels off in between 90–120 min. Also curves for dye uptake in terms of K/S value vs. dyeing time as well as K/S value vs. dyeing temperatures, support the present observation showing a similar trend exhibiting the maximum surface color strength (K/S value) at about 80 °C and for 90 min of dyeing time for mordant system (b) and (b′). The dye uptake at different temperatures is dependent on heat of dyeing. Heat of dyeing (ΔH) for each of the present case of dyeing of bleached jute and cotton fabrics with JFW extract has been found to be positive (Table 11.13 and Table 11.14), indicating that the dyeing in this case for both jute and cotton is an endothermic process. So, gradual raising of the dyeing temperature will lead to higher dye affinity up to a certain temperature limit, above which the dye uptake will gradually reduce or levels off and less dye will be absorbed above a certain temperature or at equilibrium and practically there is a decrease in dye affinity ($-\Delta\mu$) and rate of dyeing above 90 °C i.e., in the range of 90–120 °C in each case. In case of double pre-mordanting systems (a) and (a′) for bleached jute and cotton fabrics pre-mordanted using harda and $Al_2(SO_4)_3$, higher dissociation of $Al_2(SO_4)_3$ at higher temperature of dyeing or for higher dyeing time, expectedly may increase the retardation effects in rate of dyeing and hence, practically the dyeing rate is found to be measurably lower in each case of pre-mordanting systems (a) and (a′) than the same for pre-mordanting systems (b) and (b′) for jute and cotton respectively.

11.7.2 Dye Affinity

The chemical affinity ($-\Delta\mu$) or dye-affinity values for the colorants (dye) from JFW extract towards bleached jute and cotton fabrics double pre-mordanted with different fiber-mordanting systems (a), (a′), (b) and (b′), subsequently dyed at pH 11.0 following optimized conditions of dyeing at two different dyeing temperatures (60 °C and 90 °C) is shown in Table 11.13 and Table 11.14. It is observed from the relevant data that there is a low but measurable increase in chemical affinity or dye affinity values for increase in dyeing temperature from 60 to 90 °C for both bleached jute and cotton fabrics for different fiber-mordant systems (a), (a′), (b), and (b′). However, there are little or almost no significant changes in dye-affinity for dyeing either for higher duration or for using higher dye concentrations. The

Table 11.12 Data showing dye exhaustion to the fiber for different dyeing time indicating rate of dyeing for application of jackfruit wood extract as natural dye on bleached jute and cotton fabrics using different double pre-mordanting systems (a), (a′),(b) & (b′).

Time of dyeing (minutes)	$[D]_f$, g/Kg, for jute harda+$Al_2(SO_4)_3$	$[D]_f$,g/Kg, for jute) harda + $FeSO_4$	$[D]_f$, g/Kg, for cotton harda + $Al(SO_4)_3$	$[D]_f$,g/Kg, for cotton harda + $FeSO_4$
15	4.87	6.01	2.01	2.5
30	6.71	7.25	3.5	2.89
60	7.35	7.81	4.45	4.39
90	8.01	8.21	4.8	5.01
120	8.03	8.22	5.53	5.3

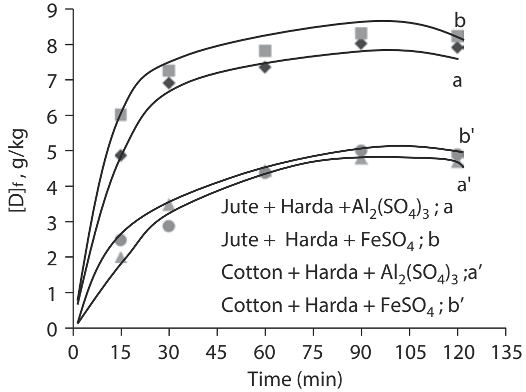

Figure 11.7 Dye exhaustion curves for different dyeing time.

measurable increase in chemical affinity/dye affinity in the present cases, for increase of dyeing temperature for the differently pre-mordanted cellulosic and ligno-cellulosic fibers can be viewed as an effect of the additional input of thermal energy to increase the rate of dyeing in this endothermic dyeing process (Δ H being positive in each case).

11.7.3 Dyeing Absorption Isotherm

The absorption isotherms [i.e., the plots of the amount of dye exhausted to the fiber (D_f) and concurrent amount of dye available in the dyeing solution (D_s) for absorption] for dyeing at optimum dyeing temperature (at 90 °C) for bleached jute and cotton fabrics after pre-mordanting with different fiber-mordant systems (a), (a′), (b) and (b′) respectively are shown in Figure 11.8 (a and a′) and Figure 11.8 (b and b′). The best fit absorption isotherms in the present cases for different fiber-mordanting systems (a), (a′), and (b′) are found to be linear indicating the partition mechanism of dyeing being more alike to Nernst Absorption Isotherm. This type of linear Nernst absorption isotherm is observed generally for dyeing of non-polar disperse dyes to hydrophobic polyester fibers. For dyeing of jute fabric with red sandal wood extract, this was found by Samanta *et al.* as well as the same was found for dyeing of wool with logwood and Brazil wood as natural dyes [12] and as for dyeing of wool and nylon with red sandal wood extract [13]. Hence, the mechanism of dye absorption in this case is though found to be like absorption of disperse dyes in polyester but it may be presumed that in the present case, jute and cotton being hygroscopic fibers, the absorption of non-polar dye through hydrophobic interaction is of marginal importance. Hence the major dye absorption is presumed to

Table 11.13 Experimental values of thermodynamic parameters for dyeing of jute and cotton with Jackfruit wood color extract after double pre-mordanting with 20% harda and 20% $Al_2(SO_4)_3$ applied in sequence [premordanting system (a) & (a′) and (b) and b’].

$[D]_f$ g/Kg		$[D]_s$ g/lts		$-\Delta\mu$ kJ/mol		ΔH kJ/mol	ΔS J/mol/ °K	K Cals ΔG	
at T_1	at T_2	at T_1	at T_2	at T_1	at T_2	$(T_2—T_1)$	at T_2	at (T_1)	at (T_2)
Jute									
4.50	6.25	0.0325	0.01	7.15	9.75	21.71	32.94	−10.94	−11.93
5.50	7.00	0.035	0.015	7.30	9.38	15.78	17.63	−5.85	−6.38
5.75	7.75	0.0425	0.0225	7.12	8.99	13.63	12.78	−4.24	−4.62
6.50	8.50	0.045	0.03	7.20	8.72	9.67	2.61	−0.85	−0.93
6.75	8.75	0.055	0.0375	7.01	8.48	9.30	2.25	−0.73	−0.80
Cotton									
1.25	2.5	0.0625	0.02	5.37	7.57	19.05	31.62	−10.51	−11.45
2.00	3.75	0.06	0.037	5.98	7.32	8.89	4.32	−1.42	−1.55
2.50	4.5	0.072	0.046	5.83	7.28	10.26	8.20	−2.72	−2.87
3.00	5.25	0.087	0.054	6.02	7.27	7.85	1.59	−0.52	−0.56
3.20	6.0	0.097	0.065	5.96	7.21	7.91	1.92	−0.63	−0.69

$[D]_f$ – Conc. of dye in fiber g/kg, $[D]_s$ – Conc. Of dye in solution g/l, – $\Delta\mu$ – Chemical Affinity, ΔH– Heat of dyeing or enthalpy and ΔS – Entropy of dyeing, T_1 = 333 °K(60 °C) and T_2 = 363 °K (90 °C).

Table 11.14 Experimental values of thermodynamic parameters for dyeing of jute and cotton with Jackfruit wood color extract after double pre-mordanting with 20% harda and 20% $FeSO_4$ applied in sequence [premordanting system (b) & (b′)].

$[D]_f$ g/Kg		$[D]_s$ g/lts		-Δμ kJ/mol		ΔH kJ/mol	ΔS J/mol/ °K	K Cals ΔG	
at T_1	at T_2	at T_1	at T_2	at T_1	at T_2	for (T_2-T_1)	at T_2	at (T_1)	at (T_2)
Jute									
3.25	4.50	0.0325	0.015	6.76	8.81	15.99	19.77	–6.56	–7.16
5.00	7.00	0.035	0.017	7.19	9.23	15.45	17.13	–5.68	–6.20
5.75	7.50	0.0425	0.025	7.12	8.81	11.63	7.64	–2.57	–2.80
6.25	7.75	0.050	0.030	7.03	8.61	10.50	5.23	–1.73	–1.88
6.30	8.25	0.069	0.052	6.65	7.98	8.11	0.35	–0.10	–1.18
Cotton									
1.00	3.00	0.036	0.03	5.77	7.30	11.21	10.77	–3.57	–3.89
1.75	3.75	0.055	0.0425	5.93	7.19	8.06	2.47	–0.81	–0.88
2.75	4.50	0.083	0.049	5.98	7.20	7.56	0.99	–0.32	–0.35
3.40	5.10	0.099	0.0541	6.01	7.23	7.53	0.82	–0.26	–0.29
4.80	6.70	0.125	0.063	6.15	7.38	7.50	0.33	–0.10	–0.11

$[D]_f$–Conc. Of dye in fiber g/kg, $[D]_s$ – Conc. Of dye in solution g/l, -Δμ- Chemical Affinity, ΔH- Heat of dyeing or enthalpy and ΔS-Entropy of dyeing, T_1=333 °K(60 °C) and T_2= 363 °K (90 °C).

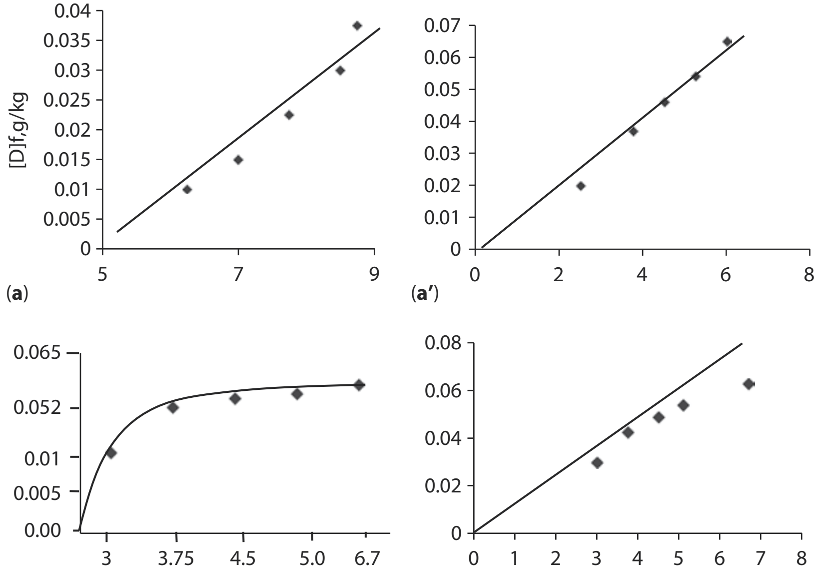

Figure 11.8 (a and a′): Dyeing isotherms for bleached jute fabrics dyed with jackfruit wood extract at 90 °C [Jute: (a) 20% harda + 20% $Al_2(S0_4)_3$; (b)Jute: 20% harda + 20% $FeSO_4$]. (b & b′): Dyeing isotherms for bleached cotton fabrics dyed with jackfruit wood extract at 90 °C [Cotton: (a′) 20% harda + 20% $Al_2(S0_4)_3$ and (b′) Cotton 20% harda +20% $FeSO_4$].

occur through hydrogen bonding interaction in these cases. However, in case of fiber-mordant system (b), i.e. bleached jute fabric double premordanted with 20% harda and 20% $FeSO_4$ applying in sequence show a non-linear langmuir absorption isotherm, which is more alike to the absorption isotherm of dyeing wool with acid dye, indicating the formation of co-ordinated complex in this case. It may be presumed that jute fiber having —COOH group in hemicelluloses might have attracted Fe^{++} ions from $FeSO_4$ mordant during second mordanting to form Jute-hemicellu—COO^-….Fe ion complex and this (Jute— $COO^-)_2$….Fe^{++}mordanted complex perhaps facilitates absorption of more and more of the said non-polar/ionic-mordantable colour component (morol) of JFW, in a fashion like wool absorbs acid dyes following the langmuir absorption isotherm.

11.7.4 Heat (Enthalpy) of Dyeing

For dyeing of bleached jute and cotton fabrics after double pre-mordanting with selective fiber-mordanting systems (a), (a′), (b) and (b′), heat (enthalpy) of dyeing is found to be positive, showing initial high value and later decreases gradually to a moderate or low values either for increase in dyeing time/ dyeing temperature or dye concentrations. Thus, these dyeing processes may be considered as endothermic and hence, in these cases, dye should be adsorbed with the increase of dyeing temperature up to a certain temperature limit (90 °C in present cases), above which the dye uptake either reduces or almost levels off, after the desorption of dyes to occur above a certain temperature limit. From the relevant data shown in Table 11.14, it is observed that between the temperature range of 60 to 90 °C, the ΔH value (a measure of strength of forces or bonds of attraction which bind relevant dyes to the fiber [14]) in the present case ranges between 21.71 to 9.30 kJ/mol for fiber-mordanting system (a), between 15.99–8.11 kJ/mol for fiber-mordanting system (b), between 19.05 to 7.91 kJ/mol for fiber-mordanting system (a′) and between 11.21 –7.50 kJ/mol for fiber- mordanting system (b′). ΔH values gradually decreases with either increased dye uptake or higher dyeing period. These observed results of ΔH values indicate that most probably a week dye-fiber force has been taken place in the present cases for both jute and cotton fabrics, as these experimental ΔH values almost matches with the range of bond energy (8.4 – 41.9 kJ/mol) [14] of hydrogen bond formation. Moreover, as the dyeing proceeds using higher concentrations of dye or with higher dyeing time, due to quick saturation of hydrogen bond formation utilizing the –OH groups of dyes and fibers, it blocks the possibility of formation of dye-fiber-co-ordinated complex utilizing the dye sites and hence, the ΔH values gradually decrease with increased dye uptake or higher dyeing time. Among all the selective fiber–mordanting systems (a), (a′), (b), and (b′), the absorption isotherm for fiber-mordanting system (b) is found to be different than other systems studied, while for heat of dyeing for different fiber-mordanting systems (a) and (b) for jute show always higher ΔH value than the same for fiber-mordant systems (a′) and (b′) for cotton. Jute fiber having–COOH group in hemicellulose can ionize in the solution as jute-cellu-COO^- ion to attract metal ions of mordants and also the mordant able dyes.

11.7.5 Entropy of Dyeing and Gibb's Free Energy

Entropy of dyeing is observed to be initially high, which however decreases significantly for increase of dye concentrations or for higher time of dyeing for both selectively double pre-mordanted jute and cotton fabrics. As change in entropy (ΔS) along with change in enthalpy (ΔH) are the main indicator of driving force leading to dye absorption and fixation, it is understood from both the ΔH and ΔS data shown in Table 11.13 and Table 11.14 for selective fiber-mordanting systems (a), (a′), (b), and (b′)

in the present cases that there are always a measurable decrease in ΔH and ΔS values with increase in dye concentration or higher time of dyeing, perhaps due to decrease in further dye-fiber interactions and fixation occurring mostly through hydrogen bonding for fiber–mordanting systems (a), (a′) and (b′) and occurring through co-ordinated complex formation for fiber-mordanting system (b), particularly when the dye saturation and equilibrium are established. However, slowing down of rate of dyeing (Figure 11.7) above 60 °C dyeing temperature with reduction in slope of dye-exhaustion curves above 60 °C and reduction in dye exhaustion above 90 °C dyeing temperature may be viewed as effect of rapid dye absorption on pre-mordanted jute and cotton fabrics by physical absorption in case of fiber-mordanting systems (a), (a′) and, (b′) and by chemi-sorption in case of fiber-mordanting system (b) up to 60 °C achieving the dye saturation quickly within this temperature range and slow dye absorption at 60 °C to 90 °C dyeing temperature. And thereafter almost no physical or chemical absorption of dye molecules occur in the fiber surface or voids without any further chemical interaction or complex formation showing much reduction in ΔH and ΔS values only due to possible desorption of the dye molecules at higher temperature or for higher dyeing time.

However, ΔG values (Gibb's free energy) [15] being negative in all these cases for all the fiber-mordanting systems both at 60 °C and 90 °C, indicate that there is still some possibility of chemical reaction/co-ordinated complex formation among the fiber, mordant, and the dye molecules in some other favorable conditions of dyeing and this may be true even for the case of fiber-mordanting system (b).

11.8 Study of Compatibility of Binary and Ternary Mixture of Natural dyes to Obtain Compound Shade

Compatibility of a pair of dyes can be judged by different approaches [13–16,], which has been described in our earlier communication [9]. However, the method of plotting ΔC vs. ΔL and/or K/S vs. ΔL values for two sets of progressive shades obtained by varying dyeing time/temperature (set-I) and varying total dye concentrations (set-II), may be considered to be more rational and practical, as the other methods of test of compatibility [13–16] are based on assumption that the dyes are non-interacting type and rate of dyeing for a dye does not change in presence of other dye, which is not practically true. Moreover, all the dyeing process variables also influence the dyeing results for dyeing with mixture of dyes [13] and hence it is preferable to use a method of the test of compatibility where results of dyeing are derived by dyeing of the substrate with mixture of dyes under practical conditions of dyeing as compared to dyeing of the samples with individual dye and then to predict the compatibility from rate of dyeing or other dyeing results. Besides the test of compatibility by conventional method, in the present work, a newer method of assessing relative compatibility rating (RCR) for binary mixture of dyes has been proposed, where a newer index called Color Difference Index (CDI) has been postulated and the same has been utilized for assessing the RCR of selective binary mixtures of those natural dyes

Double pre-mordanted bleached cotton fabric samples were dyed with aqueous extract of either single or selected binary mixture of purified natural dyes in varying proportions (100:0, 75:25, 50:50, 25:75 and 0:100 applying 1% owf purified dye extract obtained from 40% (based on weight of solid source material for each dye) aqueous dye extract after concentrating to semi-solid mass and then purifying as said for obtaining comparable results at 100 °C using MLR 1:50 for 60 min adding 10 g/L sodium chloride as only additive. In each case, after the dyeing is over, the dyed samples were repeatedly washed with hot and cold water and then subjected to soap-washing (to remove the unfixed dyes, if any) using 2 gpl neutral soap solution at 60 °C for 15 min followed by repeated water wash and atmospheric drying under sun. After dyeing two sets of such sample, the K/S value and other colorinteraction parameters were measured.The observed results in terms of Surface Color strength, Color difference value, Differences in Hue and Chroma, brightness Index, metamerism index etc and related parameters of premordanted cotton fabrics dyed with selective single and binary pair of mixture of natural dye at comparable shade depth are shown in Table 4.10 and Table 4.11

11.9 Test of Compatibility for Selected Binary Mixture of Natural Dyes

11.9.1 Conventional Method of Test of Compatibility(Method-I)

Following binary mixtures of the purified natural dyes (taking 50:50) mixture of the corresponding purified dye powder obtained from corresponding 20% to 100% aqueous dye-extracts (based on the weight of corresponding source material for each dye) were applied on premordanted cotton fabric using standard dyeing technique as stated above in item 2.5 using varying time and temperature profile:

- Mixture M1: JFW + Manjistha (JFW & MJ)
- Mixture M2: JFW + Marigold (JFW & MG)
- Mixture M3: JFW+ Red sandal wood (JFW & RSW)
- Mixture M4: JFW + Babool wood (JFW & BL)
- Mixture M5: JFW + Sappan wood (JFW & SW)

In Set I, (progressive depth of shade developed by varying dyeing time and temperature profile during dyeing), for each binary mixture (M1-M5), five separate small pre-mordanted cotton fabric samples were dyed using EEC make Laboratory beaker dyeing machine with temperature controller for varying time periods (for 10 to 60 min in 10 min steps) and varying dyeing temperatures (60 °C to 100 °C in 10 °C steps), by withdrawing one dyed sample from the dye bath at the interval of 10 min from 60 °C onwards maintaining the heating rate of 1 °C/min. The penultimate sample was taken out after 50 min at 100 °C and the last one at the end of the dyeing process after completion of 60 min dyeing.

In Set II (progressive depth of shade developed by varying total concentrations of dye mixture) for each binary mixture, five separate small pre-mordanted cotton fabric samples were dyed by applying 20% to 100% dye concentrations with increment of twenty percentage points for M1-M5 each taken in equal proportion (50:50) at 100 °C for 60 min.

For both Set I and Set II, after dyeing, all the dyed fabric samples were subjected to normal washing, soaping, and rinsing before final air-drying. The differences in the CIELAB coordinates namely, ΔL, Δa, Δb and ΔC for all dyed fabric samples for both Set I and II, with respect to the standard undyed fabric sample, were obtained from separate measurement of the same using the above said computer aided Macbeth 2020 plus reflectance spectrophotometer and associated software. By this conventional method of test of compatibility, the compatibility of a selected binary mixture of dyes can be judged from degree of closeness and overlapping of the two curves for the above said two sets of dyed samples (set I & set II) having progressive depth of shade as observed from plots of ΔC vs. ΔL or plots of K/S vs. ΔL.

11.9.2 Newer Proposed Method of Test of Compatibility (Method-II)

An alternative method of assessing RCR of binary mixture of natural dyes applied on jute fabric has been proposed and validated. Applying the same concept, the same has been employed for RCR for application binary mixtures of dyes on bleached and mordanted cotton fabric. After application of different proportions of binary mixture of natural dyes on the same cotton fabric, the magnitudes of the respective ΔE, ΔC, ΔH, and MI values irrespective of their sign and direction may be utilized to obtain a newer empirical index called CDI by the following proposed empirical relationship:

$$CDI = \frac{\Delta E \times \Delta H}{\Delta C \times MI}$$

The closer the CDI values for binary mixture of dyes applied on the same fabric under the comparable conditions of dyeing, the higher is the compatibility rating (between 0 to 5, where rating 5 is maximum representing excellent compatibility and rating 1 is minimum representing worst compatibility, while rating 0 (zero) represents completely non-compatibility). Proposed compatibility grades and RCR system may be represented as follows:

Compatibility Grades	Relative Compatibility Rating (RCR)	Highest values of differences between maximum CDI values and individual CDI values for dyeing using different proportions of mixtures of selective binary mixture of dyes applied on the same fabric under the comparable dyeing conditions.
Excellent	5	>0 but ≤ 0.05
Very good	4–5	>0.05 but ≤ 0.10
Good	4	>0.10 but ≤ 0.20
Moderate	3–4	>0.20 but ≤ 0.30
Average	3	>0.30 but ≤ 0.40
Fair	2–3	>0.50 but ≤ 1.00
Poor	2	>1.00 but ≤ 5.00
Very poor	1–2	>5.00 but ≤ 10.0
Worst	1	> 10.0 but ≤15.0
Non-Compatible	0	>>15.00

Now, this is to test or validate in the present work that how much agreement or closer results be obtained from the said conventional methods of test of compatibility (i.e., by ΔC vs. ΔL or K/S vs. ΔL plots) and this newer RCR system of test of compatibility for the said natural dyes used.

Besides, the analysis of compatibility of selected binary mixture of natural dyes by conventional method of test of compatibility, a new method of RCR of selected binary mixtures of natural dye has been postulated (as detailed in experimental part) and compared with the results of conventional methods of test of compatibility for judging the effectiveness of the proposed newer method for the same.

Binary mixtures of dyes vary considerably in their response to dyeing processes. A given binary mixture may exhibit compatibility under one set of dyeing conditions but prove incompatible under another set. Regular build-up of the individual dyes on a particular fiber does not always guarantee similar behavior when applied together. One conventional method (method-I) and proposed newer method (method-II) of test for compatibility of binary mixture of the selected natural dyes have been used and compared in the present work. In the conventional method, the closeness and degree of overlap were judged between two sets of curves (set-I and set-II) in the plots of ΔC vs. ΔL or K/S vs. ΔL for two sets of progressive depth of shade produced by dyeing pre-mordanted cotton with the selected binary mixture of natural dyes taken in equal proportion. The set-I samples were prepared using the dyes in equal proportions (50:50) for various dyeing times (10 to 60 min in 10-min steps) and dyeing temperatures (60 to 100 °C in 10 °C steps). The set –II samples were prepared using varying total dye concentrations (20% to 100% in 20% steps). However, it is felt highly essential to test the compatibility of different binary mixtures of natural dyes by some form of quantitative term or grading system of RCR that will provide the dyers an option for selecting appropriate mixture dyes to match a target compound shade. Therefore, an easy method of determining RCR (detailed in the experimental part) applicable for binary mixture of natural dyes has been established with the help of a new empirical index called color difference index [$(\text{CDI} = (\Delta E \times \Delta H) / (\Delta C \times \text{MI})$] reported earlier [17–18].

The closer the CDI values for dyeing with different proportions (75:25, 50:50, 25:75) of the selected binary mixture of natural dyes under the same dyeing conditions, the higher is the compatibility rating for the same. To test the degree of fitness of this newer proposed method, the test results of the compatibility between the two methods (methods I & II) have been compared. The degree of closeness or overlapping between set-I & set-II samples for each binary mixture of natural dyes (M1 to M5) though cannot be quantified but can be graded as 1–5 as shown by Datye and Mishra [13] depending on residual shade buildup in both set-I and set-II, assessment of degree of closeness or overlapping of the curves. Hence, the results of both methods I and II are comparable.

Figure 11.9 shows the plots of K/S vs. ΔL (plots a to e) and plots of ΔC vs. ΔL (plots a′ to e′) respectively for two sets (set-I & set-II) of dyed materials having progressive shade depth (Set I - samples are dyed by using different temperature and time profiles and Set II- samples are dyed by varying total dye concentrations) for five separate binary mixtures (M1-M5) of natural dyes.

In case of binary mixture M1 (JFW: MJ), for plots (a) of K/S vs. ΔL, the two curves for set-I & II do not show always a similar run, from beginning

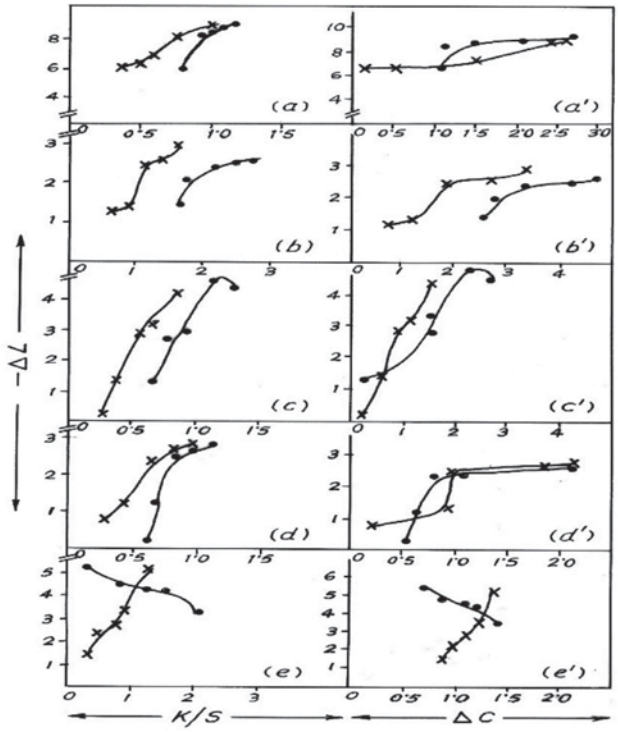

Figure 11.9 Plots of K/S vs.ΔL (a-e) and ΔC vs.ΔLfor dyeings of five separate pairs (M1 to M5) of natural dyes on premordanted cotton fabrics.M1-a and a$^{|}$ M2-b and b$^{|}$ M3-c and c$^{|}$ M4-d and d$^{|}$ M5-e and e$^{|}$

Set I: X samples dyed under different time and temperature profiles.

Set II: X samples dyed with different total concentrations of binary pairs of dyes.

to the end of the buildup of color, initially there is a reasonable gap following a distinct path, which however becomes narrower and closer almost touching each other at the end of dyeing, at dyeing equilibrium. In this case, for K/S vs. ΔL plot in set I curve, the color build up was slow at the beginning at lower temperature, while in set II curve, the color build up was moderately fast for use of higher temperature from initial stage of dyeing. Moreover, the observed deviations in these two sets of curves may also be due to the differences in the molecular weights of these two dyes. However, after sufficient time of dyeing, both in set I and set II curves, the color build up and increase in darkness become almost at par and hence the two curves meets each other at the end at dyeing equilibrium. Whereas, for plots (a′) of ΔC vs. ΔL, the two curves for set-I & II though do not show similar pattern but runs together, where the two ends of concave path of set-I curve touches the set-II curve showing a distinct deviations in their path. Plots of set I curve and set II curve follow a similar rate of color build up with minor deviations showing maximum in increase in darkness at the middle of dyeing cycle for set-I probably due to the differences in major hue of these two dyes, which gives maximum darkness by sufficient absorption of manjistha at half dyeing cycle and thereafter showing decrease in darkness due to slow but higher absorption of JFW and consequent color suppression effect. As per Figure 11.9a and Figure 11.9a′, this pair of dyes may be subjectively said to have a fair to moderate compatibility. In the new RCR system, this pair of dyes exhibit Grade 3–4 (i.e., moderate) RCR (vide Table 11.12).

In the case of binary mixture M2 (JFW: MG), the two curves for set-I & set-II in the plots (b) of K/S vs. ΔL, and for plots (b′) of ΔC vs. ΔL, the two curves for set-I & set-II do not show exactly a similar pattern from beginning to the end for buildup of color showing minor up and down deviations from time to time particularly for set II curves, while there are steady increase in darkness of the shade for both the plots (b) of K/S vs. ΔL and plots (b′) of ΔC vs. ΔL for set-I curves. As per plots (b), this pair of dyes may be subjectively considered as poor to fair compatible. In the newer RCR system, this binary mixture of dyes exhibits Grade 2–3 (i.e. fair) RCR (Table 11.12). This newer method is showing very much similar result as compared to the results of compatibility obtained by both ΔC vs. ΔL plots and K/S vs. ΔL plots. The observed gaps between the set-I and set-II curves both in ΔC vs. ΔL plots and K/S vs. ΔL plots may be considered as an influence of dulling effect due to the closeness of the hues of these two dyes and hence whatever may be the time of dyeing and concentrations of dyes, the dulling effect dose not diminishes in the whole dyeing cycle and increase in darkness goes parallelly in both the sets maintaining always a certain gap barring overlapping of the set-I and set-II curves for both K/S vs. ΔL plots and ΔC vs. ΔL plots, showing a poor to fair compatibility.

In case of the binary mixture M3 (JFW: RSW), for plots (c) of K/S vs. ΔL, the two curves for set-I and set-II show almost a parallel run showing a similar higher rate of increase in darkness in both the curves. The depth of shade (K/S value) and corresponding darkness (ΔL) of shade build up one in much similar fashion with maintaining a constant deviation and gap between set-I and set-II curves, indicating subjectively a moderate to fair compatibility between this binary mixture of selected dyes. Whereas for plots (c′) of ΔC vs. ΔL, for the same binary mixture of dyes, the two curves for set-I & II show a small but varying gap; initially one touching the other and gradually widening the gap one goes away from other. Thus it may be observed from ΔC vs. ΔL plot that the change in hue (ΔC) and darkness (ΔL) of shade do not build up systematically and both the hue and darkness changes continuously with the increase in dye concentration as well as with the progress in dyeing time almost up to the end indicating a moderate to average compatibility between this pair of dyes. In the newer RCR system, this pair of dyes exhibits Grade 3 (i.e., Average) RCR (Table 11.12). Thus the conventional and the newer (RCR) method show very similar results to one another.

In case of the binary mixture M4 (JFW: BL), for plots (d) of the K/S vs. ΔL, the two curves for set-I and set-II run in such a fashion that though initially they show a reasonable gap but finally they almost tend to meet each other at the end point, where the curve for set-I and set-II ends indicating subjectively a fair to average compatibility. For plot (d), the degree of darkness achieved by using different dye concentration (set II) are found to be relatively higher than the degree of darkness achieved by increase in dyeing time and temperature and thus, there is a reasonable gap between the curves for set-I and set-II at initially, which gradually diminishes for increase in color strength with more and more dyeing time up to the dyeing equilibrium/ saturation level. In the corresponding plots (d′) of ΔC vs. ΔL, however, the curves crosses each other after certain dyeing time, and they almost overlap each other and follow the same path indicating an average to good compatibility. The plot (d′) show a similar build up of degree of darkness of shade for both set I and set II, showing minor positive and negative deviations initially probably due to the initial dulling effect of babool due to the presence of low of molecular weight gallic acid in it being preferentially absorbed at higher rate than the color constituents of these dyes; which however disappears after the absorption of gallic acid is completed. The said dulling effect is evident by observing the UV-visible spectra of babool (Figure 11.1) in comparison

Table 11.15 Color strength, brightness Index and related parameters of pre-mordanted cotton fabrics dyed with natural dye individually at comparable shade depth.

		Color parameters of dyed fabrics without after treatment						
Dyes used[a]	**Color obtained**	**K/S at 420 nm**	**CV % of K/S**	**ΔE**	**ΔC**	**ΔH**	**MI**	**BI**
Nil (Bleached Cotton)	White	0.01	–	–	–	–	–	92.06
JFW	Yellow	0.65	3.12	7.65	8.75	–0.65	1.41	26.70
MJ	Reddish yellow	1.28	2.32	16.31	6.70	–13.56	4.89	30.88
MG	Golden beige	4.32	2.37	8.10	10.27	–0.85	2.32	31.42
RSW	Reddish yellow	1.28	3.14	8.01	2.29	–6.95	2.48	43.95
BL	Light beige	1.28	2.42	9.90	1.87	–4.79	2.32	44.32
SW	Peach	1.47	3.56	10.01	0.64	1.87	0.21	7.51

[a] Applying 1% owf purified dye powder in each case (using a fixed concentration of purified dye powder obtained from 40% aqueous extract) for obtaining comparable results.

with other natural dyes where babool shows much less peak height at 602 nm as well as showing another small hump at 550 nm giving rise to the dulling of the main hue. The good degree of overlapping observed at the latter stage of dyeing cycle in plot (d′) may be thus explained by nearer molecular weights of these two dyes [16]. In the newer proposed (RCR) method binary mixture of (JFW: BL) exhibits Grade 3 (i.e., Average) RCR (Table 11.12). Thus, the result of method-I (conventional) and method-II (RCR) are well in agreement.

In case of the binary mixture M5 (JFW: SW), for both the plots (e) of K/S vs. ΔL, and plots (e′) of ΔC vs. ΔL, the two sets of curves in each case for set-I and set-II, cross each other at the mid-point thus, they do not show a systematic build up of color either with increased concentration of dyes (Set II) and also with increased dyeing temperature and time (Set I).

Thus this binary mixture of dyes (JFW: SW) are totally incompatible with one another when applied on pre-mordanted cotton fabric. In the newer (RCR) method, mixture of (JFW: SW) exhibits Grade 0 (i.e. Non-compatible) RCR. Observed non-compatibility of JFW: SW mixture may be due to the combined effect of larger differences in molecular weights of the said two dyes along with wide variations of the main hues of these two individual dyes.

Data for cotton fabric dyed three proportions (75:25, 50:50, and 25:75) of selected binary mixture showed different color parameters. Comparison of the values for change in chroma (ΔC) shows that the changes in chroma values for the combination M2 (JFW: MG) is the maximum comparing the ΔC data for all the three proportions (75:25, 50:50 and 25:75) of selected binary mixture of natural dyes used. The values for change in hue angle (ΔH) are found to be negative for M1, M2, M3 and M4, while the same is positive for M5. The data for metamerism index show the minimum MI values for the combination M5 (JFW: SW) for all the three proportions of the selected binary mixture of dyes.

The results of the proposed newer system of RCR are in good agreement with the results of conventional test based on plots of compatibility ΔC vs. ΔL and K/S vs. ΔL. According to the RCR system, the order of relative degree of compatibility of the selected binary mixture of natural dyes is JFW: MJ > JFW: RSW ≥ JFW: BL ≥ JFW: MG >>> JFW: SW. Thus, this newer proposed RCR system may be useful to identify compatible binary mixture of natural dyes to be applied in various proportions on cotton to obtain desired compound and uncommon soothing shades, providing the dyers an option for selecting suitable dye-combinations to match a target shade. This newer RCR system is easy to adapt, saves time as well as it does not require any precision temperature controlled dyeing unit.

Table 11.16 Color strength, brightness Index and related parameters of pre-mordanted cotton fabrics dyed with selected binary pairs of mixture of natural dyes in different proportions.

Dye used[a]	Colour obtained	Colour parameters of dyed fabrics without after treatment						
		K/S at 420 nm	CV % of K/S	ΔE	ΔC	ΔH	MI	BI
For 75:25 Proportions of binary pairs of dyes								
M1 (JFW: MJ)	Light reddish yellow	0.81	1.92	8.29	1.90	−6.71	2.52	30.88
M2 (JFW: MG)	Yellow	2.36	1.83	8.24	7.81	−2.34	2.99	12.57
M3 (JFW: RSW)	Light reddish yellow	0.79	2.42	5.42	0.80	−3.39	1.35	31.42
M4 (JFW: BL)	Pale yellow	0.44	2.09	6.76	3.12	−2.98	1.17	31.42
M5 (JFW: SW)	Light peach	0.89	2.31	12.51	2.87	2.35	0.85	20.14
For 50:50 Proportions of binary pairs of dyes								
M1 (JFW: MJ)	Reddish yellow	0.88	2.21	8.95	2.18	−7.21	2.60	31.42
M2 (JFW: MG)	Golden yellow	2.89	2.10	8.30	9.75	−1.08	2.92	15.60
M3 (JFW: RSW)	Reddish yellow	0.91	3.04	6.26	1.05	−5.06	1.74	40.20

M4 (JFW: BL)	Pale yellow	0.59	2.33	7.01	2.78	−3.47	1.59	34.10
M5 (JFW: SW)	Light peach	1.10	3.36	12.25	1.67	2.25	0.58	16.54
For 25:75 Proportions of binary pairs of dyes								
M1 (JFW: MJ)	Reddish yellow	0.96	2.37	14.93	3.89	−11.99	4.05	34.41
M2 (JFW: MG)	Golden beige	3.56	3.56	8.18	10.17	−0.97	2.81	20.00
M3 (JFW: RSW)	Reddish yellow	1.07	3.10	7.32	1.56	−6.84	1.89	42.01
M4 (JFW: BL)	Light beige	0.83	2.43	7.60	2.37	−3.70	2.03	41.48
M5 (JFW: SW)	Peach	1.27	1.47	10.77	0.87	2.04	0.35	12.04

[a] Applying 1% owf purified dye powder in each case (using a fixed concentration of purified dye powder obtained from 40% aqueous extract) for obtaining comparable results.

Table 11.17 Color difference index (CDI) and relative compatibility rating (RCR) for application of selected binary pairs of natural dyes to premordated cotton fabrics.

Dye combinations[a]	**CDI for selected binary pairs of dyes**			**RCR**	**Compatibility grade**
Proportions	75:25	50:50	25:75		
M1 (JFW: MJ)	11.61	11.38	11.36	3–4	Moderate
M2 (JFW: MG)	0.82	0.31	0.27	2–3	Fair
M3 (JFW: RSW)	17.01	17.33	16.98	3	Average
M4 (JFW: BL)	5.52	5.50	5.84	3	Average
M5 (JFW: SW)	12.05	28.45	72.15	0	Non-compatible

[a] Applying 1% owf purified dye powder in each case (using a fixed concentration of purified dye powder obtained from 40% aqueous extract) for obtaining comparable results.

11.10 Some Recent Studies on Natural Dyes for Textiles

Khan *et al.* [19] studied the effect of *Rheum emodi* L. as natural dye with ferrous sulphate, stannous chloride, and alum mordant on color strength, color fastness, and anti-microbial properties (showing more than 90% bacterial reduction for both bacterial and fungal population.

Coloration of textiles with self-dispersible carbon nanoparticles as nano pigments natural color is reported by Li and Sun [20]. Andres *et al.* [21] reported the method of identification of Carbon Black in Military Textiles can be done using Infrared Techniques to discriminate military textile with or without carbon black. A semi durable simultaneous natural dyeing and antimicrobial finishing of woolen yarns using gallunt extract is reported by Shahid *et al.* [22].

Effect of tin chloride as mordant for dyeing woolen yarn with henna leaves (*Lawsoniainermis*) and madder (*Rubiacordifolia*) on color strength, color fastness, and antifungal activity, against *Candida glabrata* was investigated by Yusuf *et al.* [23], where, henna leaves show its effectivity against *Candidaglabrata* but madder shown no antifungal activity. Sustainable prospects with brief processing sequences and chemistry of natural colors with respect to absorption isotherms and dyeing kinetics etc., have been well discussed and reviewed by Yusuf *et al.* [24]. Close loop Environmental sustainability was reported by Singh *et al.* [25] for utilization of floral waste generated from temples, as a waste management measure through waste reduction and reutilization of floral waste (after utilizing color extracts as natural dye) was reutilized in production of vermin-composite as organic fertilizer for agriculture.

Besides use of natural resources for textile dyeing, cosmetic attributes of algae and its uses in the food, cosmetics, pharmaceuticals as nutraceutical industries have been reported in a review by Ariede *et al.* [26]. Similarly Antiproliferative and antioxidant activity of extracts of *Chrozophoratinctoria* (L) A. Juss for therapeutical uses is reported by Oke-Altuntas [27]. Vankar, Shukla, Wijayapala, and Samanta [28] have reported innovative silk dyeing using different enzymes (protease, amylase, xylanase, pectinase, phytase) as bio-mordants for room temperature dyeing of silk with madder (*Rubiacordifolia*) replacing metal mordants with conservation of energy and time, in a time step process and found encouraging good results. Samanta A K and Aggarwal P [29], have reported characterization of few important natural dyes (Jack fruit, Red sandal wood, Sappan wood, madder, marigold, and babool bark) after their extraction and purification, in terms of UV-absorbance FTIR-spectroscopy; thermal degrading pattern of different temperatures (includes dyeing temperatures) by DSC and color yield (color strength) and color fastness properties against – washing, light and rubbing (dry and wet).

Isolation, application, and bio-chemical characteristics of color component from *Tecomastans* (flower) and its dyeing with stannous chloride as mordant, shows good yellow color shade with reasonable color yield (color strength) with fluorescence decay profile of their natural colorant is reported by Arunkumar [30].

11.11 Conclusions

The important areas of scientific and technological aspects of natural dyeing mainly studied here for cotton and jute fabrics in terms of characterization of purified extracted natural dyes by scientific analysis, study of effect of mordanting on color strength, study of dyeing process variables for optimizing dyeing conditions to get reproducible shades and finally, development of compound shades after study of compatibility of binary pair of dyes for use of mixture of dyes by both conventional method and newer method developed from this laboratory has lead to generate more precise technological control over natural dyeing of cotton and jute textiles without any ambiguity or without dependence on individual skill of artisan. Two plates on such samples of natural dyed cotton and jute samples dyed with mixture of natural dyes are shown in Plate-A and B for a glimpse over the effect of such controlled dyeing after these scientific studies.

References

1. Gulrajani, M.L., Gupta, D., *Natural Dye and their Application to Textiles*, pp.50–55, Dept of Textile Technology, Indian Institute of Technology, Delhi, 1992.
2. Samanta, A.K., Konar, A., *Technical Handbook on Natural Dye and Colouration*, pp.97–113 (ch-4), DJFT,IJT,CU, Nov-2012.
3. Kamat, S.Y., Alat, D.V., Natural dyes, a dyeing craft. *Indian Text. J.*, 100, 66–69, 1990.
4. Samanta, A.K., Agarwal, P., Application of natural dyes on textiles. *Indian J. Fibre Text. Res.*, 34, 384–399, 2009.
5. Samanta, A.K., Singhee, D., Sethia, M., Application of single and mixture of selective natural dyes on cotton fabrics-a scientific approach. *Colourage*, 50(10), 29–42, 2003.
6. Chavan, R.B., Revival of natural dyes-A word of caution to environmentalists. *Colourage*, 42(2), 27, 1995.
7. Chavan, R.B., Revival of natural dyes-A word of caution to environmentalists. *Clothesline*, 4(1), 96, 1995.
8. Gulrajani, M.L., Present status of natural dyes. *Indian J. fibre Text. Res.*, (special issue), 1&2, 26, 2001.
9. Singh, O.P., Natural Dyes: The pros and cons. *Indian Text. J.*, 110(4), 42, 2000.
10. Pan, N.C., Chattopadhyay, S.N., Day, A., Dyeing of jute with natural dyes. *Indian J. Fibre Text. Res.*, 28(3), 339–342, 2003.
11. Samanta, A.K., Aggarwal, P., Dutta, Physio-chemical studies on dyeing of jute textileswith natural dye extracted from red sandalwood. *J. Inst. Eng. (1), Text. Eng.*, 87, 16–26, 2006.
12. Arshid, F.M., Desai, J.N., Duff, D.J., Giles, C.H., Jain, S.K., Macnral, I.R., A Study of Certain Natural Dyes I-The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres. *J. Soc. Dyers Colour.*, 70, 392–401, 1954.
13. Gulrajani, M.L., Bhaumik, S, Oppermann, W, Hardtmann, G, Dyeing of red sandlewood on wool and nylon. *Indian J. Fibre Text. Res.*, 28 (3), 191, 2003.
14. Shukla, S.R., Dhuri, S.S., The effect of dye characteristics on their compatibility in mixtures as assessed through colour coordinates. *J. Soc. Dyers Colour.*, 109, 402–405.1993.
15. Shukla, S.R., Dhuri, S.S., Improving the compatibility of disperse dye mixtures using leveling agents- assessment through colour coordinates. *J. Soc. Dyers Colour.*, 108, 395–399, 1992.
16. Shukla, S.R., Dhuri, S.S., Assessing the compatibility of disperse dye mixtures by the use of colour coordinates. *J. Soc. Dyers Colour.*, 108, 139–144, 1992.

17. Samanta, A.K., Aggarwal, P., Singhee, D., Datta, S., Application of single and mixture of Red sandalwood amd other Natural dyes for dyeing of jute fabric: studies on colour parameters/colour fastness and compatibility. *J. Text. Inst.*, 100(7), 565–587, 2009.
18. Samanta, A.K., Konar, A., Dyeing of Textiles with natural dyes, in: *Natural Dyes*, E. Perrin Akcakoca Kumbasar (Ed), pp. 29–56, InTech OA Publiser, Croatia, Oct 2011.
19. Khan, S.A., Ahmed, A., Khan, M.I., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., Antimicrobial activity of wool yarn with Rheum Emodi L. (Indian Rhubarb). *Dyes Pigm.*, 95(2), 206–214, 2012.
20. Li, D., Sun, G., Coloration of Textiles with Self-Dispersible Carbon Black Nanoparticles. *Dyes Pigm.*, 72(2), 144–149, 2007.
21. Andres, J.R., Hidalgo-Gato, R., Lopez-Higuera, J.M., Madruga, F.J., Identification of Carbon Black in Military Textiles using Infrared Imaging Techniques. *Optik- Optics Photonics J.*, 3(4A), 27–30, 2013.
22. Shahid, M., Ahmed, A., Yusuf, M., Khan, M.I., Khan, S.A., Manzoor, N., Mohammad, F., Dyeing, fastness and antimicrobial properties of woollen yarns dyed with gallnut (QuercusinfectoriaOliv.) extract. *Dyes Pigm.*, 95(1), 53–61, 2012.
23. Yusuf, M., Shahid, M., Khan, M.I., Khan, S.A., Khan, M.A., Dyeing studies with henna and madder: A research on effect of tin chloride mordant. *J. Saudi Chem. Soc.*, 19(1), 64–72, 2015.
24. Yusuf, M., Shabbir, M., Mohammad, F., Natural Colorants: Historical, Processing and Sustainable process. *Nat. Prod. Bioprospect.*, 7(1), 123–145, 2017.
25. Singh, P., Borthakur, A., Singh, P., AwasthiSh, Pal, D.B., Srivastava, P., Tiwary, D., Mishra, P.K., Utilization of temple floral waste for extraction of valuable products: A close loop approach towards environmental sustainability and waste management, *Pollution*, 3(1), 39–45. 2017.
26. Ariede, M.B., Candido, T.M., Jacome, A.L.M., Velasco, M.V.R., Carvalho, J. C.M.de, Baby, A.R., Cosmetic attributes of algae-A Review, *Algal Res.*, 25, 483–487, 2017.
27. Oke-Altuntas, F., Ipekcioglu, S., Yaglioglu, A.S., Behcet, L., Demirtas, I., Phytochemical analysis, antiproliferative and antioxidant activities of Chrozophoratinctoria: A natural dye plant. *Pharmaceut. Biol.*, 55, 966–973, 2017.
28. Vankar, P.S., Shukla, D., Wijayapala, S., Samanta, A.K., Innovative silk dyeing using enzyme and Rubiacordifolia extract at room temperature. *Pigm. Resin Technol.*, 46(4), 296–302, 2017.
29. Samanta, A.K., Aggarwal, P., Konar, A., Datta, S., Characterization and application of purified selective natural dyes on jute. *Int. Dyer*, 193(3), 25–33, 2008.
30. Arunkumar, P., Yogamoorthi, A., Isolation, application and biochemical characterization of colour component from TecomaStans: A new cost effective and eco-friendly source of natural dye. *Int. J. Nat. Prod. Res.*, 4(1), 9–11, 2014.

12

Bio-Colorants as Photosensitizers for Dye Sensitized Solar Cell (DSSC)

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Abstract

A solar cell is a device that converts light energy particles (photons) with specific wavelengths to electricity. Dye-sensitized solar cells (DSSCs), novel solar cells are also called Graetzel cells. Today researchers are paying attention towards light harvesting elements, especially low-cost bio-colorants from natural sources which are being used as photosensitizers instead of high cost metal complex sensitizers. Other advantages are good performance, flexibility, low energy payback time etc. This chapter overviews the development of natural dyes and their effect on various performance parameters of DSSCs.

Keywords: DSSC, bio-colorants, natural dyes, semiconductor

12.1 Introduction

With increasing demand of fossil types of fuel, many researchers are trying to find reliable, clean and equitable substitutes for finite energy resources. The use of excessive fossil fuels causes a serious of environmental problems that harms to human health and the constraints of social progress. The one of the most promising strategies aiming is photovoltaic (PV) technology to deal with this problem by harvesting sunlight and thus, clean and affordable solar electricity obtained [1].

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However, in the first generation, the most developed PV solar cells that fully dominate the market and commercial in nature are single or multi crystalline silicon based solar cells. In second generation, modification and development of the PV systems such as lower manufacturing cost, efficiency improvement etc. Finally, the third generation, comprising of technologies such as concentrating the PV and organic PV cells that are still in the developmental phase or have not widely commercialized yet. The DSSCs may be considered to be a part of third generation cells [2].

DSSCs are structurally simple and the materials used are generally low cost. A typical DSSC consists of a transparent conducting oxide (TCO) glass substrate, a wide band-gap semiconductor (usually a nano-crystalline TiO_2 film which is deposited on the TCO glass substrate), a dye sensitizer anchored on to the surface of TiO_2 film, a redox mediator which is a volatile electrolyte, containing iodine/triiodide (I^-/I_3^-) redox couple, and a platinum-coated TCO glass substrate as a counter electrode (CE) [3].

The concept of DSSC was first proposed by Gratzel and his coworkers in the year 1991 [4]. The first DSSC developed was found to absorb visible light up to approximately 800 nm and the energy conversion efficiency exceeding 7%. By far, the efficiency of DSSCs sensitized by Ru compound adsorbed on these miconductor nano-crystalline TiO_2 has reached 11–12% [5]. In present, although the power conversion efficiency of the DSSC is lower, the types of DSSCs are still the potential to produce a much higher efficiency in future [6].

The performance of DSSC mainly relies on the dye sensitizer. The dye absorption spectrum and the anchor age to the surface of the semiconductor TiO_2 are important parameters for determining DSSC efficiency. The absorption of light in the DSSC is achieved through sensitizer embedded in TiO_2 architecture. The sensitizer can be comprised of inorganic dye molecules, organic dye molecules, and metal–organic dye molecules. Organic metal complexes and organic dyes have been successfully employed to sensitize nano-crystalline semiconductor. The most successful sensitizers in terms of efficiency and stability are based on ruthenium (Ru) bipyridyl compounds [7]. Moreover, these dyes are also having advantageous characteristics such as excellent stability, higher absorption in the visible range of solar spectrum, excellent electron injection, and efficient metal-to-ligand charge transfer [8]. This metal-to-ligand charge transfer takes place at much faster rate than the back reaction, where the electron recombines with the oxidized dye molecule rather than flowing through the circuit and performing work. Even though Ru based dyes are capable of yielding conversion efficiencies greater than 10%, their preparation normally requires multi-step procedures and time consuming chromatographic methods [9].

In DSSCs, TiO_2, ZnO, Nb_2O_5, $SrTiO_3$, and SnO_2 metal oxide wide band gap semiconductors have been used as the most photo anodic materials and among them TiO_2 has been extensively studied. ZnO is considered as an alternative to TiO_2 due to their similar electrochemical properties, energy band structure, and optical properties. The DSSCs offer the major progress of higher conversion efficiency up to 11% based on Ru dye and 12% based on porphyrin dye. The photo current efficiency mostly depended on the dye molecules but they are still limited by the week absorption of the dye sensitizer.

12.2 Operational Principle of the DSSCs

DSSCs are a PV semiconductor device that converts directly solar radiation into electrical energy. The system consists of the following operational components [10].

- An anode (transparent) treated with a TCO layer such as fluorine dope tin oxide and Indium doped tin oxide made up of a glass sheet. However, there are reports available for some alternative low cost materials used as TCO such as graphene, aluminium doped zincoxide (AZO) and doped TiO_2.
- Mesoporous metal oxide layer, which acts as a photo anode usually developed from TiO_2 nanoparticles.
- To enhance light absorption, covalently a monolayer charge transfer dye (sensitizer) which is anchored into the photo anode.
- For dye regenerating in an organic solvent, an electrolyte (mostly iodide-triiodide electrolyte) that undergoes redox reaction
- To facilitate electron collection, a CE, generally a glass sheet coated with a catalyst such as platinum.

In DSSCs, the dye sensitizer that are adsorbed on the surface of mesoporous TiO_2 layer absorb the incident photons and gets excited from the HOMO to the LUMO levels which an electron is injected, when exposed to sunlight into the conduction band of the mesoporous oxide film. These excited dye molecules inject an electron into the conduction band of the mesoporous photo anode network and the dye molecules that loose an electron get oxidized. These injected electrons travel through the TiO_2 layer to the external load to reach the CE. These electrons are then transferred to the electrolyte where the oxidized dye receives electron from I^- ion to replace the lost electron and simultaneously, the iodide molecules are oxidized to triiodide ions (I_3^-). Finally, regeneration of I^- ion takes place at CE (cathode), and migration of electron through the external load completes the circuit.

The operating cycle can be summarized in chemical reaction terminology as

$$S\text{ (on TiO}_2) + hv \rightarrow \text{S}^*\text{ (on TiO}_2) \tag{1}$$

$$\text{S}^*\text{(on TiO}_2) \rightarrow \text{S (on TiO}_2) + e^-\text{ (TiO}_2) \tag{2}$$

$$2\text{S}^+\text{ (on TiO}_2) + 3I^- \rightarrow 2\text{S (on TiO}_2) + I_3^- \tag{3}$$

$$I_3^- + 2e^-\text{ (Pt)} \rightarrow 3I^- \tag{4}$$

$$S^+\text{ (on TiO}_2) + e^-\text{ (TiO}_2) \rightarrow S\text{ (on TiO}_2) \tag{5}$$

$$I_3^- + 2e^-\text{ (TiO}_2) \rightarrow 3I^- \tag{6}$$

$$\text{S}^*\text{(on TiO}_2) \rightarrow S\text{ (on TiO}_2) \tag{7}$$

The operation of the DSSCs continue as a cyclic process until the light illumination stops, which can be shown by a simple schematic diagram of DSSCs shown in the Figure 12.1.

In DSSCs, it is well known that the photo conversion efficiency (η) depends on the short circuit photocurrent density (J_{SC}), the open circuit photo voltage (V_{OC}), the cell fill factor (FF) and the incident light of the intensity. The overall performance of the DSSCs can be described in terms of cell efficiency (η) and FF

$$FF = \frac{V_{\max}\, J_{\max}}{V_{oc}\, J_{sc}} \tag{8}$$

$$\eta = \frac{V_{oc} J_{oc}}{P_{in}} \times 100\% \tag{9}$$

Where,

V_{oc} = Open circuit voltage (V),
J_{sc} = Short circuit current density (mA/cm^2)

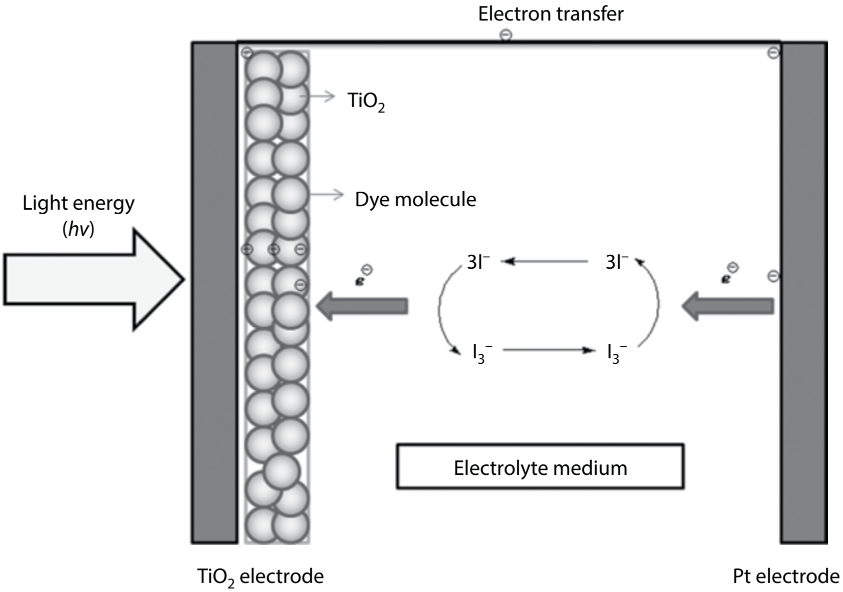

Figure 12.1 Schematic diagram for DSSC.

P_{in} = Incident light power (W/m^2)
J_{max} = Maximum current
V_{max} = Maximum voltage

12.3 DSSC Components

DSSC converts visible light into electricity based on the sensitization of wide band gap semiconductors and is primarily comprised of photoelectrode, redox electrolyte and CE. Other materials include TCO and sealing agents. DSSC components have gone under various developments over the years in order to enhance the efficiency of the cell.

12.3.1 Semiconductor Film Electrode

Oxides such as TiO_2, ZnO, SnO_2, and chalcogenides have been extensively studied as photo-electrodes due to their wide application in energy storage and environmental remediation. In a DSSC system, the typical semiconductor (TiO_2), 10–12 μm mesoporous film with 20 nm diameter particles with an internal surface area of 1000 cm^2 per 1 cm^2 have porosity of 50%, can absorb the entire incident light and their power conversion efficiency can reach up to 11.2% [11]. The need for absorbing more incident light in DSSC is the driving force for the development of mesoscopic semiconductor material. There are several criteria to be considered in selecting the photo electrode in DSSC,

1. it should be transparent to avoid visible light absorption, and has sufficiently high surface area for maximum amount of dye adsorption,
2. it should match with the excited dye (LUMO) to facilitate electron injection,
3. it should provide high charge carrier mobility to collect the photoelectrons efficiently,
4. it should be easy to synthesize, stable, cheap, and environmental friendly.

Metal oxides such as titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), and niobium oxide have been used as the semiconductor materials for the photoelectrodes. A photoelectrode made of materials such as silicon and cadmium sulfide decomposes under irradiance in solution owing to photo-corrosion. In contrast, TiO_2 is cheap, readily available, non-toxic and also has good stability in photo-electrochemical systems even under extreme operating conditions. It aids in yielding highest values of open circuit voltage (V_{oc}), short circuit current (I_{sc}), incident photon-to-current conversion efficiency and efficiency (η) when used as semiconductor electrode. Its conduction band edge coincides well with the excited electronic level of anthocyanin containing dyes, which is an important condition to be satisfied for the injection of electrons from the dye molecule to the semiconductor. Dye adsorption and microstructure of the TiO_2 film are important properties when it is used as photoelectrode for DSSCs. TiO_2 occurs in three crystalline forms – rutile, anatase, and brookite [12]. Anatase appears as pyramid-like crystals and is stable at low temperatures whereas needle-like rutile crystals are dominantly formed in high temperature processes. Among these three forms, anatase is preferred over the other two forms in DSSC application. The anatase has certain beneficial properties such as high dielectric constant (n = 80) which provides good electrostatic shielding of the injected electron from the oxidized dye and it helps to prevent the recombination before reduction of the dye occurs by the redox couple, high refractive index (n = 2.5) that promotes diffuse scattering of light inside the porous photoelectrode which in turn enhances the absorption of light, high band gap (3.2 eV) to make anatase to be chemically more stable at low temperature, and high packing density which leads to fast electrons transport in the photoelectrode [13]. While Rutile phase absorbs only 4% of the incident light in the near-UV region, and band gap excitation generated holes that act as strong oxidants reducing the long-term stability of the DSSCs. Brookite is difficult to produce and is therefore not considered in DSSC application. The band-gap of anatase is 3.2 eV at an absorption edge of 388 nm and that of rutile is 3.0 eV at an absorption edge of 413 nm [14].

The common techniques employed in the preparation of TiO_2 films include the doctor blade technique, screen printing, electrophoretic deposition, and tape casting method.

12.3.2 Electrolyte

Electrolyte is one of the most important parts in the DSSC. The role of the electrolyte in DSSC is to inject electrons into the conduction band of the semiconductor to assist in the regeneration of dye. At the same time, electrolyte behaves as a charge transfer medium to transfer positive charges toward the CEs.

The properties of the electrolyte are important for maintaining the long term stability of DSSC. Thus the electrolyte needs to have the following characteristics:

1. For diffusion of electrons, a high electrical/ionic conductivity, and low viscosity.
2. good interfacial contact with the nano-crystalline semiconductor and the CE,
3. does not degrade the dye molecules,
4. is transparent to visible light (no absorption of light),
5. non-corrosive to the CE.

There are mainly three types of electrolytes used for DSSC. They are (i) liquid electrolyte (ii) solid-state electrolyte, and (iii) quasi-solid electrolyte.

12.3.2.1 Liquid Electrolyte

The Liquid electrolytes can be further divided into two classes. They are (i) organic solvent based electrolytes (ii) ionic liquid electrolytes.

12.3.2.1.1 Organic Electrolytes

Organic electrolyte component including the solvent, redox couple, and additives affect the DSSCs performance. There are many redox couples such as I^-/I_3^-, Br^-/Br_3^-, $SCN^-/(SCN)_2^-$, $SeCN/(SeCN)_3^-$ *and* $Fe\ (CN)_6^{3/4}$ etc. However, $I_3\ /I^-$, is considered as an ideal redox couple because it has good solubility, high efficiency, easy to fabricated, rapid dye regeneration process, low absorbance of light in the visible region, suitable redox potential, and a very slow recombination kinetics between the TiO_2 injected electrons and I_3^-. Liquid electrolyte is another basic component of organic solvent that is responsible for the diffusion and dissolution of the I_3/I^- ions. A number of solvents have been studied in DSSCs, such as acrylonitrile (AcN), ethylenecarbonate (EC), propylene carbonate (PC), 3-methoxypropionitrile (MePN) and N-methylpyrrolidone (NMP) [15]. The use of solvent free ionic liquid based electrolyte, including of 3 alkylimidazolium based salts that achieving the efficiency of 8.2% [16].

The DSSCs performances mostly depended on the donor number (DN) of the solvent. With increasing the DN, increases the open circuit voltage (V_{oc}) and decreases the short circuit current density (J_{sc}) values by lowering the concentration of tri-iodide that reduces the dark current and therefore yields a high photo voltage (V_{oc}) [17]. The additives in the electrolyte increase the PV properties. The most efficient additives are 4-tert-butypyridine (TBP), guanidinium thiocyanate (GuNCS), and N-methylbenzimidazole (NMBI). It absorbs on the photo electrode/electrolyte interface and they block the reduction sites, hence keeping the electron acceptor molecules away from the contact, which in turn, prevents the recombination of injected electrons with the tri-iodide ions.

Nevertheless, the concentration of the redox couple affects the DSSC efficiency as well. A low concentration of redox couple cannot maintain a required level of electrolyte conductivity whereas a high concentration of redox couple absorbs the visible light and results in high rate of recombination [18].

12.3.2.1.2 Ionic Electrolyte

The second type of liquid electrolyte is the room temperature ionic liquid electrolyte. Covalent (organic) electrolyte has high evaporation rate because of their high volatility. The long stability is hampered due to high evaporation rate and leakage based on covalent electrolytes. Ionic liquids at room temperature have been employed in order to minimize the above problem successfully. They are a group of organic salts containing cations such as imidazolium, pyridinium, and anions from the halides or pseudo halides. Simultaneously, they act as a solvent and as an ionic liquid. The ionic liquid electrolytes show high ionic conductivity, good chemical and thermal stability at room temperature and a negligible vapour pressure, which are favourable for an efficient DSSC. Commonly, the most ionic liquid (1L) used for DSSCs, including N,N′bis-alkyl-substituted imidazolium iodides [19]. Due to the decrease of Vander waals forces, it has been found that the viscosity of these salts decrease with decreasing alkyl chain length. However, increase of viscosity decrease the conductivity of 1L electrolytes. A disadvantage of liquid electrolyte is that it may limit device stability because the liquid may evaporate when the cell is imperfectly sealed. Penetration of water or oxygen molecules and their reaction with the electrolyte may also worsen cell performance. Liquid electrolytes also make the construction of multi-cell modules difficult because cells must be connected electrically yet separated chemically, preferably on a single substrate. Among all of the solid-state cells, the one containing a p-type semiconductor possessed the advantage of easy preparation and higher stability while the cells employing polymer electrolytes showed higher efficiency and wider practical future use with the proper encapsulation.

12.3.2.2 Solid State Electrolytes

The key problem in liquid electrolyte is evaporation and leakage that reduces drastically the long-term stability of DSSC. Solid state electrolytes have been developed for performance improvement and stability. Here, p-type semiconductor or a hole transfer material as the only component replaced with the liquid electrolytes. The structure of the band gap p-type semiconductor must be compatible with the HOMO level of the photosensitizer and the n-type semiconductor of the conduction band.

An inorganic hole transfer material such as copper based compound including CuI, CuBr, and CuSCN have been commonly in use because of their good conductivity [20]. Because of easy deposition and the low cost, the organic hole transporting materials (HTMs) have some advantages over inorganic HTMs including 2,2′,7,7′-tetrakis (N,N-di-p-methoxyphenylamine) 9,9′-spirobifluorene (OMeTAD) that has an efficiency of only 0.74% (under white-light illumination of 4 mW/cm^2) [21]. The high rate of charge recombination and poor contact between photo-electrode and HTM are the main factors which lead to a low efficiency in DSSC with solid-state electrolyte. However, by introducing a redox couple into the solid-state electrolyte, conversion efficiency can be improved that acts as a transport medium.

12.3.2.3 Quasi-Solid Electrolyte

This type of electrolyte solves the problem associated with poor contact between the photo-electrode and the HTM in solid-state electrolyte.

Quasi-solid electrolyte is a composite of a polymer and liquid electrolyte which can penetrate the photoelectrode to make a good contact. Interestingly, this has long term stability, high electrical conductivity and especially good interfacial contact when compared to the other types of electrolyte because of the unique network structure of polymers. It mostly depends on the molecular weight and the morphology of the polymer because of high mobility of charge in the amorphous phase of polymers. However, the quasi-solid electrolyte has one particular disadvantage; it is strongly dependent on the working temperature of the solar cell, where high temperatures cause a phase transformation from gel state to solution state.

12.3.3 Counter Electrode

The CE is where the redox mediator reduction occurs. The oxidized ions in electrolyte diffuse toward the CE and accept electrons from the external circuit. The prerequisite of a material used as CE should have a low charge transfer resistance, and high exchange current densities to cause the reduction of the oxidized form of the charge mediator. At the same time, it aids to carry the photocurrent over the whole width of the DSSC. Therefore, the CE must be well conducting and exhibits a low overvoltage for reduction of the redox couple. Till now, Pt has been the preferred material for the CE since it is an excellent catalyst for I_3^- reduction [22, 23]. The Pt CE is ~200 nm in thickness, and it can be fabricated by sputtering, screen-printing or pyrolysis of H_2PtCl_6 solution onto the TCO substrate. The platinized TCO substrate exhibits electro catalytic activity, which improves the reduction of I_3^- by facilitating electron exchange, and it has a high light-reflection due to the mirror-like effect of Pt. However, Pt is a rare metal, hence not cost effective for large-scale production. Besides the high cost Pt corrodes with the redox mediator I_3^- which leads to the generation of platinum iodides like PtI_4 which is undesirable [24]. This means the Pt CE has a durability issue. Therefore, other materials such as carbon nanotube, graphite, conductive polymer etc., are being investigated as an alternative to Pt [25]. An interesting low cost alternative for Pt is carbon (C), because it combines sufficient conductivity and heat resistance as well as corrosion resistance and electrocatalytic activity for the I_3^- reduction. Porous C electrodes are easily prepared from graphite powder, which consists of plate like crystals that, on deposition from a liquid dispersion and drying, will preferentially align in the plane of the CEs, resulting in a high conductivity in this plane. Pt/C black CE for DSSC and achieved 6.72% efficiency under one sun illumination. Pt/C black electrode showed the same efficiency and lower cost compared with Pt electrode alone [26].

12.3.4 Photosensitizers

The photosensitizer (dye) has the role in absorbing and converting the solar energy to electrical energy. The dye is chemically bound to the TiO_2 surface (the semiconductor). The selected dye should meet several requirements to be considered as an efficient photosensitizer:

- An intense absorption in the visible region.
- Strong adsorption onto the semiconductor surface.
- Efficient electron injection into the conduction band of the semiconductor.
- It should possess several O or –OH groups capable of chelating to the Ti (IV) sites on the TiO_2 surface.

Likewise, it must be rapidly regenerated by the mediator layer to avoid electron recombination processes and be fairly stable, both in the ground and excited states. The ideal sensitizer for a PV cell converting standard air mass 1.5 sunlight to electricity must absorb all light below a threshold wavelength of about 900 nm, which is equivalent to a semiconductor with a band gap of 1.4 eV [27]. Overall, the cell performance is subjected to a number of factors but fundamental considerations relating to the dye are how efficiently:

- The molecules absorb incident photons.
- Photons are converted to electron–hole pairs.
- Separation and collection occurs.

The sensitizers are mainly categorized into three groups; metal complex sensitizers, metal-free organic sensitizers, and natural sensitizers.

12.3.4.1 Metal Complex Sensitizer

The metal complex sensitizers have both anchoring and ancillary ligands. The anchoring ability of sensitizers to TiO_2 semiconductor depends on the anchoring ligands, while the ancillary ligands tune up the overall properties of the sensitizers. The modification of these two ligands is to improve the efficiency of the solar cell performance. The finest PV performance in terms of both conversion yield and long term stability has so far been achieved with polypyridyl complexes of Ru developed by the Grätzel group: N3, N719 and 'black' dyes. Further to superior light harvesting properties and durability, a significant advantage of these dyes lie in the metal–ligand charge transfer transition through which the photoelectric charge is injected into TiO_2. Since 1993, N3 dye (cis-RuL2-$(NCS)_2$), is the standard model for efficient charge-transfer sensitizer in porous network of nanocrystalline TiO_2 particles. In Ru complexes, this transfer takes place at a much faster rate than the back reaction, in which the electron recombines with the oxidized dye molecule rather than flowing through the circuit and performing work [28]. Although, metal complex sensitizers (e.g. Ru (II) based sensitizers) provide a relatively high efficiencies and stability, several problems also associated with them. As Ru metals are very expensive and derived from relatively scarce natural resources corresponds to a relatively heavy environmental burden. These problems can be overcome by applying metal-free organic dyes in DSSCs instead of metal complex sensitizers.

12.3.4.2 Metal-Free Organic Sensitizer

The main advantage associated with organic dyes is the ease in structural modifications which can lean to improvement in DSSC efficiency from 4% to 9% [29]. In addition, organic sensitizers usually show considerably higher extinction coefficients compared to metal-based complexes such as Ru complex sensitizers. The general design of a metal-free organic sensitizer is a donor acceptor- substituted π-conjugated bridge (D-π-A). The properties of a sensitizer vary on the electron- donating ability of the donor part and the electron-accepting ability of the acceptor part, as well as on the electronic characteristics of the π bridge. At present, most of the π-bridge conjugated part in organic sensitizers are based on oligoene, coumarin, oligothiophene, fluorene, and phenoxazine. The donor part have been synthesized with a dialkyl amine or diphenylamine moiety while using a carboxylic acid, cyanoacrylic acid or rhodanine-3- acetic acid moiety for the acceptor part [29].

However, the organic dyes also have several disadvantages, which raise the question as whether they are suitable for long-term use in DSSCs. The major drawbacks associated with metal free organic sensitizers are:

1. Strong π-stacked aggregates between D–π–A dye molecules on TiO_2 surfaces, which reduces the electron-injection yield from the dyes to the CB of TiO_2,
2. Low absorption bands compared to metal-based sensitizers, which lead to a reduction in the light absorption capability,
3. Considerably low stability due to the sensitizers tendency to decay with time,
4. Long tedious purification process, and

5. Dyes themselves could be toxic or their by-products may act as environmental pollutants.

Hence, it is possible to use natural dyes as alternative photosensitizers with appreciable efficiencies. Their advantages over synthetic dyes include easy availability, abundance in supply, can be applied without further purification, environment-friendly and they considerably reduce the cost of devices.

12.3.4.3 Natural Sensitizer/Natural Dye/Natural Pigments

An alternative way to produce cost-effective dyes on a large scale is by extracting natural dyes from plant sources. Naturally available fruits, flowers, leave, bacteria etc exhibit various colors and contain several pigments that can be easily extracted and employed in DSSC. Moreover, natural dyes (natural pigments) have a number of beneficial features such as, simple preparation technique, complete biodegradation, easy access, high availability, high purity grade, environmental friendliness and most importantly, high reduction in the use of noble metals and a low production cost. These plant pigments exhibit electronic structure that interacts with sunlight and alters the wavelengths that are either transmitted or reflected by the plant tissue. This process leads to the occurrence of plant pigmentation and each pigment is described from the wavelength of maximum absorbance (λ_{max}) and the color perceived by humans. The performance of natural dye sensitizer in DSSC has been evaluated by open circuit voltage (V_{oc}), short circuit current (J_{sc}), *FF*, and energy conversion efficiency (η) (Table 12.1). Several pigments have been the famous subjects of research. Natural colorants have a hydroxyl group in their structure and exhibit water solubility. Several colorants do not have solubilizing group; hence, a temporary solubility group is generated during application. The natural photosensitizers (natural dye) are classed mainly as carotenoids, flavonoids, chlorophyll (Chl), and anthocyanin. These natural dyes are relatively easy to extract from natural products when compared to synthetic dyes [30].

12.3.4.3.1 Carotenoids

Carotenoids area large family (over 600 members) of isoprenoids that provide many fruits, flowers as well as in certain microorganisms with distinctive red, orange and yellow colors and have important roles in photosynthesis protection. Carotenoids comprise of a C40 polyene backbone that is often cyclized to generate terminal ionone rings. This structure allows carotenoids to absorb short-wave visible light. Carotenoids can be categorized into two major classes known as xanthophylls (contains oxygen),

Table 12.1 Photochemical parameters of natural dyes based DSSCs.

Dye bearing plants	**λ_{max} (nm)**	**J_{sc} (mAcm^{-2})**	**V_{oc} (V)**	**FF**	**η (%)**
Leaves					
Herba artemisiaescopariae	669	1.03	0.48	68.2	0.34
Chinese holly	–	1.19	0.60	65.4	0.47
Vernonia amygdalin (Bitter Leaf)	400	0.07	0.34	0.81	0.69
spinach	437	0.47	0.55	0.51	0.13
Ipomoea	410	0.91	0.54	0.56	0.28
Festuca ovina	420,660	1.18	0.54	0.69	0.46
Brassica olercea (Red cabbage)	537	0.50	0.37	0.54	0.13
Allium cepa (Redonion)	532	0.51	0.44	0.48	0.14
Punica granatum (Pomegranate)	412, 665	2.05	0.56	0.52	0.59
Shiso	440, 600	3.56	0.55	0.51	1.01
Jathopha curcas Linn (Botuje)	400	0.69	0.05	0.87	0.12
Lawsonia inermis (Henna)	518	1.87	0.61	0.58	0.66
Ficus reusa	670	7.85	0.52	0.29	1.18
Rhoeo spathacea	670	10.9	0.50	0.27	1.49
Garcinia subelliptica	670	6.48	0.32	0.33	0.69
Anethum graveolens	666	0.96	0.57	40.0	0.22
Parsley(*Petroselinum crispum*)	666	0.53	0.44	34.0	0.07
Arugula	666	0.78	0.59	42.0	0.20
Seeds					
Coffee	–	0.85	0.55	68.7	0.33
Oryza sativa L. indica (Black Rice)	560	1.14	0.55	0.52	–

(*Continued*)

Table 12.1 Cont.

Dye bearing plants	**λ_{max} (nm)**	**J_{sc} (mAcm^{-2})**	**V_{oc} (V)**	***FF***	**η (%)**
Bixa arellana L. (achiote)	474	1.1	0.57	0.59	0.37
Others					
Green algae	666	0.13	0.41	21.0	0.01
Kelp	465	8.20	0.38	0.38	1.19
Flowers					
Begonia	540	0.63	0.53	72.2	0.24
Rhododendron	540	6.26	0.35	47	0.96
Marigold	487	0.51	0.54	83.1	0.23
Perilla	665	1.36	0.52	69.6	0.50
China loropetal	665	0.84	0.51	62.6	0.27
Yellow rose	487	0.74	0.60	57.1	0.26
Flowery knotweed	435	0.60	0.55	62.7	0.21
Petunia	665	0.85	0.61	60.5	0.32
Violet	546	1.02	0.49	64.5	0.33
Chinese rose	516	0.90	0.48	61.9	0.27
Rose	–	0.97	0.59	65.9	0.38
Lily	–	0.51	0.49	66.7	0.17
Hibiscus sabdariffa L.	520	1.63	0.40	0.57	0.3
Clitoria ternatea	580	0.37	0.37	0.33	0.05
Erythrina variegata	451,492	0.78	0.48	0.55	–
Rosa xanthine	560	0.64	0.49	0.52	–
Hibiscus surattensis	545	5.45	0.39	0.54	1.14
Nerium olender	539	2.46	0.40	0.59	0.59
Hibiscus rosasinesis	534	4.04	0.40	0.63	1.02
Sesbania grandiflora	544	4.40	0.41	0.57	1.02
Ixora macrothyrsa	537	1.31	0.40	0.57	0.30

(*Continued*)

Table 12.1 Cont.

Dye bearing plants	λ_{max} **(nm)**	J_{sc} **(mAcm^{-2})**	V_{oc} **(V)**	***FF***	η **(%)**
Red *Bougainvillea glabra*	482,535	2.34	0.26	0.74	0.45
Violet *Bougainvillea glabra*	547	1.86	0.23	0.71	0.31
Red *Bougainvillea spectabilis*	480	2.29	0.28	0.76	0.48
Violet *Bougainvillea spectabilis*	535	1.88	0.25	0.73	0.35
Fruits					
Tangerinepeel	446	0.74	0.59	63.1	0.28
Fructus lycii	447,425	0.53	0.68	46.6	0.17
Mangosteen pericarp	389	2.69	0.68	63.3	1.17
Raspberries	540	0.26	0.42	64.8	1.50
Grapes	560	0.09	0.34	61.1	0.38
Citrus sinensis (Red Sicilian)	515	3.84	0.34	0.50	–
Solanum melongena (Eggplant)	522	3.40	0.35	0.40	–
Cheries	500	0.46	0.30	38.3	0.18
Capsicum	455	0.23	0.41	0.63	–
Kopsia flavida TiO_2	550	1.20	0.52	0.62	–
Berberies buxifolia Lam (Calafate) TiO_2	533	6.20	0.47	0.36	–
Myrtus cauliflora Mart (Jaboticaba)	520	7.20	0.59	0.54	–
Hylocereus polyrhizus (Dragonfruit)	535	0.20	0.22	0.30	0.22
Wild Sicilian (Prickly Pear)	465	8.20	0.38	0.38	1.19
Chaste tree fruit	548	1.06	0.39	0.48	
Mulberry	543	0.86	0.42	0.43	
Cabbage-palm fruit	545	0.37	0.44	0.61	
Ivy gourd fruits	458, 480	0.24	0.64	0.49	0.09

and carotenes (purely hydrocarbons and has no oxygen). Carotenoids bind to the TiO_2 as a monolayer with 8-apo-β-caroten-8-oic acid bond. Nevertheless, the optimal length of carotenoids consists of seven conjugated π bounds. Along with these discoveries, carotenoids were successfully used in DSSCs as sensitizers. The highest reported ECE (energy conversion efficiency) with single carotenoids is 2.6% [31], while the ECE of solar cells with a combination of carotenoids and Chl derivatives is 4.2% [32]. The raw natural dyes are better than those of the purified or commercial analogs because of the presence of natural extracts, such as alcohol sand organic acids, which assist dye adsorption, prevent electrolyte recombination, and decrease dye accumulation.

12.3.4.3.2 Chlorophyll

Chlorophyll (Chl) is a green pigment found in the leaves of most green plants, algae, and cyanobacteria. Chls are the principal pigments in natural photosynthetic systems. Their functions include harvesting sunlight, converting solar energy (to chemical energy), and transferring electrons. Chl has maximum absorption at 670nm because of an attractive compound that acts as a photosensitizer in the visible light range. Furthermore, Chls do not contain a heavy metal ion, and are thus suitable photo sensitizers from the environmental view point. Chls are highly symmetrical metal-complexes of magnesium ion that consist of a tetrapyrrolic macrocycle, encompassed by several pigments with common structural elements. Six different types of Chl pigment exist and the most occurring type is Chl α. Chlorophylls (Chl a and Chl b) are derived from chlorophyllides (Chl a and Chl b) and pheophytins (Pheo a and Pheo b). They absorb light from red, blue, and violet wavelengths with maximum absorption at 670 nm while reflecting green. Chls and their derivatives are inserted into DSSC as dye sensitizers because of their beneficial light absorption tendency modes; the most efficient of which is Chl α (chlorine2) derivative-methyl trans- 32-carboxy-pyropheophorbide α. The very first evidence of using Chl derivatives for photosensitization of nanoporous TiO_2 was reported by Kay and Grätzel [33].

Generally, the carboxylic acid groups in the photosensitizers establish an electronic coupling with the conduction band of TiO_2, which in turn helps to anchor the dye molecules and to inject electrons efficiently to the conduction band of TiO_2. Thus, the carboxylic acid groups are essential elements in a dye for it to make a DSSC efficient. However, Chl-a, Chl-b and the pheophytins do not make strong bonds with the TiO_2 surface, due to the weak interaction of the phytylester group and keto carbonyl groups. Chlorophyll c1 (Chl-c1) and Chlorophyll c2 (Chl-c2) with terminal carboxylic acid groups are able to connect through a conjugated double bond of the porphyrin macrocycle thus making a strong bond with the TiO_2 surface. A strong bond is needed to ensure electron is efficiently injected into the TiO_2 conduction band, and prevents gradual electron leakage by the electrolyte. Interestingly, the most efficient mode of Chl s as sensitizer is Chl α (chlorine2) derivative- methyltrans- 32-carboxypyropheophorbide α. Chl-a derivative has an ability to bind with TiO_2 and ZnO surfaces via different modes such as the bidentate chelating and monodentate modes [34].

12.3.4.3.3 Flavonoids

Flavonoids are the most important floral pigments associated with the angiosperms and they provide most of the colors in the visible spectrum. In many flowers, the development of a certain colour is initiated with the production and accumulation of flavonoid chromophores, and thereafter the other intrinsic andextrinsic factors determine the actual colour of the flower. Moreover, flavonoids are responsible for attracting insects to the plants, protecting plants from UV-B, signalling between plants microbes, and regulating auxin transport. Flavonoids has a chemical structure comprising of a C6-C3-C6 carbon framework with two phenyl rings connected by a three-carbon bridge that usually forms a third ring or more specifically a phenyl benzo pyran functionality. Usually the colour of the particular flavonoid is dependent on the degree of oxidation of the C-ring. They can, however, be further sub grouped into three classes depending on the position of the linkage of the aromatic ring to the benzopyrano (chromano) moiety. All the three sub-groups share a common chalcone precursor, since they are being biogenetically and structurally related to each other. Over 5000 naturally occurring flavonoids have been extracted from various plants, and divided according to their chemical structure as follows: flavonoids (2-phenylbenzopyrans), isoflavonoids (3-benzopyrans) and neoflavonoids (4- benzopyrans) [35]. The flavonoids (2-phenylbenzopyrans) itself has the following subclasses; anthocyanins, aurones, chalcones, flavones and flavonols. Among them, the anthocyanins play a major role in DSSC as sensitizers, while chalcones, aurones, flavones, and flavonols serve a more limited role as sensitizers.

However, most of the naturally existing flavonoid pigment molecules are characterized by having unbound or loosely bound electrons, whereas the amount of energy required for excitation of such electrons to a higher energy level is lower comparing to the others. Therefore, those pigment molecules can be energized by light within the visible range. The adsorption of flavonoid to the mesoporous TiO_2 surface is fast, displacing an OH^- counter ion from the Ti sites that combines with a proton donated by the flavonoid structure. Flavonoid pigmentation is based on the primary and secondary structures of flavonoids, and influenced by pH and the structures arising from self-association and inter and intra molecular interactions. The flavonoid dye extracted from Botuje (Jathopha curcas Linn) can be used as a DSSC sensitizer. This solar cell is sensitized to achieve up to J_{sc} 0.69 mAcm^{-2}, V_{oc} 0.054V, and *FF* 0.87, with a cell conversion efficiency (η) of 0.12% [36].

Nevertheless, even with similar structural characteristics, not all the flavonoids can absorb the visible light but only some have the ability while those that do not have that ability appears as colorless molecules. In that sense, the different pigment colors depend on the particular wavelengths of visible light that are absorbed by the particular molecule.

12.3.4.3.4 Anthocyanin

The sensitization of wide band gap semiconductors utilizing natural pigments is often a scribed to anthocyanin. Anthocyanins are the most abundant and wide spread pigment type of the flavonoids and they are the most important group of water-soluble pigments in plants. They absorb light at the longest wavelengths and are the basis for most orange, pink, red, magenta, purple, blue, and blue-black color to the flowers, fruits, and leaves of plants. The hue and structure of anthocyanins depend on pH and the presence of co-pigments. Anthocyanins are glycoside with an anthocyanidin (flavonoid) C6-C3-C6 skeleton. Particularly, the most common anthocyanidins are pelagonidin (orange), cyanidin (orange-red), delpinidin (blue-red), peonidin (purplish-red), petunidin (blue-red) and malvidin (blue-red). In an equilibrium solution, the anthocyanin occurs in four molecular forms; as the flavylium cation, the quinoidal base, the hemiacetal base, and chalcone. The relative amounts of these four forms vary with either pH of the solution or the structure of the anthocyanin. When the pH is < 2, anthocyanins exist as the stable flavylium cation. In fact, it is a very unique and one of the most important characters in the anthocyanin chemical structure which leads to a high absorption response at low pH. Anthocyanin molecule have carbonyl and hydroxyl groups bound to conductor TiO_2 surface, which excite electron transfer from the sensitizer (anthocyanin molecules) to the conduction band of porous TiO_2 film [37].

Table 12.1, summarizes the latest PV parameters such as λ_{max}, J_{sc}, V_{oc}, *ff*, and η, from a range of natural dyes as photosensitizers.

12.4 Conclusion and Future Outlook

Bio-colorants from natural sources are believed to be non-toxic, low cost, easily available, and biodegradable. These can be extracted from plant parts like leaves, flowers, roots, and barks in the form of carotenoids, flavonoids, anthocyanins, Chl s etc. However, the synthetic dyes and pigments have superior sensitization over natural dyes/pigments. Therefore, on the basis of considerable works of several scientific communities, due to environmental concerns, natural dyes/pigments can be used as photosensitizers in DSSCs. Hence, bio-colorants as light harvesting elements in DSSCs can contribute to a sustainable alternative for the future research dimension of energy production and conservation.

References

1. Eisenberg, R., Nocera, D.G., Preface: Overview of the forum on solar and renewable energy. *Inorg. Chem.*, 44, 6799–801, 2005.
2. Cuce, E., Riffat, S.B., Young, C-H., Thermal insulation, power generation, lighting and energy saving performance of heat insulation solar glass as a curtain wall application in Taiwan: a comparative experimental study. *Energy Convers. Manag.*, 96, 31–8, 2015.
3. Sharma, S., Siwach, B., Ghoshal, S.K. and Mohan, D., Dye sensitized solar cells: From genesis to recent drifts. Renew. Sustain. *Energy Rev.*, 70, 529–537, 2017.
4. O'Regan, B., Grätzel, M., A low-cost, high-efficiency solar-cell based on dye sensitized colloidal TiO_2 films. *Nature*, 353, 737–40, 1991.
5. Buscaino, R., Baiocchi C., Barolo, C., Medana, C., Gratzel, M., *et al.* A mass spectrometric analysis of sensitizer solution used for dye sensitized solar cell. *Inorg. Chim. Acta*, 361, 798–805, 2008.
6. Nogueira, A.F., Longo, C., De Paoli, M-A., Polymers in dye sensitized solar cells: Overview and perspectives. Coord. *Chem. Rev.*, 248, 1455–68, 2004.
7. Gokilamani, N., Muthukumarasamy, N., Thambidurai, M., Ranjitha, A., Velauthapillai, D., Utilization of natural anthocyanin pigments as photosensitizers for dye-sensitized solar cells. *J. Sol- Gel Sci. Technol.*, 66, 212–9, 2013.
8. Al-Ghamdi, A.A., Gupta, R.K., Kahol, P.K., Wageh, S., El. Shirbeeny, W., Improved solar efficiency by introducing grapheme oxide in purple cabbage dye sensitized TiO_2 based solar cell. *Solid State Commun.*, 183, 56–9, 2014.
9. Maldonado-Valdivia, AI., G alindo, E.G., Ariza,M.J., Garcia-Salinas, M.J., Surfactant influence in the performance of titanium dioxide photo electrodes for dye- sensitized solar cells. *Sol. Energy*, 91, 263–72, 2013.
10. Gong, J., Liang, J., Sumathy, K., Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials. Renew. Sustain. *Energy Rev.*, 16, 5848–60, 2012.
11. Calogero, G., Marco, G.D., Cazzanti, S., Caramori, S., Argazzi, R., Carlo, A.D., *et al.* Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits. *Int. J. Mol. Sci.*, 11, 254–67, 2010.

12. Tang, X., Qian, J., Wang, Z., Wang, H., Feng, Q., Liu, G., Comparison of low crystallinity TiO_2 film with nanocrystalline anatase film for dye-sensitized solar cells. *J. Colloid Interface Sci.*, 330(2), 386–91, 2009.
13. Park, N.G., Van, De., Lagemaat, J., Frank, A.J., Comparison of dye-sensitized rutile- and anatase-based TiO_2 solar cells. *J. Phys. Chem. B*, 104(38), 8989–94, 2000.
14. Kalyanasundaram, K., Grätzel, M., Applications of functionalized transition metal complexes in photonic and optoelectronic devices. Coord. *Chem. Rev.*, 177, 347–414, 1998.
15. Fukui, A., Komiya, R., Yamanaka, R., Islam, A. and Han, L., Effect of a redox electrolyte in mixed solvents on the photovoltaic performance of a dye-sensitized solar cell. *Sol. Energy Mater. Sol. Cells*, 90(5), 649–58, 2006.
16. Bai, Y., Cao, Y., Zhang, J., Wang, M., Li, R., Wang, P., *et al.*, High-performance dyesensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nat. Mater.*, 7, 626–30, 2008.
17. Wu, J., Lan, Z., Lin, J., Huang, M. and Li, P., Effect of solvents in liquid electrolyte on the photovoltaic performance of dye-sensitized solar cells. *J. Power Sources*, 173(1), 585–91, 2007.
18. Mehmood, U., Rahman, S.U., Harrabi, K., Hussein, I.A. and Reddy, B.V.S., Recent advances in dye sensitized solar cells. *Adv. Mater. Sci. Eng.*, 2014, 12, 2014.
19. Wang, P., Zakeeruddin, S.M., Moser, J-E, Grätzel, M., A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells. *J. Phys. Chem. B*, 107, 13280–5, 2003.
20. Wu, J., Lan, Z., Hao, S., Li, P., Lin, J., Huang, M., Fang, L. and Huang, Y., Progress on the electrolytes for dye-sensitized solar cells. *Pure Appl. Chem.*, 80, 2241–58, 2008.
21. Bach, U., Lupo, D., Comte, P., Moser, J.E., Weissortel, F., Salbeck, J., *et al.*, Solid-state dyesensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies. *Nature*, 395, 583–5, 1998.
22. Luque, A.S.H., Handbook of photovoltaic science and engineering. In: Dye-sensitized solar cells, 2nd ed., K. Hara, S. Mori (Eds.), John Wiley & sons Ltd, UK, 2011.
23. Narayan, M.R., Review: dye sensitized solar cells based on natural photosensitizers. Renew. Sustain. *Energy Rev.*, 16(1), 208–15, 2012.
24. Syrrokostas, G., Siokou, A., Leftheriotis, G. and Yianoulis, P., Degradation mechanisms of Pt counter electrodes for dye sensitized solar cells. *Sol. Energy Mater. Sol. Cells*, 103, 119–27, 2012.
25. Andrade, L., Ribeiro, H.A., Mendes, A., *Dye-sensitized solar cells*: *An overview Encyclopedia of inorganic and bioinorganic chemistry*. John Wiley & Sons Ltd., 2011.
26. Li, P., Wu, J., Lin, J., Huang, M., Huang, Y., Li, Q., High performance and low platinum loading Pt/carbon black counter electrode for dye-sensitized solar cells. *Sol. Energy*, 83, 845–849, 2009.

27. Wan, H., *Dye sensitized solar cells, literature seminar*. AL, United States of America: The University of Alabama, 2004.
28. Ryan, M., Progress in ruthenium complexes for dye sensitised solar cells. *Platinum Metals Rev*., 53, 216–8, 2009.
29. Ooyama, Y., Harima, Y., Molecular designs and syntheses of organic dyes for dye sensitized solar cells. *Eur. J. Org. Chem*., (18), 2903–34, 2009.
30. Kumara, N.T.R.N., Ekanayake, P., Lim, A., Liew, L.Y.C., Iskandar, M., Ming, L.C., etal., Layered co-sensitization for enhancement of conversion efficiency of natural dye sensitized solar cells. *J. Alloys Compd*., 581, 186–91, 2013.
31. Wang, X.F., Koyama, Y., Nagae, H., Yamano, Y., Ito, M. and Wada, Y., Photocurrents of solar cells sensitized by aggregate-forming polyenes: enhancement due to suppression of singlet–triplet annihilation by lowering of dye concentration or light intensity. *Chem. Phys. Lett*., 420(4–6), 309–15, 2006.
32. Wang, X.F., Matsuda, A., Koyama, Y., Nagae, H., Sasaki, S.I., Tamiaki, H. and Wada, Y., Effects of plant carotenoid spacers on the performance of a dye sensitized solar cell using a chlorophyll derivative: enhancement of photocurrent determined by one electron-oxidation potential of each carotenoid. *Chem. Phys. Lett*., 423(4–6), 470–5, 2006.
33. Kay, A., Grätzel, M., Artificial photosynthesis. 1. Photosensitization of TiO_2 solar cells with chlorophyll derivatives and related natural porphyrins. *J. Phys. Chem*., 97(23), 6272–7, 1993.
34. Wang, X.F., Kitao, O., Hosono, E., Zhou, H., Sasaki, S.I. and Tamiaki, H., TiO_2 and ZnO-based solar cells using a chlorophyll a derivative sensitizer for light-harvesting and energy conversion. *J. Photochem. Photobiol. A*: *Chem*., 210(2–3), 145–52, 2010.
35. Marais, J.P., Deavours, B.E.T.T.I.N.A., Dixon, R.A. and Ferreira, D., The stereochemistry of flavonoids, in: *The Science of Flavonoids*, E. Grotewold (Ed.), pp. 1–46, Springer, New York, 2006.
36. Boyo, A.O., Abdulsalami, I.O., Oluwa, T., Oluwole., S.O., Umar, A., Development of dye sensitized solar cells using Botuje green leaves (*Jathopha Curcas* Linn). *Sci. J. Phys*., 2013.
37. Hao, S., Wu, J., Huang, Y.,Lin, J., Natural dyes as photosensitizers for dye-sensitized solar cell. *Sol. Energy*, 80 (2), 209–14, 2006.

PART III

ADVANCED MATERIALS AND TECHNOLOGIES FOR COLORATION AND FINISHING

13

Advanced Materials and Technologies for Antimicrobial Finishing of Cellulosic Textiles

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Abstract

Due to the increased demands for eco-friendly textile wet-processes and products as well as for developing innovative multifunctional cellulosic textiles taking in consideration quality, ecology and economy concerns, utilization of green antimicrobial finishing materials, along with careful selection and implementation of the best available technologies in textile finishing are growing rapidly and more promising economic, environment, and social benefits are expecting. This chapter highlights the wet processing of cellulosic textiles and their inherent drawbacks. Chemistry of traditional antimicrobial agents, application methods, and their disadvantages are addressed. Main requirements for proper antimicrobial agents, chemistry, mode of interaction, antimicrobial effects, and positive impacts of advanced bioactive agents along with emerging technologies, as eco-friendly alternatives to the traditional ones, are also covered. Full evaluation and diverse applications of developed antimicrobial cellulosic textiles are described. Finally, recent progress and future trends in multi-functional protective cellulosic fabrics are discussed.

Keywords: Cellulosic textiles, advanced materials, emerging technologies, eco-friendly processing, antimicrobial textiles, evaluation and potential applications

13.1 Cellulosic Fibers

Cellulose polymer is one of the most abundant and cheap polysaccharides obtained from natural sources. Cellulose is biodegradable, biocompatible,

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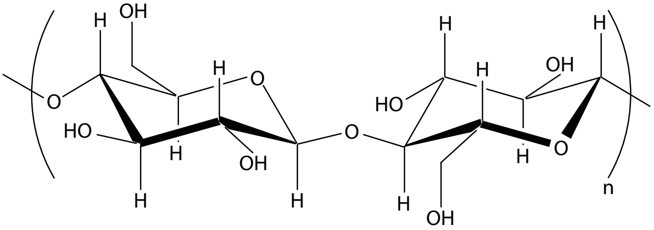


Figure 13.1 Chemical structure of cellulose.

and renewable. Its properties can be tailored to be fitted with various fields [1]. Cellulose is linear chains polymer composed of β-D-glucopyranose units connected by β-1,4-glycosidic linkage (Figure 13.1). The degree of polymerization is strongly dependent on the source of cellulose. It reaches approximately 10,000 in wood and 15,000 in native cotton [2]. This linear polymer contains three pendant –OH groups per anhyroglucose unite. Two of the –OH groups are secondary and attached at C3 and C4. The third one is primary ($-CH_2OH$) and attached to C-6. The latter –OH group is more reactive so most of the chemical modification of cellulose, e.g. esterification, etherification, copolymer grafting, have occurred on this group to confer cellulose new favorable properties. [3-5]. Cellulosic fibers are potentially used in textile industry individually and in combination with each other because of their softness, absorbent, and comfortability properties. Cellulosic fibers could be naturally occurring such as cotton, flax, jute, or regenerated like viscose, bamboo, rayon, lyocell, and tencel. Regenerated fibers are obtained from chemical transformation of cellulose from tree wood, inner pith, and leaves from bamboo plants using an eco-friendly aqueous solvent i.e. N-methyl-morphlene N-oxide [2].

Cellulosic substrates are usually modified to improve their properties, confer them new functionalities and to increase their global consumptions [4]. This modification could be (i) physically (ii) physico-chemically e.g. plasma, corona, laser and/or (iii) chemically treatments.

13.2 Wet Processing of Cellulosic Textiles

13.2.1 Pre-Treatment

Figure 13.2 demonstrates the key steps in wet processing of cotton cellulose textiles. Pretreatment of natural cellulosic fibers is necessary to remove the latent impurities such as noncellulosic impurities e.g. wax, fats, pectin,

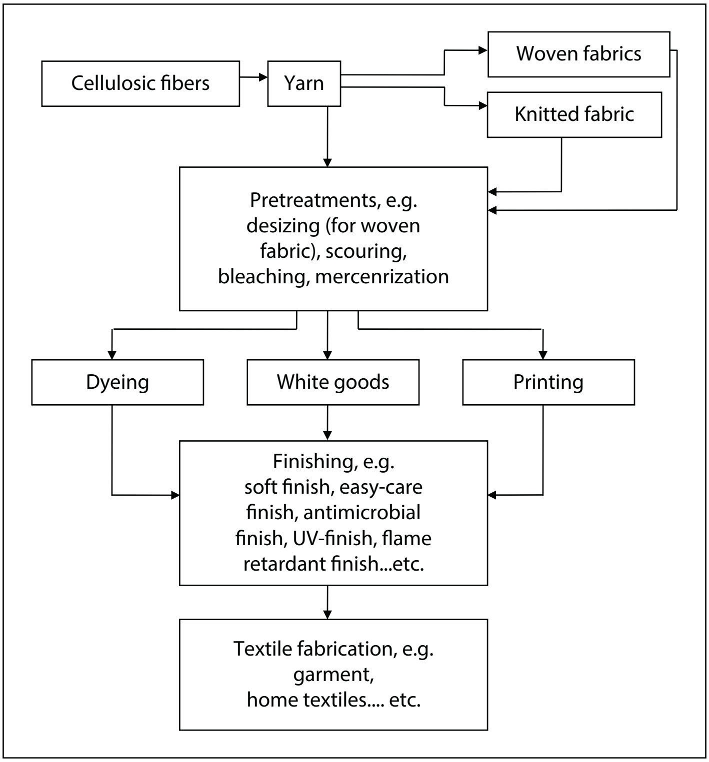


Figure 13.2 Key steps in wet processing of cotton cellulose textiles.

lignin, and seed husks. Furthermore, this process is used to eliminate the added chemicals during spinning, weaving, or knitting processes e.g., spinning oils, sizes, and lubricants. Pretreatment steps improve the properties of the cellulosic fibers such as enhancing the wettability of fibers, improving the degree of whiteness by removing the coloring materials and leading to a uniform successive coloration and/or finishing processes with maintaining the physico-mechanical properties of the treated fabrics. Pretreatment process consists of the following stages [6, 7]:

- Singeing to obtain and get soft fabric surface by removing protrusive fibers ends.
- Desizing to remove sizing materials, e.g., starch, CMC, PVOH…etc.
- Scouring to swell the cellulosic fibers, seed husks, and to enhance the wettability via removal of hydrophobic noncellulosic impurities.

- Bleaching to eliminate the pre-swell seed husks, oxidize natural coloring matters and get rid of any remnant size, e.g., starch and polyvinyl alcohol.
- Mercerizing to improve dye ability, tensile strength, and dimensional stability as well as to increase luster, especially in case of using chain mercerization.
- Optical brightening especially in case of seeking of high degree of whiteness.

More than 50% of all drawbacks that appear during the subsequent wet processing i.e., dyeing, printing, and finishing, are attributed to wrong or inadequate pretreatment processes.

Application of cleaner production opportunities to pretreatment processes is highly demanded for eco-friendly textile processes and products taking in consideration product quality, ecology and economy concerns.

13.2.2 Coloration

An efficient pretreatment steps are essentially required for subsequent coloration of cellulosic substrates, dyeing and/or printing, for attaining significant improvements in coloration properties, i.e. high color yield, remarkable fastness properties, along with achieving right- first- time reproducibility.

The most common coloring agents for dyeing and/or printing of cellulosic substrates are direct, reactive, vat, and sulfur dyes along with pigment colorant [8, 9].

Utilization of eco-friendly colorants and greener coloration auxiliaries, modification of existing processes and equipments, and developments of right- first- time production technology to achieve highly production processes and environmentally friendly cellulosic dyeings or prints with minimal environmental impacts with reasonable costs represent the main prerequisites for sustainable products[10, 11].

13.2.3 Finishing

Cellulosic substrates are biodegradable, hydrophilic, comfort, and eco-friendly in nature. However, they certainly lack many of desired functional properties like antimicrobial performances, UV protection, self-cleaning, flame retardant, insect repellent, easy care, dimensional stability, water and oil repellent…etc. [4]. Therefore, development of innovative functional textile auxiliaries as well as application techniques with the goal of imparting innovative functional and comfort properties to cellulosic substrates, especially in the final step of textile processing taking into account type of substrate, quality and desired end-use of the finished product in environmentally friendly ways, cost/benefit ratio and available technology are greatly demanded [12].

Textile finishing techniques can be broadly classified into mechanical, chemical, and bio-finishes which are applied individually or in combination with each other to achieve the desired fabric properties and to create an expanded array of multi-functionalization of cellulosic textiles, which in turn expands their potential applications and utilizations in novel textile products. The most common textile finishes and imparted functional properties are summarized in (Table 13.1).

Among the various functional finishes listed in Table 13.1 and to cope with increasing awareness of ecological and environmental concerns, as well as on hygiene and well-being, antimicrobial functionalization of cellulosic substrates have received much attention in recent years. To cater for these demands, this chapter discusses mainly antimicrobial finishes of cellulosic textile with focuses on type, chemistry, advantages, and disadvantages of currently used antimicrobial agents, mode of action, positive impacts of using new generation of antimicrobial agents, full evaluation and expected diverse application of functionalized textiles as well as future prospects for high performance functional finishes.

13.3 Antimicrobial Finishing of Cellulosic Textiles

The global competitions for developing advanced antimicrobial cellulosic textiles increase the challenges for developing new antimicrobial agents. Cellulosic fibers are commonly attached by microorganisms present in air, water and by direct contact with skin. Moreover, the fabrics surfaces create a favorable environment for microorganisms' growth that can lead to biodeterioration, irritation, odor problems, staining and degradation of cellulosic fabrics [62]. The destructive influence of microorganisms not only concerns the cellulosic fabrics, but it extends to the negative impact on the user's life and also the environment. Therefore, the demand for developing cellulosic textiles having the ability to kill or inhibit microorganisms, maintaining the quality of the cellulosic fabrics from microbial degradation and reducing the release of body odor is rapidly growing [63]. For this respect, antimicrobial agents are applied onto textile products to impart them the antimicrobial activity. This process is usually described as antimicrobial finishing [64].

Depending on the nature of the antimicrobial agents, the mechanism of how they can affect on the microorganisms usually include killing or

Table 13.1 Possible Functional Finishes for Cellulosic Textiles.

Type of finish	Positive impact	References
1. Mechanical		
Calendering	Improve flatness and glase of the fabric	[13, 14]
Embossing	Produce a pattern	
Raising	Provide greater warmth to the wearer	
Sanforizing	Control the shrinkage of woven or knitted fabrics	
2. Chemical finishes e.g.		
Soft finish	Improve the fabric softness	[15-21]
Soil release finish	Facilitate removal of soils during laundering	[22–24]
Stain & oil resistance finish	Prevent soil & stains from being attached to fabrics	[18, 20, 25–27]
Easy care finish	Improve fabric resiliency & provide easy care performance	[21, 28–31]
Self-cleaning finish	- Impart lotus effect to the surface - Decolorize stains via photocatalayzation	[32–34]
Odor-resistant finish	Adsorb or remove unpleasant odors via entrapping into the grafted β-CD cavities through host-guest interactions	[35]
Antimicrobial finish	- Prevent the growth and/or kill harmful microorganism, e.g. pathogenic bacteria - Protect both the consumer & textile itself - Enable cellulosic to remain fresh from longer time	[36–45]
Insect repellent finish	- Protect human beings from the bite of mosquitoes - Offer safety from mosquito borne diseases	[46]
UV-protection finish	- Improve the UV-protection especially the harmful UV-B rays - Block, scatter and/or absorb the UV-A & UV-B rays to avoid skin cancer	[47–53]

(*Continued*)

Table 13.1 Cont.

Type of finish	Positive impact	References
Radiation protection finish	- Achieve radiation, both ionizing & non-ionizing, shielding - Gain protection	[54]
3. Bio-finishes		
Cellulases	- Impart durable softness to cellulosic substrates without adversely affecting hydrophilicity	[55–61]
Lipases or esterases	Enhance hydrophilicity & wettability of polyester	

inhibition of the growth of the microorganisms by one or more of the following [7, 12, 65, 66]:

- Damaging the microorganisms cell wall.
- Inhibiting the synthesis of cell wall, proteins and nucleic acids.
- Changing the cell wall permeability.
- Inhibition of enzyme action by killing or inhibiting the microorganism.
- Disruption of cytoplasmic membranes of bacterial cells via physical and/or ionic phenomena.
- Subsequent release of the cytoplasmic constituents

The mode of action of the different antimicrobial agents is very important. It explains how the antimicrobial agents work. Antimicrobial agents that are not chemically bonded to the textile fibers (leaching type) act by controlled release mechanism and their antimicrobial activity can be attributed to their gradual release, but the continuous leaching of these types of antimicrobial agents led to the decrease of their concentration and therefore decay their antimicrobial activity. On the contrary, antimicrobial agents that are chemically bonded to the fibers (non-leaching type) make a barrier against the microorganisms. However, the efficiency of these antimicrobial agents could be limited by the dead microorganisms which cover the bio-barrier and cause its deactivation [67].

Figure 13.3 shows the different types of antimicrobial agents and the advantages and the disadvantages of each type.

13.3.1 Criteria for Proper Antimicrobial Agents

The rapid growth in the production of antimicrobial cellulosic fabrics has led to many opportunities for developing novel technologies to enhance their antimicrobial activity [68]. Nevertheless, most of the traditional antimicrobial agents have lot of disadvantages such as low antimicrobial activity, low durability or self-toxicity, in addition to their influence on the environment and the biological systems [68, 69]. Therefore, the demand for developing new antimicrobial agents is very important. The new antimicrobial agents should achieve several criteria such as being effective against a broad range of harmful microorganisms without having negative impacts on human heath, friendly microorganisms, nonpathogenic bacteria, and the environment. Moreover, they should not influence adversely on the comfortability of the fabric, be colorless, odorless and compatible with other textile finishing agents. They should be resistance to the influence of the environment and the processing conditions, and be durable for repeated washing cycles [6].

13.3.2 Best Available Techniques

Different approaches have been used for conferring cellulosic textiles the antimicrobial activity. Generally, the antimicrobial activity can be attained

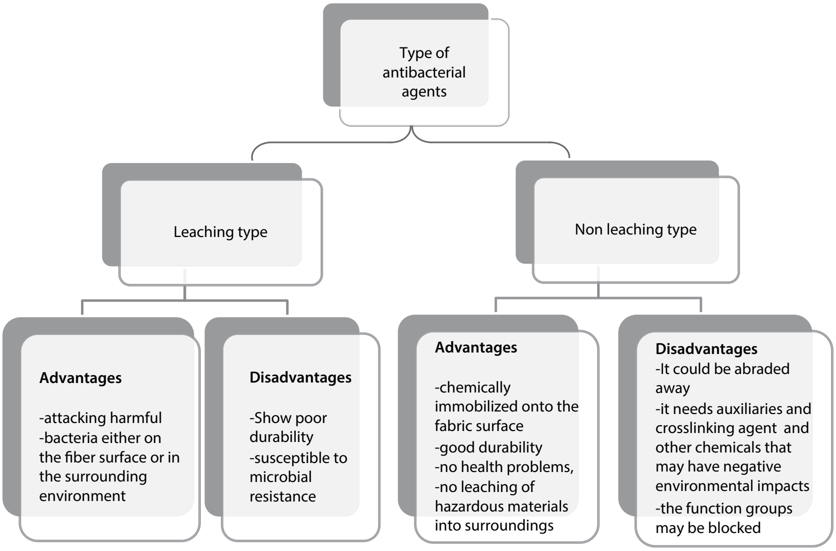


Figure 13.3 Different types of action of antimicrobial agents.

either by incorporating the antimicrobial agent into the polymer solution before extrusion or in the spinning bath, as in case of polyester, or by an after-treatment processes e.g., exhaustion, pad-dry-cure, coating technology, chemical or physical modification of the fabric, spraying or foaming technique; or by using sol-gel or encapsulation processes.

The method of treating the cellulosic textiles with antimicrobial agents is strongly dependent on the chemical nature of the antimicrobial agents, the structure of fabric, the type of fiber and the required performance of the final product [70-73].

13.4 Traditional Antimicrobial Finishing Chemicals, Application Methods, and Disadvantages

The antimicrobial agents could be chemically synthesized or it could be naturally occurring. For decade several antimicrobial agents were used for cellulosic fabric finishing e.g., quaternary ammonium compounds, polybiguanides, N-halamines, triclosan, and, chitosan, etc. [74].

13.4.1 Synthetic Antimicrobial Agents

13.4.1.1 Quaternary Ammonium Compounds

Quaternary ammonium derived compounds (QACs) (Figure 13.4) have been used for decades as antimicrobial agent for cellulosic textile finishing. These compounds showed abroad activity against Gram-negative and Gram-positive bacteria, moulds, and yeasts [75]. Their antimicrobial activities emerge from the interaction between the cationic ammonium groups and the membrane cell of the microorganism. This interaction leads to the formation of surfactant-microbe complex and interruption in the function of the microorganisms [76]. Nevertheless, the application of QACs on cellulosic fabrics showed lot of drawbacks like the poor binding of these

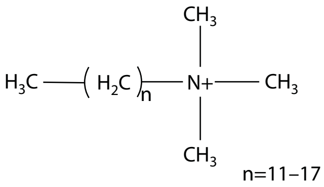


Figure 13.4 Example for the quaternary ammonium compound.

compounds to the cellulosic chains, therefore their physical linkage to the fiber led to poor durability of QACs. To overcome these drawbacks, new QACs were developed by incorporating them in polymer structure via synthesizing new monomer containing quaternary ammonium group which polymerize to give polycationic compound [77].

QACs based liquid solution could be applied onto textile materials using different techniques e.g., padding, spray, or foam-deposition methods. Recently, many researchers have taken the advantage of sol-gel method to incorporate QACs within silica network on the textile fibers surface physically [75, 78]. Gao *et al.* have synthesized zinc oxide sol containing quaternary ammonium salts (DMDAAC-ZnO) from zinc acetate and diallyl dimethyl ammonium chloride using sol–gel method. Cotton fabric was finished using the sol containing quaternary ammonium. The antibacterial activity of the treated fabric was evaluated qualitatively and quantitatively. The treated fabric revealed antibacterial activity against *E. coli* with inhibition rate of 72.6 % [78]. Following the successful approach of incorporation of QACs with ZnO on the surface of cellulosic textile, cotton fabric was finished with sol containing QAC -TiO_2 NPs by Messaoud *et al.* the finished fabric showed strong antibacterial activity on cotton-based fabrics against both Gram-negative and Gram-positive bacteria [75].

13.4.1.2 Poly (Hexamethylenebiguanide) (PHMB)

Poly (hexamethylenebiguanide) (PHMB) is polycationic amines, which belongs to polybiguanide compounds (Figure 13.5). Due to its high antimicrobial activity, PHMB is widely used as bacteriocide agents against many pathogens in medical and cosmetics fields and also for finishing cellulosic fabrics. PHMB could bind to cellulosic fabrics by the electrostatic interaction with the anionic carboxylic group resulted from the pretreatment processes of the cellulosic fabrics. This electrostatic linkage is weak and led to the liberation of free PHMB. Dyeing of cellulosic fabrics with anionic dye provide sulfonic acid sites which could interacted with PHMB and reduce the release of free PHMB [79, 80].

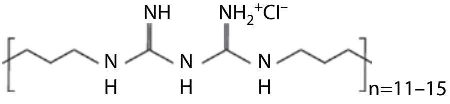
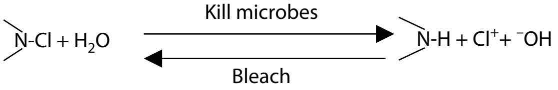


Figure 13.5 Chemical structure of poly(hexamethylenebiguanide)

13.4.1.3 N-Halamine Compounds

N-halamine compounds (Figures 13.6-13.8) have gained great interest in recent several decades, due to their excellent disinfection efficacies against microbes including fungi, viruses, and bacteria, within a short contact time. N-halamine compounds usually contain one or more nitrogen–halogen linked by covalent bonds [81]. This high antimicrobial ability is because of the oxidative chlorine which is formed after the chlorination of N-halamine compounds. The oxidative chlorine could oxidize the receptors in the cell and cause the death of the microorganisms. The antimicrobial ability makes N-halamines a desired choice for antibacterial finishing of textiles. Jiang *et al.* have finished cotton fabric with monochloro-s-triazine-based N-halamine using exhaustion method and the treated fabric could inhibit the growth of *S. aureus* and *E. coli* with reduction rate of 100% [1], according to the following reaction.



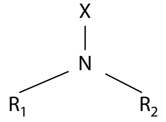


Figure 13.6 General chemical structure of N-halamine compounds. R_1, R_2 = H or Cl or Br or organic group or inorganic group. X = Cl or Br or I [81].

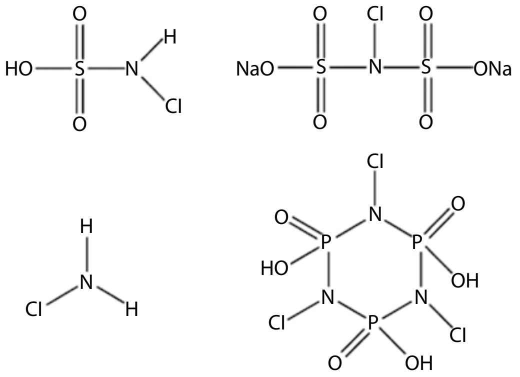


Figure 13.7 Different examples of inorganic N-halamine compounds [81]. Reprinted from "Antimicrobial NHalamine Polymers and Coatings: A Review of Their Synthesis, Characterization, and Applications", F. Hui, 2013, *Biomacromolecules, 14*, p. 586, Copyright 2013. American Chemical Society.

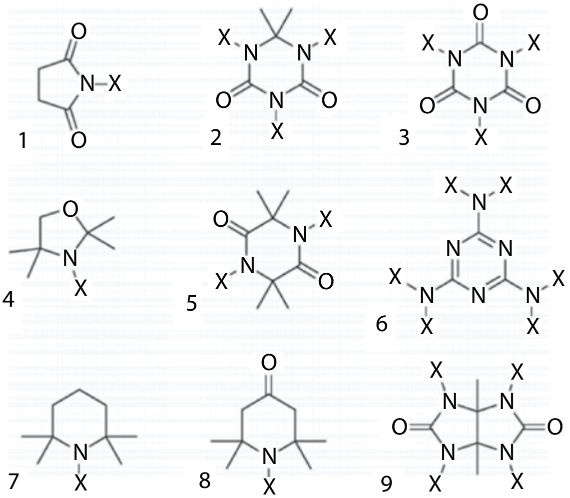


Figure 13.8 Different examples of organic cyclic N-halamine compounds [81]. Reprinted from Antimicrobial N-Halamine Polymers and Coatings: A Review of Their Synthesis, Characterization, and Applications", F. Hui, 2013, *Biomacromolecules, 14*, p. 586, Copyright 2013. American Chemical Society.

13.4.1.4 Triclosan

Triclosan (2,4,4-hydrophenyl trichloro (II) ether) (Figure 13.9) is well known antiseptic and disinfectant agent. It has a broad spectrum against both gram-negative and gram positive bacteria but it has poor activity against fungi. Triclosan inhibits the growth of bacteria by blocking the fatty acid synthesis needed for membrane cell building and lipid synthesis. Moreover, triclosan disrupt the cell wall of the microorganism by an electro chemical mode of action which causes metabolites leakage and disabling other cell functions. Due to the antibacterial properties of triclosan, it has found widespread use in different products including toothpastes, deodorants, soaps, polymers, and fibers [82]. Despite the fact that triclosan has tendency to form endocrine disruption, moreover, it was found that aquatic species including algae, invertebrates and some types of fish were more sensitive to TCS relative to mammals. Serious concerns were raised for triclosan in fibrous material finishing as a direct consequence of continuous release of triclosan to the environment by repeated washing cycles which negatively impacted the aquatic life [83].

13.4.2 Natural Antimicrobial Agents

The awareness of healthcare is continuously increasing and wide range of researches has been done to obtain eco-friendly antimicrobial cellulosic textile

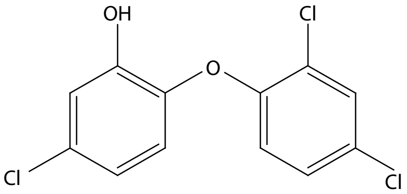


Figure 13.9 Chemical structure of triclosan.

products taking into account both the ecological and environmental concerns. Due to the toxicity and non-degradability of most synthetic antimicrobial agents, many R&D efforts have been done to replace the harmful antimicrobial agents with natural and biodegradable [84, 85]ones based on sustainable biopolymers e.g., chitosan, or natural products e.g., extracts of herbs.

This part will focus on the using of biopolymer and natural product as antimicrobial agents to produce eco-friendly antimicrobial cellulosic textiles.

13.4.2.1 Chitosan

Chitosan (Figure 13.10) is obtained by deacetylation of chitin. This cationic biopolymer is widely used in medical field especially in artificial skin, blood anticoagulants, drug-delivery systems, food industry, and antioxidant due to its biodegradability, compatibility, nontoxicity, and broad spectrum antimicrobial activity. Chitosan in its cationic form has antimicrobial activity against different bacteria and fungi by inhibiting the normal metabolism of the microorganisms and causing death of their cells. The disadvantage of using of chitosan as antimicrobial agents to finish cellulosic textiles was the poor adhesion of chitosan to the textile surface i.e., poor durability. This problem was solved by the chemical modification of chitosan to improve the bonding force between chitosan and textiles [86]. Chitosan contains two hydroxyl groups and one amino which could diversify the modification of chitosan. Quaternization of chitosan amino group enhanced the antimicrobial activity against different microorganisms in addition to improving its water solubility [87]. Another approach was the grafting of chitosan onto cellulosic fabrics by UV curing method [88] or by using proper crosslinker e.g., 1,2,3,4–buthanetetracarboxylic acid BTCA. The negatively charged carboxyl groups of BTCA used as reactive binding sites for amino groups of chitosan to increase its concentration on the fabric[89, 90]. Most of chitosan derivatives showed high antibacterial activity against both *E. coli* and *S. aureus* in addition to high durability. Table 13.2 reviews the use of chitosan/chitosan derivatives for finishing cellulosic fabrics and the antimicrobial activity of the product.

Table 13.2 Using of Chitosan/Chitosan Derivatives for Antimicrobial Functionalization of Cellulosic Substrates.

Antimicrobial agent	Properties	Treated fabric	Finishing formulation and finishing technique	Feature of the fabric	Ref.
I. Chitosan					
Chitosan	Cationic polymer has high compatibility, nontoxicity biodegradability, strong antimicrobial agent	Cotton	- Chitosan/photointiator - impregnation for 12 h, drying for 10 min at 80 °C–100 °C and finally UV-curing for 30–60 sec, in inert atmosphere.	All the treated fabrics showed high antibacterial activity	[91]
Chitosan		Viscose	- Chitosan/BTCA - Viscose samples were impregnated with the help of a foulard/drying in microwave.	The combination chitosan/BTCA supported by microwaves drying led to increase the proportion of amino groups on the fabric which enhance the antibacterial activity of the fabric against *E coli* and *C. albicans* by 100%	[90]

Chitosan	Cationic polymer has high compatibility, nontoxicity biodegradability, strong antimicrobial agent	Cotton	- Chitosan/1,2,3,4-butane tetracarboxylic acid (BTCA) as crosslinker/ sodium acetate trihydrate as a catalyst - Pad-dry-cure	- Cotton fabrics were treated with different Mwt chitosan which could be achieved by subjecting high molecular weight chitosan to enzymatic hydrolysis - The treated cotton fabrics showed antimicrobial activity against both gram-positive and gram-negative bacteria and yeast tested over 10 washes	[89]
Chitosan		Cotton	- Chitosan/radical Photoinitiator Darocur1173 - The fabrics were impregnated in the mixture for 12 h, drying for 10 min at 100 °C and finally UV-curing.	Cotton fabrics was grafted with chitosan using UV-curing which enhance the chitosan presence even after the washing and revealed great antibacterial efficiency of the fabric against both *E. coli* and *S. aureus*.	[88]

(*Continued*)

Table 13.2 Cont.

Antimicrobial agent	**Properties**	**Treated fabric**	**Finishing formulation and finishing technique**	**Feature of the fabric**	**Ref.**
Chitosan		Viscose/spandex blend	- Chitosan - Surface modification and in situ immobilization of chitosan using non-thermal oxygen plasma	Air or oxygen Plasma treated viscose fabric was finished with chitosan. Oxygen treated fabric showed antibacterial activity against *S. aureus* and *E. coli* higher than that of the air plasma treated fabric or untreated fabric.	[92]
II. Modified chitosan					
O-quaternized-N,N-biethyl-N-benzyl ammonium chitosans chloride (O-QCTS-DEBn) O-quaternized-N-chitosan Schiff bases (O-QCTSS) O-quaternized-N-benzyl-chitosans (O-QCTS-Bn).	- Water soluble chitosan derivatives - Bearing double functional groups - Enhance the antimicrobial activity of chitosan	Cotton	- Chitosan derivatives is 3% (owf), citric acid crosslinker (14%, o.w.f), NaH2PO2 catalyst (6%. owf). - Pad-dry-cure	- The treated fabric exhibited high antimicrobial activity and good washing resistance against *E. coli* and *S. aureus* - The antimicrobial efficiency of O-QCTSS treated fabric was still over 75% after 20 washing cycles which was better than that of the fabric treated with the other derivatives.	[87]

1-Hydroxymethyl-5,5-dimethylhydantoin chitosan	- Enhanced the antimicrobial activity toward different microorganisms - Enhance the stability of chitosan in wide range of pH	Cotton	- Chitosan/BTCA as crosslinker/ sodium hypophosphite as a catalyst - Pad-dry-cure	The synthesized chitosan derivative was grafted onto cotton fabrics using BTCA crosslinker. Treated cotton swatches led to exceptional antibacterial activity against *S. aureus* and *E. coli*	[86]
N-benzyl-N,N-diethyl Chitosan Quaternary Ammonium BDCQA	- Water soluble chitosan derivatives - Increase the number of Quaternary Ammonium in chitosan - Enhance the antimicrobial activity of chitosan	Cotton	- γ-Mercaptopropyl trimethoxysilane / BDCQA - Padding for different time	Cotton treated BDCQA exhibited broad spectrum and high antibacterial activity against gram negative, gram positive and drug-resistance bacteria. The antibacterial activity was over 95 % even after 20 laundering cycles.	[69]

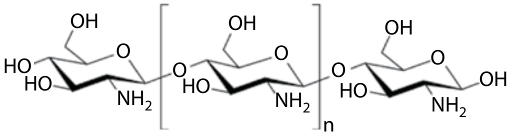


Figure 13.10 Chemical structure of chitosan.

13.5 Advanced Antimicrobial Agents

13.5.1 Antimicrobial Agent Based on Natural Products

Medicinal plants and extracts from herbs have been used as antimicrobial agents in different fields. They are biodegradable and renewable biocides. There are many extracts and essential oils from different medicinal plants that are widely known for their antibacterial and fungicidal properties, e.g., *Menthapiperita, Thymus vulgaris, Origanum compactum*, *Salvia* etc. Their antimicrobial activity could be due to the presence of different groups e.g., phenolics, saponins, flavonoids, coumarins, alkaloids terpenoids, and tannins [93]. These eco-friendly antimicrobial agents are very good candidates used to replace the carcinogenic and toxic synthetic antimicrobial agents to impart antimicrobial activity to the different textiles products. Thyme essential oil was used for finishing cellulosic fabrics and it led to very promising antimicrobial activity [62].

Table 13.3 illustrates some examples of antimicrobial agents from natural products.

The antimicrobial efficiency of Aleovera finished cellulosic textiles was studied. It was found that *Aloe vera* gel was effective enough for imparting good antibacterial activity and less adhesion of both gram-positive and negative bacteria to different cellulosic fabrics [68]. Nadiger *et al.* have finished cotton fabric with different concentration of *Aloe vera* and 1,2,3,4-butanetetracarboxlic acid as a crosslinking agent using pad-dry-cure technique. The attaching of *Aloe vera* to hydroxyl group of cotton was confirmed using IR and scanning electron microscopy. The antibacterial activity of the treated samples was evaluated qualitatively by AATCC-147 method. The concentration 3 % (w/v) of *Aloe vera* gel was effective enough for imparting good antibacterial activity and less adhesion of both gram-positive and negative bacteria (Figure 13.11) [68]. Khurshid *et al.* have used exhaustion method for the finishing of bleached cotton fabric with three different natural antimicrobial agents; aloe gel, neem extract and their hybrid combination; using different concentration at 5, 7, and 10%

Table 13.3 Some Antimicrobial Agents Based on Natural Products for Antimicrobial Functionalization of Cellulosic Textiles.

Type of natural products	Antimicrobial agent	Main active ingredients	Treated fabrics	Application method	Feature of the fabric	Ref.
1. Plant extract	i. Aloe vera	200 active compounds, including 20 minerals, 18 amino acids and 12 vitamins	Towel	Fabric samples were treated with aloe gel, neem extract and their hybrid combination via exhaustion method at pH 5, and liquor ratio of 1:20 for 30 minutes Then the samples were dried at 80 °C for 15 minutes in a tumble drying machine.	The samples revealed that they have antibacterial activity against *E. coli* and *S. aureus*, and antifungal activity against *Aspergillus niger*. The antimicrobial activity of the hybrid combination was more effective and durable to washing up to 20 washing cycle	[74]
		Acemannan, the polysaccharide responsible for the anti-inflammatory behavior and antimicrobial effect	Nonwoven cotton	- Fabrication of oxidized pectin (OP)-gelatin-aloe vera (OP-Gel-Aloe) - Fabrication of (OP-GelCurcumin) - Fabrication of OPGel-Aloe Curcumin - cotton samples were then dipped into the solution separately and then dried at room temperature	The OP-Gel-Aloe and OP-Gel-Curcumin dressings exhibited ~83% and ~93% efficiency, respectively and the antibacterial efficacy was reduced for OPGel-Aloe Curcumin The results revealed that OP-Gel-Aloe biocomposite dressings had a strong potential for wound management.	[94]

(*Continued*)

Table 13.3 Cont.

Type of natural products	Antimicrobial agent	Main active ingredients	Treated fabrics	Application method	Feature of the fabric	Ref.
	ii. Tulsi leaves	Eugenol	Cotton	Methanolic extract of Tulsi by dipping method using LR 1:10 followed by drying at 80°C for 15 min	The treated cotton exhibited antimicrobial activity against the strains of *S. aureus* and *E. coli*. the results showed 73% bacterial reduction in the quantitative challenge test	[95]
		Eugenol	Cotton	Microencapsulation, and resin as cross-linking	The treated cotton showed considerable zone of inhibition and about 99% bacterial reduction in the quantitative test method	[96]
	iii. Prickly chaff flower (*Achyran thesaspera*)	Alkaloids and saponins	Cotton	Citric acid as the cross-linking agent using pad-dry-cure	The treated samples showed bacterial reduction of 92.84% and 50.29% against *S. aureus* and *E.coli*. respectively	[97]
	iv. Green tea extract	phenolic moieties, i.e. catechins	Viscose	Loading of MCT-β- cyclodextrin treatment using several technique: exhaustion, pad-dry-cure, pad-dry-steam followed by post finishing with green tea extract using exhaustion technique	The treated substrate showed a variable antibacterial activity against *S. aureus* and *E.coli*. depending on the application method of loading MCT-β-cyclodextrin: exhaustion > pad-dry-steam > pad-dry/cure	[98]

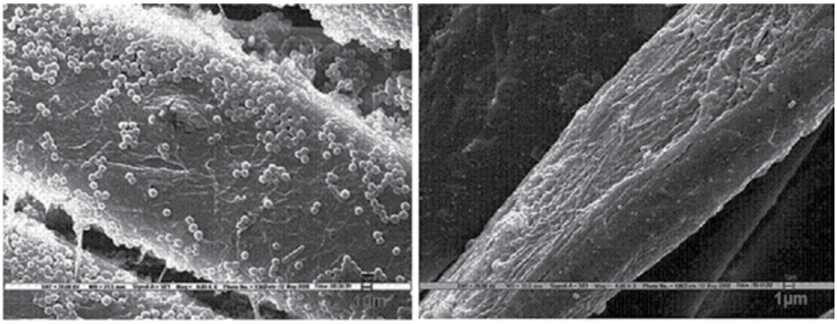
2. Essential oils	i. Neem extract	Azadirachtin	Cotton	Samples were treated with Oxygen plasma → immersing –padding-curing→treated with cross linking agent	The treated samples showed 100% reduction against both tested G+ve and G-ve bacteria (*S. aureus* and *E.coli)*	[99]
		Azadirachtin	Cotton and viscose	Incorporation of βCD into reactive printing paste followed by post treatment with methanolic solution of neem oil	The treated substrates showed a remarkable improvement in antibacterial activity against *S. aureus* and *E.coli* using the qualitative test method.	[100]
	ii. Clove oil	Eugenol	Cotton	Treatment was carried out using DMDHEU as the cross-linking agent	The treated samples showed an improvement on antibacterial activity against *S. aureus* and *K. pneumonia*	[101, 102]
	iii. Lavender	1,5-Dimethyl-1-vinyl-4-hexenyl butyrate	Cotton/PET Viscose/ PET	The fabrics were pretreated with MCT-βCD in presence of citric acid as crosslinker followed by post finished with alcoholic solution of lavender oil	The treated substrates exhibited a good antimicrobial activity against *S. aureus* and *E.coli* even after 15 washing laundering cycles	[103, 104]

(*Continued*)

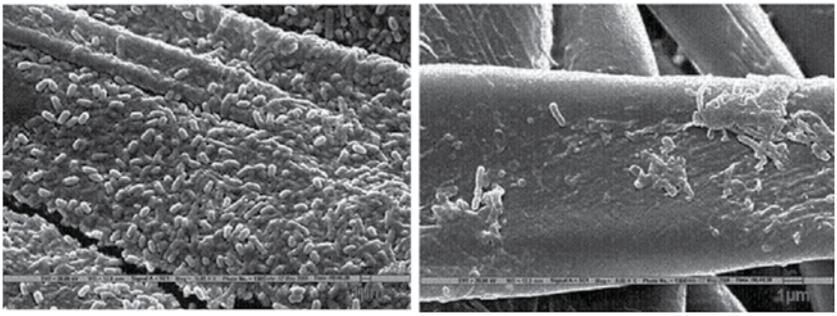
Table 13.3 Cont.

Type of natural products	Antimicrobial agent	Main active ingredients	Treated fabrics	Application method	Feature of the fabric	Ref.
3. Natural Dyes and pigments	i. Madder (*Rubia Tinctoria*)	Anthraquinones	Knitted cotton	The fabric samples were pre-mordanted with different type of mordant followed by dyeing at pH 4, and temp. 100 °C for 1hr	The dyed fabric showed an enhancement in both antibacterial activity and UV-protection properties depending on the type of the used mordant	[105]
	ii. Curcuma (*Curcuma Tinctoria*)	Diferuloye-methan				
	iii. Onion (*AliumCepa*)	Flavonoid				
	iv. Henna (*Lawsone*)	Alpha-naphtho quinones				

	v. *Quercus infectoria* (QI)	Tannin	Cotton	Dyeing in presence and absence of mordant, alum, copper, ferrous	The treated samples showed inhibiting of microbial growth by 45 to 50 % in absence of mordant and 70-90% in case of using alum and copper sulphate as mordant treated fabrics with QI alone lost its antibacterial activity after 5 laundering cycle while the mordanted treated fabric retain almost 100% from its antibacterial activity	[106]
	vi. Pomegranate	Tannins, phenolic content, alkaloid	Cotton	The cotton fabric were treated using, micro-encapsulation, resin crosslinking methods and their combination	The treated cotton fabric showed an excellent antibacterial activity depending on the used application technique. The combination of micro-encapsulation and resin finish gave the best antibacterial activity	[96, 101]



(**a**) *S. aureus* on untreated cotton (**b**) *S. aureus* on Aloe vera treated cotton



(**c**) *E. coli* on untreated cotton (**d**) *E. coli* on Aloe vera treated cotton

Figure 13.11 SEM for a, c untreated and b, d cotton treated with Aloe vera (3 %) [68]. Reprinted from "Antibacterial properties of Aloe vera gel finished cotton fabric" by S. W. Ali, 2014, *Cellulose, 21 (3)*, 2069.Copyright 2014 by Springer. Reprinted with permission.

in the presence of acetic acid. The antimicrobial analysis of these samples revealed that they have antibacterial activity against *E. coli* and *S. aureus*, and antifungal activity against *Aspergillus niger*. The antimicrobial activity of the hybrid combination was more effective and durable to washing up to 20 washing cycle [74].

Essential oils are also used to impart antimicrobial activity to textile products. Walentowska *et al.* have applied thyme essential oil (8% and 12% in methanol) onto linen/cotton blended fabric. The resulted samples exhibited very promising antibacterial activity with inhibition zones higher than 5 mm. the antifungal activity of the samples treated with both concentration, 8% and 12% of thyme inhibited the growth of mould and protect the fabric from breaking force loss [62]. To control the release of essential oils and to protect them from the surrounding environment, encapsulation technology was the appropriate selection. Complex coacervation method of both chitosan and gelatin as the outer shell was used to encapsulate patchouli oil (Figure 13.12). These microcapsules were immobilized onto

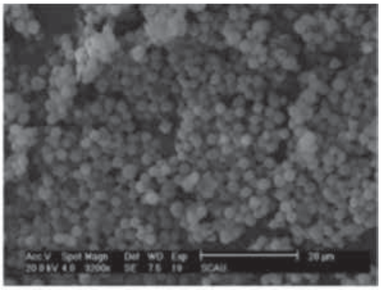


Figure 13.12 SEM photographs of microcapsules of chitosan and gelatin [107]. Reprinted from "Study on the grafting of chitosan–gelatin microcapsules onto cotton fabrics and its antibacterial effect", J. Liu, 2013, *Colloids and Surfaces B: Biointerfaces, 109*, p. 105. Copyright Elsevier B.V. Reprinted with permission.

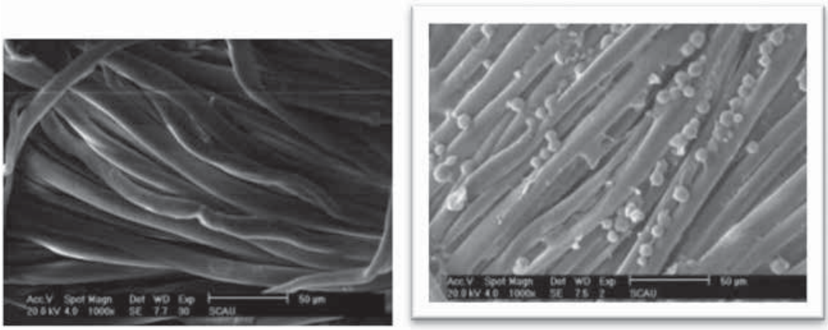


Figure 13.13 SEM photographs of cotton fabrics before and after treating with the microcapsules [107]. Reprinted from "Study on the grafting of chitosan–gelatin microcapsules onto cotton fabrics and its antibacterial effect", J. Liu, 2013, *Colloids and Surfaces B: Biointerfaces, 109*, p. 106. Copyright 2013.Elsevier B.V. Reprinted with permission.

cotton fabrics by the etherification crosslinking reaction [107]. Moreover, alginate nanocapsules containing peppermint oil were obtained by microemulsion method. These nanocapsules were applied onto cotton fabric using microwave for curing to obtain a good antimicrobial and fragrant textile (Figure 13.13) [64].

13.5.2 Advanced Antimicrobial Agents Based on Nano-Materials

Nanotechnology is an emerging field used in various disciplines and combines the principle of molecular chemistry and physics. Nanotechnology is used for the innovation of new generations of improved materials, structures and systems. Materials at nanoscale (size range of 1-100 nm) exhibit unique properties because of their very high surface area and peculiar electronic configuration. Nanomaterials are usually obtained by gas phase techniques, liquid phase techniques, or grinding method. To obtain high quality nanoparticles with controlled shapes and surface functionality, liquid phase technique is the proper method. In addition to the chemical methods used to obtain nanomaterials, greener methods are developed for synthesizing nanomaterials by using different greener chemicals e.g. biodegradable polymers, sugars, plant extract...etc. or biological systems using microorganism. The green methods are usually used to overcome the different drawbacks of the chemical methods such as the using of hazardous and aggressive reducing, capping, and/or stabilizing agents, organic solvent along with higher energy [6].

In the last few years, nanotechnology was used to improve the performance and the properties of the existing textile products and developing new smart and intelligent textile products with new functionality. Moreover, nanomaterials e.g. Ag, TiO_2, and ZnO can be dispersed during the spinning of the fibers to have nanoparticle composites, or by using ex-situ synthesis of the nanoparticles followed by the application of the nanoparticles onto the fabric using one of the different finishing techniques (Figure 13.14) [108]. *In situ* synthesis of the nanoparticle on the surfaces of fibers or fabrics is also a known. *In situ* methods are more favorable because these methods provide better control for the deposition of the NPs into the fiber/fabrics with saving time and energy [109]. Formation of cellulosic fibers/nanoparticles matrixes or deposition on the cellulosic fabric

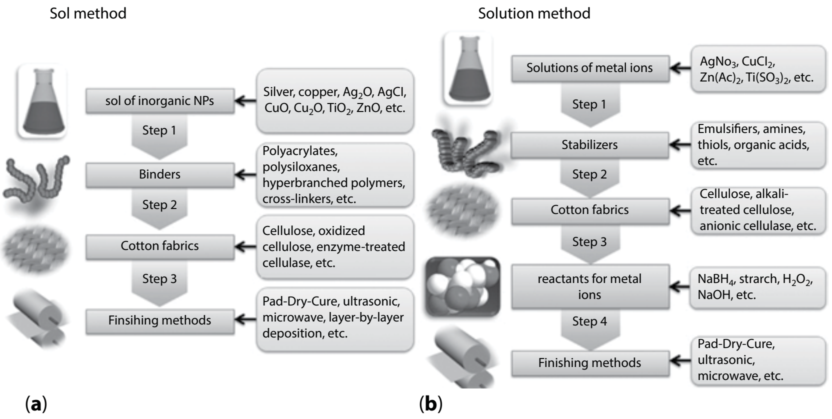


Figure 13.14 Example for the methods used for immobilizing organic NPs onto cotton surfaces [108]. "Durable antimicrobial cotton textiles modified with inorganic nanoparticles", Y.Y. Zhang, 2016, Cellulose, *23 (5)*, 2798. Copyright 2016, Springer, Reprinted with permission.

surface led to textile products with unlimited functional performance properties e.g., UV protection, self-cleaning status, super-hydrophilicity or hydrophobicity, water/oil repellency, and antimicrobial function [6, 110]. Finishing of cellulosic fabrics using nanoparticles and the out features of the finished fabrics are summarized in Table 13.4.

13.5.2.1 Silver Nanoparticles AgNPs

AgNPs are widely used as safe and non-toxic antimicrobial agent in medical field and also for antibacterial finishing of cellulosic textile. Silver has the highest electrical and thermal conductivity among all metals and it has good optical reflectivity and exhibits surface Plasmon [109]. Silver in nano or ionic form is a powerful antimicrobial agent and has the ability to destruct different gram-positive and gram-negative bacteria and fungi [112]. AgNPs can accumulate in walls or can penetrate into the cells of bacteria and react with –SH groups of enzymes which change the major cell metabolisms and inhibit the growth of bacteria. Moreover, AgNPs can form active oxygen species (ROS) and hydroxyl radicals which have the ability to oxidize the molecular structure of bacteria [111].

$$4Ag + O_2 + 2H_2O \longrightarrow 4Ag^+ + 4OH^-$$

$$H_2O + 1/2\ O_2 \xrightarrow{Ag^+ \text{ and/or Ag NPs}} H_2O_2 \longrightarrow ROS + H_2O$$

The most popular pathway for AgNPs synthesis is the reduction of Ag salts e.g. silver nitrate using reducing agent e.g. β-D-glucose, ascorbic acid etc. This reductant led to AgNPs with narrow particle size. To prevent the agglomeration of the nanoparticles, a stabilizing agent like soluble Daxad 19 is usually used. In addition to chemical reduction of silver salts, different methods were used for AgNPs synthesis e.g., thermal decomposition in organic solvents, chemical and photo reduction in reverse micelles [116]. Recently different green methods have been used for AgNPs synthesis e.g., using of cationic chitosan and anionic charged heparin polysaccharides as reducing agent/stabilizing agents by heating aqueous solutions of Ag nitrate. Ag-NPs with particles size in narrow range were obtained by using soluble starch or gelatin as reducing and stabilizing agent [6]. The application of AgNPs on cellulosic fabrics reached outstanding features in the recent years (Figure 13.15).

With the continuous growth of using AgNPs in textile finishing, the need to know the environmental impact of AgNPs becomes necessary. It was found that washing of nanosilver finished textiles led to the release AgNPs into the discharge water and create a potential health hazard to aquatic organism. It may led to lethal to small fish and cause binding/crossing the

Table 13.4 Application of Different Nanomaterials on Cellulosic Fabrics for Antimicrobial Functionalization.

Nano-material	Treated fabric	Finishing formulation and finishing technique	Feature of the fabric.	Ref.
AgNPs	Cotton	- AgNPs /BTCA - Pad-dry-cure method	The antimicrobial activity against either *E. coli* or *S. aureus* bacteria of the treated cotton fabrics improved up to 100%	[111]
AgNPs	Cotton	- Silver nitrate/ printing paste - The printed samples were cured using UV light.	Depending on the concentration of silver nitrate, all samples inhibit proliferation of *E. coli*, *B. subtilis* and *S. aureus* both before and after 10 washings, and the durability reached 50 washing cycle for most of the samples.	[112]
Ag doped TiO_2 nanoparticles and/or TiO_2 nanowires.	Cotton	- Untreated cotton fabric and PVP treated cotton/ Ag doped TiO_2 nanoparticles and/or TiO_2 nanowires - Pad-dry-cure	The cotton fabric treated with nanomaterials exhibited good antimicrobial activity against Gram positive bacteria, Gram negative bacteria and fungi.	[73]
Ag-NPs, TiO2-NPs.	Linen and linen/cotton blend (50/50%).	- The fabrics were carboxymethylated and post-treated with Ag-NPs, TiO_2-NPs, chitosan solution in citric acid, or organosilane quaternary ammonium, followed by squeezing to a wet pick-up of 80%, and microwave fixation, as an efficient internal heating than conventional method, at 1300 w for 4 min.	All the treated samples exhibited antibacterial activity against both Gram positive (*S.aureus*); G-ve: Gram negative (*E.coli*) and the activity against the Gram positive (*S.aureus*) were higher than that of Gram negative (*E.coli*) Using different formulation of the nano particles with chitosan or organosilane quaternary ammonium improve the antibacterial activity of the treated fabrics;	[4]

Ag:ZnO NPs	Bleached cotton, and blended polyester/cotton (50/50%) fabrics	- Ag/Chitosan (CS),orZnO/CS or Ag:ZnO/CS composite coatings. - Pad-dry-cure	- All samples showed good and very good antimicrobial activity with inhibition rate up to 50–95% - The antimicrobial activity of the fabrics treated with Ag-doped ZnOnanoparticles embedded in chitosan matrix has higher antimicrobial activity than that treated with both Ag/CS and ZnO/CS composite coatings.	[113]
ZnO NPs	Cotton	- ZnO NPs aqueous solution / cellulase enzyme - Sonochemical coating was carried out using an ultrasonic Transducer Ti-horn	The uniform multilayer depositions of ZnO NPs onto the fibers ensure its antibacterial activity. The outer NP layers were not firmly fixed on the textiles, 33% of the initially deposited ZnONPs was still remained on the surface of the fabric after multiple intensive washing cycles. The remaining NPs led to nearly 100% inhibition rate of *E. coli*, while the activity against S. aureus decreased by 50%.	[114]
TiO_2, ZnO and Ag NPs	Denim	- TiO_2 with rutile and anatase structures, ZnO and Ag NPs - Spraying- squeezing- drying.	- TiO_2 (rutile and anatase), ZnO and Ag NPs deposited onto denim fabric led to significant antibacterial activity against *S.aureus*, *E. coli,* - TiO_2 (rutile and anatase), had high activity against *S. aureus* only. - ZnONPs was effective against *S. aureus*, it showed moderate activity against *E. coli* - Ag exhibited excellent antibacterial activity against the different bacteria	[72]

(*Continued*)

Table 13.4 Cont.

CuO_2 NPs	Cotton	- Microcapsule containing Copper oxide nanoparticles - The fabric was immersed in a bath containing 10 ml of the microencapsule at 50 °C for 30 min.followed by padding, drying and curing.	The treated fabric showed high antibacterial efficiency compared to the untreated fabric.	[70]
CuO_2 NPs	Cotton	Cotton fabric/8% (w/w) copper salt/ 1.6% (w/w) NaOH/ 100 mL water at 80 °C	Cotton treated with Copper oxide nanoparticles shows 89% and 100% antibacterial reduction against S.aureus and 67% and 90% against *E. coli* for 0 and 2 h exposure, respectively	[115]
CuO_2 NPs	Cotton	- Oxidized cotton fabric/ $CuSO_4$ at a pH = 5.5–6 for 2 h/ NaOH solution at pH = 10 - Two other samples were prepared with both reducing agents: either hydrazine monohydrate ($NH_2NH_2{\cdot}H_2O$) or hydroxylamine(NH_2OH) /NaOH.	The antibacterial activity of Cu_2O–cotton was strongly dependant on Cu_2O. The strongest antibacterial activity was obtained from samples loaded with a Cu loading of 220 μmol/g,	[71]

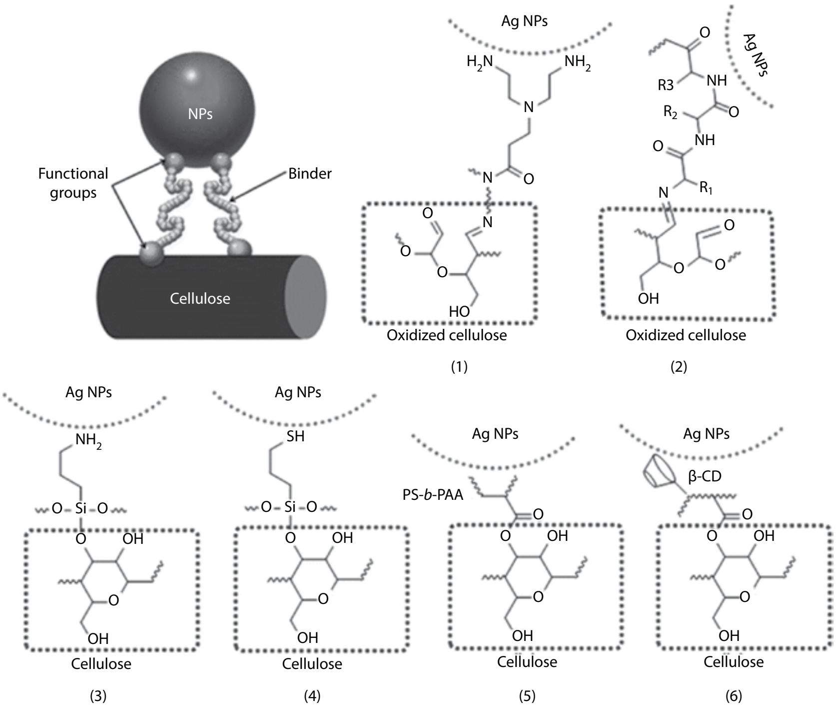


Figure 13.15 Systematic structure for the binders linking the inorganic NPs and cellulose chains by covalent bonds [108]. Reprinted from "Durable antimicrobial cotton textiles modified with inorganic nanoparticles", Y.Y. Zhang, 2016, *Cellulose, 23 (5)*, 2798. Copyright 2016, Springer, Reprinted with permission.

egg membrane and entering into the fish embryos [83] Recently, Reed *et al.* have assessed the antimicrobial activity of textile treated with AgNPs in parallel with their release during multiple life cycle stages (Figure 13.16). The release of AgNPs during multiple washing cycles is strongly dependant on the attachment method of AgNPs to textile. The toxicity analysis revealed that the residual detergent has greater adverse response than the released silver and the antimicrobial activity was not affected after multiple washing cycles and the inhibition rate was >99.9% against *E. coli* growth on the textiles. The latter results suggest the use of very low concentration of AgNPs control bacterial growth in textiles [117].

13.5.2.2 Tianium Dioxide Nanoparticle (TiO_2NPs)

TiO_2NPs are promising inorganic metal oxide due to their powerful photo catalytic properties, high activity, strong oxidizing agent, and long-term

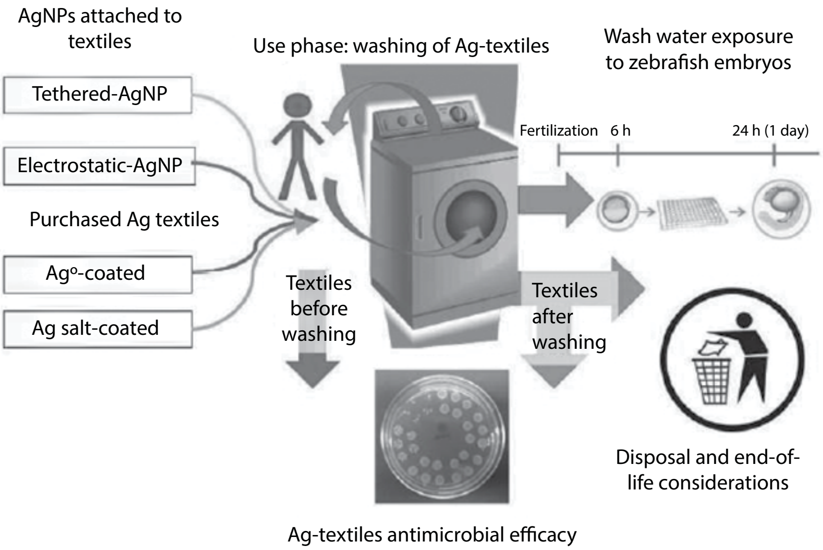


Figure 13.16 The life cycle of textile treated with AgNPs[117]. Reprinted from "Potential Environmental Impacts and Antimicrobial Efficacy of Silver and Nanosilver containing Textiles", by R.B. Reed, 2016, Environmental Science and Technology, 50 (7), graphical abstract. Copyright 2016.*American Chemical Society*. Reprinted with permission.

stability. The antibacterial properties of TiO_2NPs is attributed to the generation of reactive oxygen species (ROS) responsible for inactivation of the bacteria cell according to the following mechanisms [118]. TiO_2NPs are applied on different textiles material to emerge new textile products with self-cleaning and in hygienic properties [113]. However, the use of TiO_2 nanomaterial for textile applications has been reported rarely so far. Table 13.4 show some researches on the using of TiO_2NPs for obtaining antimicrobial cellulosic textiles [4, 73].

$$TiO_2 \xrightarrow{UV} e_{cb}^- + h_{vb}^+$$

$$h_{vb}^+ + HO_{abs}^- \longrightarrow HO^\bullet + TiO_2$$

$$h_{vb}^+ + H_2O_{abs} \longrightarrow HO^\bullet + H^+ + TiO_2$$

$$O_2 + e_{cb}^- \longrightarrow O_2^\bullet + H^+ \longrightarrow HO_2^\bullet$$

$$2\,HO_2^\bullet \longrightarrow O_2 + H_2O_2$$

13.5.2.3 Zinc Oxide Nanoparticles (ZnO NPs)

ZnO NPs are attractive metal oxide, widely used because of their good photocatalytic activity and high stability. Due to the nontoxicity of ZnO NPs and their antibacterial properties, they can be used for cosmetics, depollution, and protective medical textiles application. ZnO NPs have anti-inflammatory, drying, and antiseptic properties which encourage the use of zinc ion in wound healing, particularly for treating burns [113]. Recently several studies reported the use of ZnO NPs for imparting the cellulosic textile multi-functions like self-cleaning, UV-protection, flame retardant [119, 120] and antibacterial properties. ZnO NPs showed high antimicrobial activity against Staphylococcus aureus and *Escherichia coli.* ZnO NPs have the ability to damage the membrane cell of the microorganisms due to their photocatalytic activity similar to TiO_2 nanoparticles [118] according to the following mechanism.

$$\mathrm{ZnO} + h\nu \longrightarrow h^{+} + e^{-}$$

$$\mathrm{H_2O} + h^{+} \longrightarrow {}^{\bullet}\mathrm{OH} + \mathrm{H}^{+}$$

$$\mathrm{O_2} + e^{-} \longrightarrow {}^{-}\mathrm{O_2}^{\bullet} + \mathrm{H}^{+} \longrightarrow \mathrm{HO_2}^{\bullet}$$

$$2\mathrm{HO_2}^{\bullet} \longrightarrow \mathrm{O_2} + \mathrm{H_2O_2}$$

13.5.2.4 Cuprousoxide Nanoparticle (Cu_2ONPs)

Copper has been known as a hygienic material due to its antimicrobial properties. Copper has the ability to inhibit the growth of dangerous pathogens bacteria, moulds, algae, fungi, and viruses. It was reported that treating cotton with cationic copper imparts it with potent broad spectrum antibacterial, antiviral, and antifungal properties [121].

Recently copper(I) oxide or cuprous oxide, Cu_2O nano particles are well known for its catalytic properties, non-toxicity, ecofriendly, and antimicrobial properties [70, 71, 121]. Cotton fabric treated with Cu_2O nano particles (Figure 13.17) could be used in medical applications such as medical devices, healthcare, wound dressing, military, protective suits, personal care product [115]. Cu_2O nano particles showed strong antibacterial activity due to their high surface areas, which increase the contact of the nanoparticles with the microorganisms. Copper and copper oxides have the ability to generate hydroxyl radicals. These radical led to oxidation of proteins, cleavage DNA and RNA molecules, and damage membrane of microorganisms. Moreover, the radicals formed from excited electrons of

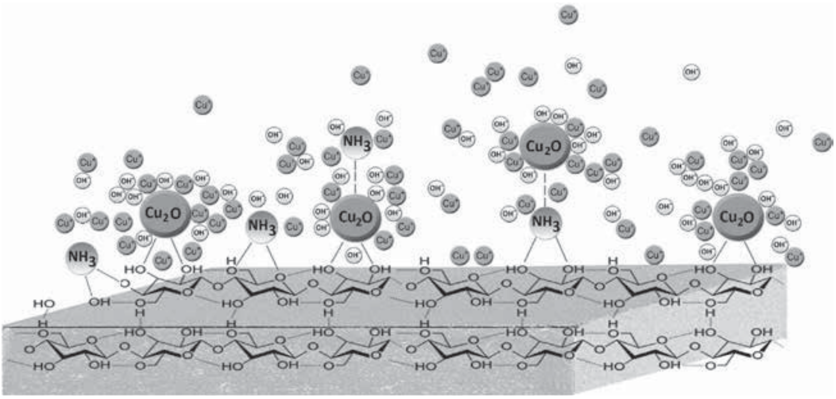


Figure 13.17 Schematic structure of cellulose nucleation and chemisorption of Cu_2O nanoparticles on fabric surface [115]. Reprinted from "Synthesis of nano Cu_2O on cotton: Morphological, physical, biological and optical sensing characterizations", A. Sedighi, 2014, *Carbohydrate Polymers, 110*, p. 491. Copyright 2014, Elsevier B.V. Reprinted with permission.

Cu_2O particles are powerful oxidizing agents; these radicals break the cell wall of microorganisms through oxidation–reduction reactions [115].

13.5.3 Nano Composites and Hybrid Materials

Table 13.5 demonstrates some nanocomposite and hybrid materials used for imparting antimicrobial function to cellulosic fabrics.

13.6 Evaluation of Antimicrobial Products

Different methods were developed to analyze the antimicrobial activity of the finished textiles [6]. Table 13.6 shows short explanation about the different testing methods.

13.7 Potential Applications

Table 13.7 lists some potential applications of antimicrobial textile products

13.8 Conclusion and Future Prospects

- Use of emerging technologies as well as sustainable and safe antimicrobial agents in antimicrobial functionalization of textile materials, taking in consideration human,

Table 13.5 Some Nanocomposite and Hybrid Materials Used for Antimicrobial Functionalization of Cellulosic Materials.

The used polymer	Type of nanocomposite/ hybrid	Treated fabric	Application method	Fabric feature	Ref.
1- Nanocomposite					
Chitosan (Cs)	Cs/Ag/ZnO nanocomposite	Cotton gauze	The samples were treated with chitosan, chitosan/Ag, chitosan/ZnO, and chitosan/Ag/ZnO separately using pad-dry cure method	Samples treated with nominated nanocomposite showed higher antibacterial activity comparing with each nanoparticles separately. Additionally chitosan/Ag/ZnO nanocomposite increased drying time, wicking ability, and water absorbency; the main parameter for wound dressing	[122]
	Cs/ZnO nanocomposites (CZNCs)		Pre-ultrasonicated for CZNCs in presence of low temperature cross-linking agent then cotton fabric was treated using pad-dry cure technique	The nano-composite coated cotton fabric showed durable antibacterial activity, UV protection properties without affecting other treated physical properties	[123]

(*Continued*)

Table 13.5 Cont.

The used polymer	Type of nanocomposite/ hybrid	Treated fabric	Application method	Fabric feature	Ref.
	CuO-Cs nanocompsite	Cotton	Pad-dry-cure method	The finished fabric samples showed an excellent anti-bacterial reached 99% and 96% bacteria reduction for *S. aureus* and *E. coli* respectively activity and withstand 30 laundering cycles	[124]
	Neem/Cs nanocomposite	Cotton	Cotton fabric samples were finished with Neem extract, Cs solution, Neem/Cs composite and Neem/Cs nanocomposite	The antibacterial activity showed a decreasing order according to the finishing bath: Neem/Cs nanocomposite > Neem/Cs composite> Neem extract > Cs solution	[125]
Cs-NPs	CsNPs/herbal-NPs nanocompsite (*Senna auriculata and Achyranthes aspera leaves*)	Cotton	Citric acid as crosslinking using pad-dry-cure technique	The nanocomposite finished cotton fabric gave higher antibacterial activity comparing with cotton samples finished with only herbal extract, chitosan or combined herbal extract and chitosan	[126]

Carboxymethylcellulose (CMC)	in presence of Fumaric acid (FA)	CMCF/Ag nanocomposite	Cotton	Cotton fabric were padded for different periods then dried at 80 °C	The treated cotton fabrics showed 99.9% reduction for both *S.aureus* and *K. pneumonia(Kp)* for all the used silver concentration. The durability to wash was negatively affected by the number of washing cycles but in reasonable range	[127]
	With poly(vinyl alcohol) PVA	CMC/PVA/ TiO_2 nanocomposites	Cotton	Fabric samples were immersed in the colloidal solutions of CMC/PVA/TiO_2 nanocomposites for 2 min→ squeezing to 100% wet pick-up →exposed to gamma irradiation (dose rate: 4.8-kGy/h)	The treated cotton fabric exhibited a good antibacterial activity, and the activity increased by increasing TiO_2 concentration	[128]
Polyacrylamide (PAAm)		Nano Cu.AAm-g-BR composite	Knitted bamboo rayon (BR)	- knitted bamboo rayon fabric grafted with acrylamide, followed by - Cu nanoparticle loaded on grafted bamboo rayon fabric	The obtained nanocomposite displayed excellent antibacterial activity against both Gram positive and Gram negative bacteria which was durable till 50 washes	[129]

(*Continued*)

Table 13.5 Cont.

The used polymer	Type of nanocomposite/ hybrid	Treated fabric	Application method	Fabric feature	Ref.
Alginate	AgNPs–alginate composite	Cotton	pad (in presence and absence of binder)– dry – cure method	The treated cotton samples showed excellent antibacterial activity against *E. coli*, *P. aeruginosa* and *S. aureus*. The presence of binder during padding enhance the durability to wash for the treated fabric samples	[130]
2- Hybrid					
Aminoterminated hyperbranched polymer (HBP-NH_2)	ZnO-Ag/HBP hybrid	Cotton	*In situ* preparation	The multifunctionalized cotton fabric samples exhibited an excellent UV- protection and antibacterial activity. The UPF value reached 55 and bacterial reduction rate against *S. aureus* and *E. coli* reached 99.99%	[131]
HSDA (water-soluble HBP)	ZnO/HSDA hybrid	Bamboo pulp fabric	Immersing	The treated fabric samples attained durable and excellent multifunctional properties.The finished fabric showed antibacterial activity reduction was 99% against the test bacteria, the UPF value reached 90	[132]

Hybrid antimicrobial coatings	Hybrid ZnO/Chitosan nanoparticles	Cotton	Sonochemical coating process	The finished fabric showed an excellent antibacterial activity and good resistance to multiple wash cycles	[133]
Hyperbranched poly (amide–amine)	HBPAA/AgNPs	Cotton Linen viscose	Pad-dry cure, using Fixapret® ECO, as fixing and crosslinking agent	The finished fabrics showed an excellent and durable antimicrobial activity against the tested bacteria	[38]
	HBPAA/AgNPs & HBPAA/ZnO-NP's hybrid	Cotton Cotton/PET	Incorporation in pigment printing paste followed by curing in microwave oven	The obtained prints exhibited sufficient antibacterial activity even after 20 washing cycles. The improvement in antibacterial properties depended on type of nanoparticles: HBPAA/ZnO-NP's hybrid > HBPAA/AgNPs	[45]

Table 13.6 Test Methods for Evaluation of Antimicrobial Activity of Textiles.

Type of test	Test method	Title
Qualitative test	AATCC 147	Antibacterial activity assessment of textile materials: Parallel Streak Method
	JIS L 1902	Test method for antibacterial activity of textiles
	SN 195920	Textile fabrics: Determination of the antibacterial activity – Agar diffusion plate test
Quantitative test	AATCC 100	Antibacterial Finishes on Textile Materials
	AATCC 30	Antifungal activity, assessment on textile materials: mildew and rot resistance of textiles
	ISO 20743	Determination of antibacterial activity of antibacterial finished products
	SN 195924	Textile fabrics: Determination of the antibacterial activity – Germ count method
	ASTM E 2149	Test method for determining the antimicrobial activity of immobilized antimicrobial agents

Table 13.7 Some Potential Applications of Antimicrobial Products.

Finished fabric	**Applications**	**Ref.**
Cotton/chitosan/ Viola Tricolor	Bioactive textiles	[134]
Carboxymethyl cotton knitted fabrics	Wound dressing	[135]
Carboxymethyl cotton gauze fabrics/Tetracycline Hydrate and Gentamicine Sulfate	Wound dressing	[136]
Cotton/sodium alginate/ AgNPs	Hospital clothing, surgical scrubs	[137]
Cotton/ AgNPs–alginate composite	Personal Protective Fabrics	[138]
Flax/AgNPs	Wound dressing	[139]
Cotton/ AgNPs	Personal Protective Fabrics	[109]
Peco fabrics/ AgNPs	Hospital clothing	[140]
Cotton/chitosan	Medical textile	[141]
Cotton/quaternary ammonium salt	Hospital clothing and hygienic inner wears	[142]
cotton/$BaFe_{12}O_{19}$NP/hydrogel	Wound dressing	[143]
Cotton/ZnO NPs	Practical textile and biomedical applications	[144]
Cotton/Polypyrrole–silver nanocomposites	Biomedical applications and sensors	[145]
Cotton/ potassium alginate/ biomedical applications and sensors	Flame retardant and antimicrobial textile	[146]
Cotton/ethanolic extract of the sea grass Halophilastipulacea and marine macroalgae	Eco-friendly natural based antibacterial and anti-inflammatory cotton fabric	[147]
Cotton/[2-(Methacryloyloxy) ethyl]trimethylammonium chloride	Hospital clothing and hygienic inner wears	[148]
Cotton/β-Cyclodextrin/ Chitosan/lavender oil	Home furnishings such as curtains, wall hangings, and table covers	[149]

(*Continued*)

Table 13.7 Cont.

Finished fabric	Applications	Ref.
Cellulose fiber/chitosan/silver ions	Antimicrobial filtration system	[150]
Cotton/Cu_2O NPs	Antibacterial cotton fabrics	[71]
Cotton/TiO_2 NPs	Antibacterial cotton fabrics	[151]
Cotton/Ag/octyltriethoxysilane	Super hydrophobic antibacterial fabrics, biomedical and general use applications	[152]
Cotton gauzes/chitosan/alginic acid sodium salt/peptides	Wound-dressings	[153]
Cotton/Curcumin/acid-catalyzed silica xerogel	Wound-dressings	[154]
Cotton/propolis or beeswax or chitosan	Medical field	[155]
Cotton/Ag NPs	Antibacterial textile	[156]
Cotton and non-woven bandages/piroxicam and vegetable oils	Wound dressing	[157]
Cotton/citric acid and diethyl-tetradecyl-[3-(trimethoxysilyl)-propyl] ammonium chloride	Antimicrobial medical textile	[158]
Cotton/chitosan	Medical and hygienic applications	[159]
Cotton and viscose/pigment prints/TiO_2NPs	Antibacterial cellulosic fabrics	[160]

production, and disposal ecology concerns, for production of highly active, durable and value added medical textile products are likely to continue in the near future.

- Multifunctional protective textile materials are still the wave of the future and the development of highly efficient protective products against chemicals, biological threats, harmful radiation, pathogenic microbes….etc with minimal negative impacts and improved cost-effectiveness will result in a wide range of potential applications.

- Multi-applications of recent advances in information technology, nano- and bio-information technologies as well as in new materials will boost the development of sustainable multifunctional textiles to meet the increasing consumer demands and awareness on hygiene and well-being in the near future.
- Surface modification of cellulosic substrates using an eco-friendly dry tools followed by subsequent treatment with carefully selected functionalizing agents to impart a wide range of individual or multifunctional properties such as antimicrobial, UV-protection, easy care, self cleaning, flame retardant, water/oil repellent, insect repellent…etc in an environment friendly way and on industrial scale manufacturing are still a challenge to those working in textile field.
- Application of proper best available techniques as well as new generation of green textile finishing auxiliaries to cellulosic materials will create an expanded array of multifunctional properties for apparel, household, technical, and smart textile products, which are increasingly demanded by the textile industry and textile consumer.
- Upgrading performance and improving cost-effectiveness of sustainable textiles taking in consideration both the environmental and toxicity requirements will be the main focus for the future.
- Last but not least, updating and revising the testing protocols adopted for full evaluation of the finishing formulation ingredients and the imparted comfort, performance, and protection properties of the functionalized textiles as well as their environmental and toxicological impacts will be of utmost importance in the future.

Reference

1. Jiang, Z., Liu, Y., Li, R., Ren, X., Huang, T. S. C. P. A. T. R., Preparation of antibacterial cellulose with a monochloro-s-triazine-based N-halamine biocide. *Polymers for Advanced Technologies*, 27, 460, 2016.
2. Wang, S., Lu, A., Zhang, L., Recent advances in regenerated cellulose materials. *Prog. Polym. Sci.*, 53, 169, 2016.
3. Siroka, B., Noisternig, M., Griesser, U.J., Bechtold, T., Characterization of cellulosic fibers and fabrics by sorption/desorption. *Carbohydr. Res.*, 343, 2194, 2008.

4. Ibrahim, N.A., El-Zairy, E.M., Eid, B.M., Emam, E., Barkat, S.R., A new approach for imparting durable multifunctional properties to linen-containing fabrics. *Carbohydr. Polym.*, 157, 1085, 2016.
5. Vuoti, S., Laatikainen, E., Heikkinen, H., Johansson, L.-S., *et al.*, Chemical modification of cellulosic fibers for better convertibility in packaging applications. *Carbohydr. Polym.*, 96, 549, 2013.
6. Ibrahim, N. A., Nanomaterials for Antibacterial Textiles A2 - Rai, Mahendra, in: *Nanotechnology in Diagnosis, Treatment and Prophylaxis of Infectious Diseases*, M. Rai, K. Kon (Eds.) pp. 191–216, Academic Press, Boston, 2015,.
7. Ibrahim, N. A., Eid, B. M., Potential Applications of Sustainable Polymers in Functionalization of Cellulosic Textile Materials, in: Vijay Kumar Thakur, Thakur, M. K. (Eds.), *Polymer Handbook of Processing and applications*, pp. 215–252, CRC Press, 2015.
8. Koh, J., Dyeing of cellulosic fibres in: *Handbook of Textile and Industrial Dyeing*, M. Clark (Ed), Woodhead Publishing, pp. 129–146, 2011.
9. Yusuf, M., Shabbir, M., Mohammad, F., Natural Colorants: Historical, Processing and Sustainable Prospects. *Nat. Prod. Bioprospect.,* 2017, *7*, 123
10. Ibrahim, N. A., Dyeing of textile fibre blends in: *Handbook of Textile and Industrial Dyeing*, M. Clark (Ed), Woodhead Publishing, pp. 147,, 2011.
11. Li, D., Sun, G., Coloration of textiles with self-dispersible carbon black nanoparticles. *Dyes and Pigments*, *72*, 144, 2007.
12. Holme, I., Innovative technologies for high performance textiles. *Color. Technol.*, 123, 59, 2007.
13. Whewell, C.S., Turner, H.A., Recent Developments In The Mechanical Finishing Of Textile Fabrics. *J. Text. Inst. Proc.*, 42, 633, 1951.
14. Paul, R., Functional finishes for textiles: An overview, *Functional Finishes for Textiles*, Woodhead Publishing, pp. 1–3, 2015.
15. Teli, M. D., Softening finishes for textiles and clothing, in: *Functional Finishes for Textiles*, R. Paul (Ed), Woodhead Publishing, pp. 123–152, 2015.
16. Hashem, M., Ibrahim, N.A., El-Shafei, A., Refaie, R., Hauser, P., An eco-friendly – novel approach for attaining wrinkle – free/soft-hand cotton fabric. *Carbohydr. Polym.*, 78, 690, 2009.
17. Ibrahim, N.A., El-Sayed, Z.M., Fahmy, H.M., Hassabo, A.G., Abo-Shosha, M. H., Perfume Finishing of Cotton/Polyester Fabric Cross-linked with DMDHEU in Presence of Softeners. *Res. J. Text. & Apparel*, 17, 58, 2013.
18. Ibrahim, N.A., Khalifa, T.F., El-Hossamy, M.B., Tawfik, T.M., Effect of Knit Structure and Finishing Treatments on Functional and Comfort Properties of Cotton Knitted Fabrics. *J. Ind. Text.*, 40, 49, 2010.
19. Ibrahim, N.A., Khalifa, T.F., El-Hossamy, M.B., Tawfik, T.M., Factors Affecting the Functional- and Comfort-related Properties of Reactive Dyed Cotton Knits. *J. Ind. Text.*, 41, 41, 2011.
20. Ibrahim, N.A., Ibrahim, D.F., Elzairy, W.M., Eid, B.M., Tawfk, T.M., Options for Enhancing Functional Properties of Knitted Cotton Fabrics. *Adv. Res. Text. Eng.*, 1, 1007, 2016.

21. Ibrahim, N. A., El-Zairy, M. R., Eid, B. M., El-Zairy, E. M. R., Emam, E. M., New finishing possibilities for producing durable multifunctional cotton/wool and viscose/wool blended fabrics. *Carbohydr. Polym.*, 119, 182, 2015.
22. Pavlidou, S., Paul, R., Moisture management and soil release finishes for textiles, in: *Functional Finishes for Textiles*, R. Paul (Ed), Woodhead Publishing, pp. 99–121,, 2015.
23. Hebeish, A., Amin, S.A., Nassar, F., Ibrahim, N.A., Hanna, H.L., Chemical Factors Affecting Soiling and Soil Release from Cotton Containing Durable Press Fabrics. III. Application of CMC During the Crosslinking Treatment. *J.Cellulose Chem. Technol.*, 16, 405, 1982.
24. Ibrahim, N. A., Hebeish, A., Dependence of soiling and soil release of easy care cotton on factors-controlling the finishing treatment. Die Angewandte Makromolekulare Chemie, 130, 111, 1985.
25. Mahltig, B., Hydrophobic and oleophobic finishes for textiles in: *Functional Finishes for Textiles*, R. Paul (Ed), Woodhead Publishing, pp. 387- 428, 2015.
26. Ibrahim, N. A., Khalil, H. M., El-Zairy, E. M. R., Abdalla, W. A., Smart options for simultaneous functionalization and pigment coloration of cellulosic/wool blends. *Carbohydr. Polym.*, 96, 200, 2013.
27. Abo-Shosha, M. H., El-Sayed, Z. M., Fahmy, H. M., Ibrahim, N. A., Synthesis of PEG/TDI/F6 Adducts and Utilization as Water/Oil Repellents and Oily Stain Release Finishes for Cotton Fabric. Polym. *Plast. Technol. Eng.*, 44, 1189, 2005.
28. Vanneste, M., 7 - Easy care finishes for textiles in: Functional Finishes for Textiles, Paul, R. (Ed), Woodhead Publishing pp. 227–256, 2015.
29. Ibrahim, N. A., Allam, E., El-Hosamy, M. B., El-Zairy, M. R., El-Zairy, W., Union Dyeing of Easy Care-Finished Wool/Viscose and Cotton/Wool Blends. Polym. *Plast. Technol. Eng.*, 45, 447, 2006.
30. Ibrahim, N. A., Allam, E. A., El-Hossamy, M. B., El-Zairy, W. M., Options for Enhancing Performance Properties of Easy-Care Finished Cellulose/Wool Blended Fabrics. Polym. *Plast. Technol. Eng.*, 47, 281, 2008.
31. Ibrahim, N. A., Refaie, R., Ahmed, A. F., Novel approach for attaining cotton fabric with multi-functional properties. *J. Ind. Text.*, 40, 65, 2010.
32. Gupta, D., Gulrajani, M. L., 8 - Self cleaning finishes for textiles in: Functional Finishes for Textiles, R. Paul (Ed), Woodhead Publishing, pp. 257–281, 2015.
33. Ibrahim, N. A., Amr, A., Eid, B. M., Mohamed, Z. E., Fahmy, H. M., Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydr. Polym.*, 89, 648, 2012.
34. Ibrahim, N. A., Amr, A., Eid, B. M., Almetwally, A. A., Mourad, M. M., Functional finishes of stretch cotton fabrics. *Carbohydr. Polym.*, 98, 1603, 2013.
35. Buschmann, H. J., Dehabadi, V. A., Wiegand, C., Medical, cosmetic and odour resistant finishes for textiles, in: *Functional Finishes for Textiles*, Paul, R. (Ed), Woodhead Publishing,pp. 303–330, 2015.

36. Nayak, R., Padhye, R., Antimicrobial finishes for textiles, in: *Functional Finishes for Textiles*, R. Paul (Ed), Woodhead Publishing, pp. 361–385, 2015.
37. Ibrahim, N. A., Eid, B. M., Abdel-Aziz, M. S., Effect of plasma superficial treatments on antibacterial functionalization and coloration of cellulosic fabrics. *Appl. Surf Sci.*, 392, 1126, 2017.
38. Ibrahim, N. A., Eid, B. M., El-Batal, H., A novel approach for adding smart functionalities to cellulosic fabrics. *Carbohydr. Polym.*, 87, 744, 2012.
39. Ibrahim, N. A., Eid, B. M., Elmaaty, T. M. A., El-Aziz, E. A., A smart approach to add antibacterial functionality to cellulosic pigment prints. *Carbohydr. Polym.*, 94, 612, 2013.
40. Ibrahim, N. A., El-Zairy, E. M., Eid, B. M., Emam, E., Barkat, S. R., A new approach for imparting durable multifunctional properties to linen-containing fabrics. *Carbohydr. Polym.*, 157, 1085, 2017.
41. Ibrahim, N. A., El-Zairy, E. M. R., Eid, B. M., Eco-friendly modification and antibacterial functionalization of viscose fabric. *J. Text. Inst.*, 108, 1406, 2016.
42. Ibrahim, N. A., Fahmy, H. M., Rehim, M. A., Sharaf, S. S., Abo-Shosha, M. H., Finishing of Cotton Fabrics with Hyperbranched Poly (ester-amine) to Enhance Their Antibacterial Properties and UV Protection. Polym. *Plast. Technol. Eng.*, 49, 1297, 2010.
43. Ibrahim, N. A., Eid, B. M., Abdel-Aziz, M. S., Green synthesis of AuNPs for eco-friendly functionalization of cellulosic substrates. *Appl. Surf. Sci.*, 389, 118, 2016.
44. Ibrahim, N. A., Eid, B. M., Khalil, H. M., Cellulosic/wool pigment prints with remarkable antibacterial functionalities. *Carbohydr. Polym.*, 115, 559, 2015.
45. Ibrahim, N. A., Abou Elmaaty, T. M., Eid, B. M., Abd El-Aziz, E., Combined antimicrobial finishing and pigment printing of cotton/polyester blends. *Carbohydr. Polym.*, 95, 379, 2013.
46. Van Langenhove, L., Paul, R., Insect repellent finishes for textiles, in: *Functional Finishes for Textiles*, Paul, R. (Ed), Woodhead Publishing pp. 333–360, 2015.
47. Kim, Y. K., Ultraviolet protection finishes for textiles, in: *Functional Finishes for Textiles*, Paul, R. (Ed), Woodhead Publishing pp. 463- 485, 2015.
48. Ibrahim, N. A., Eid, B. M., Abd El-Aziz, E., Abou Elmaaty, T. M., Functionalization of linen/cotton pigment prints using inorganic nano structure materials. *Carbohydr. Polym.*, 97, 537, 2013.
49. Ibrahim, N.A., El-Zairy, E M.R., Abdalla, W. A., Khalil, H. M., Combined UV-protecting and reactive printing of Cellulosic/wool blends. *Carbohydr. Polym.*, 92, 1386, 2013.
50. Ibrahim, N.A., Eid, B.M., Hashem, M.M., Refai, R., El-Hossamy, M., Smart Options for Functional Finishing of Linen-containing Fabrics. *J. Ind.Text.*, 39, 233, 2010.
51. Ibrahim, N., Eid, B., Youssef, M., Ameen, H., Salah, A., Surface modification and smart functionalization of polyester-containing fabrics. *J. Ind.Text.*, 42, 353, 2013.

52. Ibrahim, N.A., Refai, R., Ahmed, A.F., Youssef, M.A., New Approach for Improving UV-Protecting Properties of Woven Cotton Fabrics. Polym. *Plast. Technol. Eng.*, 44, 919, 2005.
53. Ibrahim, N.A., Gouda, M., Husseiny, S.M., El-Gamal, A.R., Mahrous, F., UV-protecting and antibacterial finishing of cotton knits. *J. Appl. Polym. Sci.*, 112, 3589, 2009.
54. Rosace, G., Radiation protection finishes for textiles, in: *Functional Finishes for Textiles,* R. Paul (Ed), Woodhead Publishing, pp. 487- 512, 2015.
55. Silva, C., Cavaco-Paulo, A. M., Fu, J. J., Enzymatic biofinishes for synthetic textiles, in: *Functional Finishes for Textiles*, R. Paul (Ed), Woodhead Publishing pp. 153–191,, 2015.
56. Ibrahim, N. A., El-Badry, K., Eid, B. M., Hassan, T. M., A new approach for biofinishing of cellulose-containing fabrics using acid cellulases. *Carbohydr. Polym.*, 83, 116, 2011.
57. Ibrahim, N. A., Fahmy, H. M., Hassan, T. M., Mohamed, Z. E., Effect of cellulase treatment on the extent of post-finishing and dyeing of cotton fabrics. *J. Mater. Process. Technol.*, 160, 99, 2005.
58. Ibrahim, N. A., Abd Allah, S. Z., Borham, H. A. T., Hassan, T. M., Economical and Ecological Biotreatment/Half Bleaching of Cotton-Containing Knit Fabrics on Industrial Scale. *Polym. Plast. Technol. Eng.*, 44, 881, 2005.
59. Ibrahim, N. A., El-Hossamy, M., Hashem, M. M., Refai, R., Eid, B. M., Novel pre-treatment processes to promote linen-containing fabrics properties. *Carbohydr. Polym.*, 74, 880, 2008.
60. Ibrahim, N., Abdel-Aziz, M., Eid, B., Hamdy, S., Abd Allah, S., Biosynthesis, Optimization and Potential Textile Application of Fungal Cellulases/Xylanase Multifunctional Enzyme Preparation from Penicillium sp. SAF6. *Biocatal. Biotransformation*, 34, 128, 2016.
61. Mostafa, F. A., Abd El Aty, A. A., Hamed, E. R., Eid, B. M., Ibrahim, N. A., Enzymatic, kinetic and anti-microbial studies on Aspergillus terreus culture filtrate and Allium cepa seeds extract and their potent applications. *Biocatal. Agric. Biotechnol.*, 5, 116, 2016.
62. Walentowska, J., Foksowicz-Flaczyk, J., Thyme essential oil for antimicrobial protection of natural textiles. *Int. Biodeterior. Biodegradation*, 84, 407, 2013.
63. Ibrahim, N. A., Eid, B. M., Abdel-Aziz, M. S., Effect of plasma superficial treatments on antibacterial functionalization and coloration of cellulosic fabrics. *Appl. Surf. Sci.*, 392, 1126, 2016.
64. Ghayempour, S., Mortazavi, S. M., Microwave curing for applying polymeric nanocapsules containing essential oils on cotton fabric to produce antimicrobial and fragrant textiles. *Cellulose*, 22, 4065, 2015.
65. Yeo, S. Y., Lee, H. J., Jeong, S. H., Preparation of nanocomposite fibers for permanent antibacterial effect. *J. Mater. Sci.*, 38, 2143, 2003.
66. Yuan Gao, Cranston, R., Recent Advances in Antimicrobial Treatments of Textiles. *Text. Res. J.*, 78, 60, 2008.

67. Tomsic, B., Klemencic, D., Simoncic, B., Orel, B., Influence of antimicrobial finishes on the biodeterioration of cotton and cotton/polyester fabrics: Leaching versus bio-barrier formation. *Polym. Degrad. Stab.*, 96, 1286, 2011.
68. Ali, S. W., Purwar, R., Joshi, M., Rajendran, S., Antibacterial properties of Aloe vera gel-finished cotton fabric. *Cellulose*, 21, 2063, 2014.
69. Feng, X., Zheng, K., Wang, C., Chu, F., Chen, Y., Durable antibacterial cotton fabrics with chitosan based quaternary ammonium salt. *Fiber Polym.*, 17, 371, 2016.
70. Anita, S., Ramachandran, T., Rajendran, R., Koushik, C. V., Mahalakshmi, M., A study of the antimicrobial property of encapsulated copper oxide nanoparticles on cotton fabric. *Text. Res. J.*, 81, 1081, 2011.
71. Errokh, A., Ferraria, A.M., Conceicao, D. S., Vieira Ferreira, L. F., *et al.*, Controlled growth of Cu_2O nanoparticles bound to cotton fibres. *Carbohydr. Polym.*, 141, 229, 2016.
72. Becenen, N., Altun, Ö., Applications of TiO_2, ZnO and Ag Nanomaterials to Denim Fabric. *J. Nanosci. Nanotechnol.*, 16 5359, 2016.
73. Hebeish, A.A., Abdelhady, M.M., Youssef, A.M., TiO_2 nanowire and TiO_2 nanowire doped Ag-PVP nanocomposite for antimicrobial and self-cleaning cotton textile. *Carbohydr. Polym.*, 91, 549, 2013.
74. Khurshid MF, A.M., Asad M, Shah SNH, Assessment of Eco-Friendly Natural Antimicrobial Textile Finish Extracted from Aloe Vera and Neem Plants. *Fibres Text. East. Eur.*, 23, 120, 2015.
75. Messaoud, M., Chadeau, E., Chaudout, P., Oulahal, N., Langlet, M., Quaternary Ammonium-based Composite Particles for Antibacterial Finishing of Cotton-based Textiles. *J. Mater. Sci. Technol.*, 30, 19, 2014.
76. [Gilbert, P., Moore, L. E., Cationic antiseptics: Diversity of action under a common epithet. *J. Appl. Microbiol.*, 99, 703, 2005.
77. Caillier, L., de Givenchy, E.T., Levy, R., Vandenberghe, Y., *et al.*, Synthesis and antimicrobial properties of polymerizable quaternary ammoniums. *Eur. J. Med. Chem.*, 44, 3201, 2009.
78. Gao, D.-G., Chen, C., Ma, J.-Z., Lv, B., Jia, X.-L., Preparation, characterization and application of ZnO sol containing quaternary ammonium salts. *J. Solgel Sci. Technol.*, 65, 336, 2013.
79. Ashraf, S., Akhtar, N., Ghauri, M. A., Rajoka, M. I., *et al.*, Polyhexamethylene biguanide functionalized cationic silver nanoparticles for enhanced antimicrobial activity. *Nanoscale Res. Lett.*, 7, 267, 2012.
80. Kawabata, A., Taylor, J. A., The effect of reactive dyes upon the uptake and anti bacterial action of poly(hexamethylene biguanide) on cotton. Part 2: Uptake of poly(hexamethylene biguanide) on cotton dyed with β-sulphatoethylsulphonyl reactive dyes. *Dyes Pigm*,, 68, 197, 2006.
81. Franck Hui, Debiemme-Chouvy, C., Antimicrobial N-Halamine Polymers and Coatings: A Review of Their Synthesis, Characterization, and Applications. *Biomacromolecules*, 14, 585–601, 2013.
82. Dhiman, G., Chakraborty, J. N., Antimicrobial performance of cotton finished with triclosan, silver and chitosan. *Fashion Text.*, 2, 13, 2015.

83. Uddin, F., Environmental concerns in antimicrobial finishing of textiles. *Inter. J. Text. Sci.*, 1A, 15, 2014.
84. Shahid, M., Ahmad, A., Yusuf, M., Khan, M. I., *et al.*, Dyeing, fastness and antimicrobial properties of woolen yarns dyed with gallnut (Quercus infectoria Oliv.) extract. *Dyes and Pigments*, *95*, 53, 2012
85. Ariede, M. B., Candido, T. M., Jacome, A. L. M., Velasco, M. V. R., *et al.*, Cosmetic attributes of algae - A review. *Algal Research,*, *25*, 483, 2017
86. Cheng, X., Ma, K., Li, R., Ren, X., Huang, T. S., Antimicrobial coating of modified chitosan onto cotton fabrics. *Appl. Surf. Sci.*, 309, 138, 2014.
87. Fu, X., Shen, Y., Jiang, X., Huang, D., Yan, Y., Chitosan derivatives with dual-antibacterial functional groups for antimicrobial finishing of cotton fabrics. *Carbohydr. Polym.*, 85, 221, 2011.
88. Ferrero, F., Periolatto, M., Ferrario, S., Sustainable antimicrobial finishing of cotton fabrics by chitosan UV-grafting: from laboratory experiments to semi industrial scale-up. *J. Clean Prod.*, 96, 244, 2015.
89. Hebeish, A., Abdel-Mohdy, F. A., Fouda, M. M. G., Elsaid, Z., *et al.*, Green synthesis of easy care and antimicrobial cotton fabrics. *Carbohydr. Polym.*, 86, 1684, 2011.
90. Šauperl, O., Volmajer-Valh, J., Viscose Functionalisation with a Combination of Chitosan/BTCA Using Microwaves. *Fibres Text. East. Eur.*, 21, 24, 2013.
91. Ferrero, F., Periolatto, M., Antimicrobial Finish of Textiles by Chitosan UV-Curing. *J. Nanosci. Nanotechnol.*, 12, 4803, 2012.
92. Karthikeyan, N., Vijayalakshmi, K. A., Vignesh, K., Functionalisation of viscose fabric with chitosan particles using non-thermal oxygen plasma. Mater. *Technol.*, 31, 358, 2016.
93. [89] Gyawali, R., Ibrahim, S. A., Natural products as antimicrobial agents. *Food Control*, 46, 412, 2014.
94. [90] Tummalapalli, M., Berthet, M., Verrier, B., Deopura, B. L., *et al.*, Composite wound dressings of pectin and gelatin with aloe vera and curcumin as bioactive agents. *Int. J. Biol. Macromol.*, 82, 104, 2016.
95. Thilagavathi, G., Rajendrakumar, K., Rajendran, R., Development of eco-friendly antimicrobial textile finishes using herbs. *Indian J. Fibre Text. Res.*, 30, 431, 2005.
96. Sathianarayanan, M. P., Bhat, N. V., Kokate, S. S., Walunj, V. E., Antimicrobial finish for cotton fabrics from herbal products. *Indian J. Fibre Text. Res.*, 35, 50, 2010.
97. Thilagavathi, G., Kannaian, T., Application of Prickly Chaff (Achyranthes aspera Linn.) leaves as herbal antimicrobial finish for cotton fabric used in healthcare textiles. Natural Product Radiance, 7, 330, 2008.
98. Ibrahim, N. A., El-Zairy, E. M. R., Eid, B. M., Eco-friendly modification and antibacterial functionalization of viscose fabric. *J. Text. Inst.*, 108, 1406, 2017.
99. Vaideki, K., Jayakumar, S., Thilagavathi, G., Rajendran, R., A study on the antimicrobial efficacy of RF oxygen plasma and neem extract treated cotton fabrics. *Appl. Surf. Sci.*, 253, 7323, 2007.

100. Ibrahim, N. A., Eid, B. M., El-Zairy, E. R., Antibacterial functionalization of reactive-cellulosic prints via inclusion of bioactive Neem oil/βCD complex. *Carbohydr. Polym.*, 86, 1313, 2011.
101. Murugesh Babu, K., Ravindra, K. B., Bioactive antimicrobial agents for finishing of textiles for health care products. *J. Text. Inst.*, 106, 706, 2015.
102. Sarkar, R. K., Purushottam, D., Chauhan, P. D., Bacteria resist finish on cotton fabric using natural herbal extract. *Indian J. Fibre Text. Res.*,, 28, 322, 2003.
103. Ibrahim, N. A., Eid, B. M., Youssef, M. A., Ibrahim, H. M., *et al.*, Multifunctional finishing of cellulosic/polyester blended fabrics. *Carbohydr. Polym.*, 97, 783, 2013.
104. Hui, L., He, L., Huan, L., XiaoLan, L., Chemical composition of lavender essential oil and its antioxidant activity and inhibition against rhinitisrelated bacteria. *African J. Microbiol. Res.*, 4, 309, 2010.
105. Ibrahim, N. A., El-Gamal, A. R., Gouda, M., Mahrous, F., A new approach for natural dyeing and functional finishing of cotton cellulose. *Carbohydr. Polym.*, 82, 1205, 2010.
106. Gupta, D., Laha, A., Antimicrobial activity of cotton fabric treated with Quercus infectoria extract. *Indian J. Fibre Text. Res.*, 32, 88, 2007.
107. Liu, J., Liu, C., Liu, Y., Chen, M., *et al.*, Study on the grafting of chitosan-gelatin microcapsules onto cotton fabrics and its antibacterial effect. Colloid s Surf. *B. Biointerfaces*, 109, 103, 2013.
108. YanYan Zhang, Qing Bo Xu, Fei Ya Fu, Liu, X. D., Durable antimicrobial cotton textiles modified with inorganic nanoparticles..*Cellulose*, 23, 2791, 2016.
109. Rehan, M., Barhoum, A., Van Assche, G., Dufresne, A., *et al.*, Towards multifunctional cellulosic fabric: UV photo-reduction and *in-situ* synthesis of silver nanoparticles into cellulose fabrics. *Int. J. Biol. Macromol.*, 98, 877, 2017.
110. Sawhney, A. P. S., Condon, B., Singh, K. V., Pang, S. S., *et al.*, Modern Applications of Nanotechnology in Textiles. *Text. Res. J.*, 78, 731, 2008.
111. Montazer, M., Alimohammadi, F., Shamei, A., Rahimi, M. K., Durable antibacterial and cross-linking cotton with colloidal silver nanoparticles and butane tetracarboxylic acid without yellowing. *Colloids Surf. B. Biointerface s*, 89, 196, 2012.
112. Kozicki, M., Sasiadek, E., Kołodziejczyk, M., Komasa, J., *et al.*, Facile and durable antimicrobial finishing of cotton textiles using a silver salt and UV light. *Carbohydr. Polym.*, 91, 115, 2013.
113. Busila, M., Musat, V., Textor, T., Mahltig, B., Synthesis and characterization of antimicrobial textile finishing based on Ag:ZnO nanoparticles/chitosan biocomposites. *RSC Adv.*, 5, 21562, 2015.
114. Petkova, P., Francesko, A., Perelshtein, I., Gedanken, A., Tzanov, T., Simultaneous sonochemical-enzymatic coating of medical textiles with antibacterial ZnO nanoparticles. *Ultrason. Sonochem.*, 29, 244, 2016.
115. Sedighi, A., Montazer, M., Samadi, N., Synthesis of nano Cu_2O on cotton: Morphological, physical, biological and optical sensing characterizations. *Carbohydr. Polym.*, 110, 489, 2014.

116. Sondi, I., Goia, D. V., Matijević, E., Preparation of highly concentrated stable dispersions of uniform silver nanoparticles. *J. Colloid Interface Sci.*, 260, 75, 2003.
117. Reed, R. B., Zaikova, T., Barber, A., Simonich, M., *et al.*, Potential Environmental Impacts and Antimicrobial Efficacy of Silver- and Nanosilver-Containing Textiles. *Environ. Sci. Technol.*, 50, 4018, 2016.
118. Tam, K. H., Djuri, A. B., Chan, C. M. N., Xi, Y. Y., *et al.*, Antibacterial activity of ZnO nanorods prepared by a hydrothermal method. *Thin Solid Films*, 516, 6167, 2008.
119. El-Hady, M. M. A., Farouk, A., Sharaf, S., Flame retardancy and UV protection of cotton based fabrics using nano ZnO and polycarboxylic acids. *Carbohydr. Polym.*, 92, 400, 2013.
120. Anitha, S., Brabu, B., Thiruvadigal, D. J., Gopalakrishnan, C., Natarajan, T. S., Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO. *Carbohydr. Polym.*, 87, 1065, 2012.
121. Gabbay, J., Borkow, G., Mishal, J., Magen, E., *et al.*, Copper Oxide Impregnated Textiles with Potent Biocidal Activities. *J. Ind.Text.*, 35, 323, 2006.
122. Abbasipour, M., Mirjalili, M., Khajavi, R., Majidi, M. M., Coated Cotton Gauze with Ag/ZnO/chitosan Nanocomposite as a Modern Wound Dressing. *J. Eng. Fiber Fabr.*, 9, 124, 2014.
123. Raza, Z. A., Anwar, F., Ahmad, S., Aslam, M., Fabrication of ZnO incorporated chitosan nanocomposites for enhanced functional properties of cellulosic fabric. Mater. *Res. Express*, 3, 115001, 2016.
124. Gouda, M., Hebeish, A., Preparation and Evaluation of CuO/Chitosan Nanocomposite for Antibacterial Finishing Cotton Fabric. *J. Ind. Text.*, 39, 203, 2010.
125. Rajendran, R., Radhai, R., Hasabo, A., Vigneswaran, C., *et al.*, Synthesis and Characterization of Neem Chitosan Nanocomposites for Development of Antimicrobial Cotton Textiles. *J. Eng. Fiber Fabr.*, 7, 136, 2012.
126. Chandrasekar, S., Vijayakumar, S., Rajendran, R., Application of chitosan and herbal nanocomposites to develop antibacterial medical textile. *Biomed. Aging Pathol.*, 4, 59, 2014.
127. Bozaci, E., Akar, E., Ozdogan, E., Demir, A., *et al.*, Application of carboxymethylcellulose hydrogel based silver nanocomposites on cotton fabrics for antibacterial property. *Carbohydr. Polym.*, 134, 128, 2015.
128. Khafaga, M. R., Ali, H. E., El-Naggar, A. W. M., Antimicrobial finishing of cotton fabrics based on gamma irradiated carboxymethyl cellulose/poly(vinyl alcohol)/TiO_2 nanocomposites. J. Text. Inst., 107, 766, 2016.
129. Teli, M. D., Sheikh, J., Modified bamboo rayon–copper nanoparticle composites as antibacterial textiles. Int. *J. Biol. Macromol.*, 61, 302, 2013.
130. Zahran, M. K., Ahmed, H. B., El-Rafie, M. H., Surface modification of cotton fabrics for antibacterial application by coating with AgNPs–alginate composite. Carbohydr. *Polym.*, 108, 145, 2014.

131. Zhang, D., Zhang, G., Chen, L., Liao, Y., *et al.*, Multifunctional finishing of cotton fabric based on *in situ* fabrication of polymer-hybrid nanoparticles. *J. Appl. Polym. Sci.*, 130, 3778, 2013.
132. Zhang, G., Liu, Y., Morikawa, H., Chen, Y., Application of ZnO nanoparticles to enhance the antimicrobial activity and ultraviolet protective property of bamboo pulp fabric. *Cellulose*, 20, 1877, 2013.
133. Petkova, P., Francesko, A., Fernandes, M. M., Mendoza, E., *et al.*, Sonochemical Coating of Textiles with Hybrid ZnO/Chitosan Antimicrobial Nanoparticles. ACS Appl. *Mater. Interfaces,* 6, 1164, 2014.
134. Mocanu, G., Nichifor, M., Mihai, D., Oproiu, L. C., Bioactive cotton fabrics containing chitosan and biologically active substances extracted from plants. *Mater. Sci. Eng. C.*, 33, 72, 2013.
135. Zhao, J., Tang, Y., Liu, Y., Cui, L., *et al.*, Design carboxymethyl cotton knitted fabrics for wound dressing applications: Solvent effects. *Mater. Design*, 87, 238, 2015.
136. Abo-Shosha, M. H., Fahmy, H. M., Hassan, F. H., Ashour, A. M., Khalil, A. A., Tetracycline hydrate and gentamicine sulfate containing carboxymethylated cotton fabric suitable for moist wound healing dressings: Properties and evaluation. *J. Ind. Text.*, 38, 341, 2009.
137. Su, C.-H., Kumar, G. V., Adhikary, S., Velusamy, P., *et al.*, Preparation of cotton fabric using sodium alginate-coated nanoparticles to protect against nosocomial pathogens. *Biochem. Eng. J.*, 117, Part B, 28, 2017.
138. Zahran, M. K., Ahmed, H. B., El-Rafie, M. H., Surface modification of cotton fabrics for antibacterial application by coating with AgNPs-alginate composite. *Carbohydr. Polym.*, 108, 145, 2014.
139. Paladini, F., Picca, R. A., Sportelli, M. C., Cioffi, N., *et al.*, Surface chemical and biological characterization of flax fabrics modified with silver nanoparticles for biomedical applications. *Mater. Sci. Eng. C.*, 52, 1, 2015.
140. Hanh, T. T., Thu, N. T., Hien, N. Q., An, P. N., *et al.*, Preparation of silver nanoparticles fabrics against multidrug-resistant bacteria. *Radiat. Phys. Chem.*, 121, 87, 2016.
141. Xu, Y., Qiu, C., Zhang, X., Zhang, W., Crosslinking chitosan into H_3PO_4/HNO_3-$NANO_2$ oxidized cellulose fabrics as antibacterial-finished material. *Carbohydr. Polym.*, 112, 186, 2014.
142. Goel, N. K., Kumar, V., Rao, M. S., Bhardwaj, Y. K., Sabharwal, S., Functionalization of cotton fabrics by radiation induced grafting of quaternary salt to impart antibacterial property. *Radiat. Phys. Chem.*, 80, 1233, 2011.
143. Staneva, D., Koutzarova, T., Vertruyen, B., Vasileva-Tonkova, E., Grabchev, I., Synthesis, structural characterization and antibacterial activity of cotton fabric modified with a hydrogel containing barium hexaferrite nanoparticles. *J. Mol. Struct.*, 1127, 74, 2017.
144. Dhandapani, P., Siddarth, A. S., Kamalasekaran, S., Maruthamuthu, S., Rajagopal, G., Bio-approach: Ureolytic bacteria mediated synthesis of ZnO

nanocrystals on cotton fabric and evaluation of their antibacterial properties. *Carbohydr. Polym.*, 103, 448, 2014.

145. Firoz Babu, K., Dhandapani, P., Maruthamuthu, S., Anbu Kulandainathan, M., One pot synthesis of polypyrrole silver nanocomposite on cotton fabrics for multifunctional property. *Carbohydr. Polym.*, 90, 1557, 2012.
146. Fang, F., Chen, X., Zhang, X., Cheng, C., *et al.*, Environmentally friendly assembly multilayer coating for flame retardant and antimicrobial cotton fabric. *Prog. Org. Coat.*, 90, 258, 2016.
147. El-Rafie, H. M., El-Rafie, M. H., AbdElsalam, H. M., El-Sayed, W. A., Antibacterial and anti-inflammatory finishing of cotton by microencapsulation using three marine organisms. *Int. J. Biol. Macromol.*, 86, 59, 2016.
148. Goel, N. K., Rao, M. S., Kumar, V., Bhardwaj, Y. K., *et al.*, Synthesis of antibacterial cotton fabric by radiation-induced grafting of [2-(Methacryloyloxy) ethyl]trimethylammonium chloride (MAETC) onto cotton. Radiat, *Phys. Chem.*, 78, 399, 2009.
149. Singh, N., Yadav, M., Khanna, S., Sahu, O., Sustainable fragrance cum antimicrobial finishing on cotton: Indigenous essential oil. Sustain. *Chem. Pharm.*, 5, 22, 2017.
150. Guibal, E., Cambe, S., Bayle, S., Taulemesse, J.-M., Vincent, T., Silver/chitosan/cellulose fibers foam composites: From synthesis to antibacterial properties. *J. Colloid Interface Sci.*, 393, 411, 2013.
151. Galkina, O. L., Sycheva, A., Blagodatskiy, A., Kaptay, G., *et al.*, The sol-gel synthesis of cotton/TiO2 composites and their antibacterial properties. *Surf. Coat. Technol.*, 253, 171, 2014.
152. Shateri Khalil-Abad, M., Yazdanshenas, M. E., Superhydrophobic antibacterial cotton textiles. *J. Colloid Interface Sci.*, 351, 293, 2010.
153. Gomes, A. P., Mano, J. F., Queiroz, J. A., Gouveia, I. C., Incorporation of antimicrobial peptides on functionalized cotton gauzes for medical applications. *Carbohydr. Polym.*, 127, 451, 2015.
154. Pisitsak, P., Ruktanonchai, U., Preparation, characterization, and *in vitro* evaluation of antibacterial sol-gel coated cotton textiles with prolonged release of curcumin. *Text. Res. J.*, 85, 949, 2015.
155. Abramiuc, D., Ciobanu, L., Muresan, R., Chiosac, M., Muresan, A., Antibacterial finishing of cotton fabrics using biologically active natural compounds. *Fiber Polym.*, 14, 1826, 2013.
156. Firdhouse, M. J., Lalitha, P., Fabrication of antimicrobial perspiration pads and cotton cloth using amaranthus dubius mediated silver nanoparticles. *J. Chem.*, 2013, http://dx.doi.org/10.1155/2013/741743.
157. Silva, R., Ferreira, H., Matama, T., Gomes, A.C., Cavaco-Paulo, A., Wound-healing evaluation of entrapped active agents into protein microspheres over cellulosic gauzes. *Biotechnol. J.*, 7, 1376, 2012.
158. Budimir, A., Vukusic, S.B., Flincec, S.G., Study of antimicrobial properties of cotton medical textiles treated with citric acid and dried/cured by microwaves. *Cellulose*, 19, 289, 2012.

159. Tayel, A.A., Moussa, S.H., El-Tras, W.F., Elguindy, N.M., Opwis,K., Antimicrobial textile treated with chitosan from Aspergillus niger mycelial waste. *Int. J. Biol. Macromol.*, 49, 241, 2011.
160. Ibrahim, N.A., Abd El-Aziz, E., Eid, B.M., Abou Elmaaty, T.M., Single-stage process for bifunctionalization and eco-friendly pigment coloration of cellulosic fabrics. *J. Text. Inst.*, 107, 1022, 2016.

14

Bio-Macromolecules: A New Flame Retardant Finishing Strategy for Textiles

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Abstract

Nowadays, the seeking for new, low environmental impact flame retardants (FRs) has pushed the scientific community toward the assessment of feasibility of selected bio-macromolecules as potential FRs for textiles (namely, cotton, polyester and their blends). In fact, such products as some proteins (caseins, whey proteins, hydrophobins, …) and nucleic acids exhibit a chemical composition comprising those elements (namely, phosphorus, nitrogen and/or sulphur), which are able to provide the treated fabrics with FR features. In other words, the bio-macromolecules-treated fabrics show an enhanced resistance to flame spread and heat flux. There are different possibilities for applying such bio-macromolecules to the fabric substrates: in particular, impregnation/exhaustion methods and layer by layer treatments can be successfully exploited.

This chapter is aimed at summarizing the recent advances on the use of different bio-macromolecules as "green" FR systems, also discussing the current limitations of this "bio-strategy" and some possible perspectives for the next future.

Keywords: Flame retardant finishing, cotton, polyester, proteins, nucleic acids, layer by layer

14.1 Introduction

Flammability represents one of the current major concerns, which significantly limits the applications in the fields of textiles and related materials. According to the International Association of Fire and Rescue Services,

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from 1993 to 2014 fire statistics from 40 countries, collectively representing 2.6 billion inhabitants of the Earth, reported 3.8 million fires and 45,400 fire deaths. In particular, statistics indicate that in 32 countries, representing 15% of the world's population, 49 million calls (45.3 calls per 1000 inhabitants), 2.7 million fires (5.5% of all calls, 2.5 fires per 1000 inhabitants), 20.7 thousand fire deaths (1.9 fire deaths per 100,000 inhabitants), and 64.3 thousand fire injuries (5.9 fire injuries per 100,000 inhabitants) occurred [1]. Most of the deaths are caused by inhalation of smoke and toxic combustion gases, such as carbon monoxide; the injuries are a consequence of the exposure to the heat from fires.

Specifically referring to textiles, as well documented in the annual U.K. fire statistics, most of the fire incidents happen in the home and involve bedding, nightwear, and upholstered furniture [2].

Therefore, since 1950s, both the academic and industrial community has been involved in the design and development of efficient flame retardants (FRs) that are aimed at lowering the risk of fire: more specifically, they are able to decrease the ease of flammability of textiles by reducing the propensity of the material to ignition or slowing down the flame spread rate when required.

From an overall point of view, flaming combustion is an oxidative reaction taking place in the gas phase, thus, requesting oxygen (or air) from the surrounding atmosphere. Prior to the flaming combustion, polymer degradation has to occur: during this stage, combustible volatile species, which mingle with atmospheric oxygen, are formed and according to the exothermic character of the flame, a self-sustaining combustion cycle (Figure 14.1) can be supported when the heat transmitted to the textile surface is sufficient.

Till now, several different chemical additives usually based on halogens, boron, nitrogen, metals, phosphorus, sulphur, or on a combination of them, have been designed and produced in order to provide fibers and fabrics with FR features. It is noteworthy that the use of a specific FR is strictly related to the chemical composition and to the thermal and fire behavior of the selected textile substrate [3, 4].

As far as synthetic fibers are concerned, their suitable FRs can be directly embedded during the spinning process: to this aim, it is possible to graft them onto the polymer backbone or to perform copolymerization reactions; in addition, FRs can be applied as surface treatments either on synthetic or natural fibers/fabrics [5, 6].

Both finishing and coating methods can be successfully exploited for applying FRs to textile substrates: in particular, the finishing exploits the impregnation of the fabric in a solution or stable suspension containing the FR compound. Coating methods require the application of a continuous or

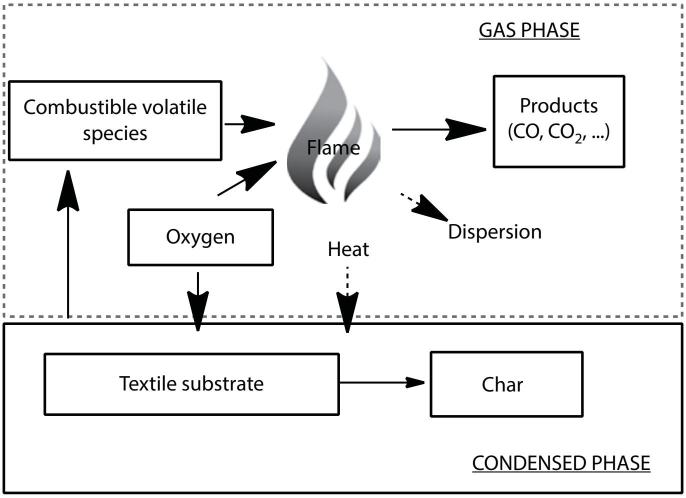

Figure 14.1 Scheme of the self-sustaining combustion cycle for textiles.

discontinuous layer/film on both the outer surface and back of the textile substrate.

The main characteristics of FRs are aimed at breaking the self-sustaining combustion cycle of the textile materials: this can be fulfilled either by achieving the extinction of the flame or by lowering the burning rate. More specifically, any FR should be able to:

- Decrease the heat developed to below the level that required for sustaining the textile combustion
- Address the pyrolysis process toward the reduction of the amount of flammable volatile species, thus favoring the formation of char, a less flammable carbonaceous residue that also behaves as a barrier between the polymer and the flame, in the condensed phase
- Separate the flame from the oxygen/air source
- Release chlorine or bromine atoms, able to act in gas phase as flame inhibitors, when the textile substrate is heated to near the ignition temperature.
- Lower the heat flow back to the textile substrate, hence limiting further pyrolysis phenomena that can give rise to additional flammable volatile species fuelling the flame
- Favor the formation of a barrier (such as an in tumescent protective coating or a char) when the textile substrate is exposed to a flame or a heat flow.

During the last 65–70 years, several FRs have been designed and developed for almost all the natural and synthetic textiles: as clearly reported by Horrocks in a quite recent review [7], from an historical point of view FRs have undergone a continuous evolution according to the main following periods:

1. The 'golden period' of FR research (1950–1980)
2. The 1980–late 1990s period
3. The 2000 onward period

During the first (and longest) period, the first patents for organophosphorus-based FRs for cotton were invented; besides, inherently FR synthetic fibers based on polymer chains bearing aromatic rings were developed and put on the market.

Unlike the second one, which was characterized by very limited research in FR textiles, the 2000 onward period saw a significant development of char-promoting FRs; these latter were often combined with phosphorus-containing species. This was also the period, during which the toxicity of bromine-based FRs was demonstrated, hence leading to the seeking for possible effective alternatives. However, the third period is also very well known for the exploitation of nanotechnology and nanomaterials (in particular in form of nanoparticles or nanolamellae) as a potential efficient strategy for creating self-assembled nanolayer ceramic films, able to protect the underlying textile substrate, hence enhancing the fire retardant behavior of this latter. In particular, two different approaches, i.e. top-down and bottom-up methods, have been effectively exploited: the latter is based on the build-up of single or aggregates/assemblies of different types of nanoparticles on the fabric surface; conversely, the former utilizes preformed (colloidal) nanoparticle stable suspensions as finishing baths for treating the fibres/fabrics (e.g. through an impregnation/exhaustion method).

There exist other possibilities for classifying FRs: one of them groups these additives on the basis of the type of elements that are specifically responsible for flame retardancy. According to this idea, FR additives comprise halogenated organic FRs (mainly brominated and chlorinated), phosphorous containing FRs, nitrogen-containing FRs and inorganic FRs.

Finally, expressly concerning the textile area, FRs can be also classified on the basis of their laundry durability: in fact, durable FRs cannot be washed off immediately when soaked in water and can resist some 50 or 100 washing cycles; in other cases, non-durable FRs may resist dry cleaning only. In addition, there also exist semi-durable FRs, which are able to tolerate water soaking and possibly a few washing cycles.

As mentioned above, the toxicity and the severe directives lately supported by EU community and USA have banned some of the halogenated FRs (such as decabromodiphenyl or pentabromodiphenyl ethers and polychlorinated biphenyls): in fact, these products have undoubtedly shown to be bioaccumulative and persistent [8]; besides, they exhibited environmentally toxic characteristics for both animals and humans [9–12].

These problems have stimulated the scientific community toward the design of such possible and less toxic alternatives as phosphorus-based FRs, which seem less toxic and may represent a suitable alternative to their halogen-based counterparts [13, 14]. In particular, specifically referring to cotton and cellulosic-rich substrates, the current attention is focused either on the production of effective halogen-free substituents for coatings and back-coated textiles or on the use of hydroxymethylphosphonium salts (Proban®) or N-methylol phosphonopropionamide derivatives (Pyrovatex®). Proban® process (schematized in Figure 14.2) is based on tetrakis (hydroxymethyl) phosphonium–urea condensate, which is applied to the fabric substrate by padding; then it is cross-linked by ammonia gas in a dedicated plant and treated with peroxides, in order to stabilize the resulting fabric substrate [15]. The good washing fastness achieved is a consequence of the deposition of the FR within the fibers due to the formation of a polymer network during the thermal treatment: this means that the FR is not covalently linked to the fabric substrate, but it is mechanically retained within the fiber interstices only. The main drawback of the Proban® process is the potential formaldehyde release during the fabric use [16].

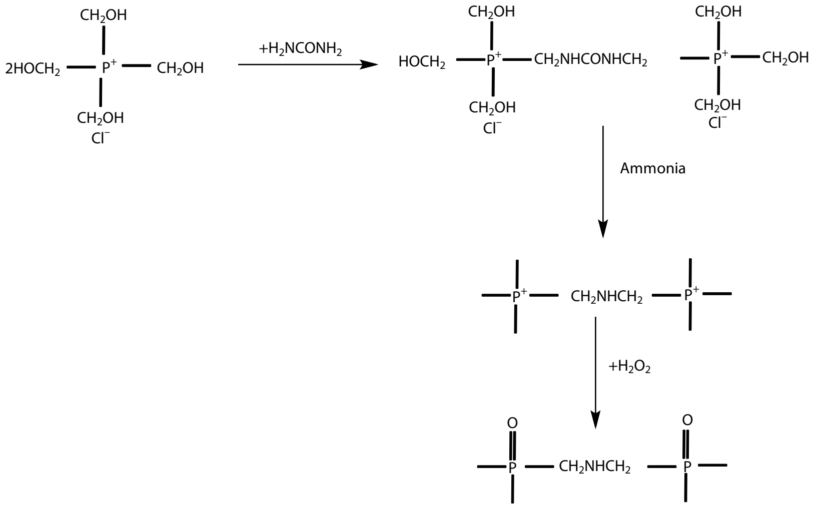

Figure 14.2 Scheme of the Proban® process.

At variance, Pyrovatex® process exploits a conventional pad-dry-cure treatment [15]: the formation of covalent links between the FR and the cellulose hydroxyl groups is provided by the use of a methylolated crosslinking agent (Figure 14.3).

Despite the formation of these covalent bonds, around 50% of the FR can be lost during the first washing cycle: this finding is ascribed to the unreacted Pyrovatex® species, which can be easily washed off; however, the remaining reacted FR is stably bound to the fabric substrate and therefore it can tolerate any of the successive laundry occasions.

Generally speaking, the possibility of replacing commercially available FRs with acceptable efficient alternative products has to accomplish with the following requirements (that are not easy to fulfill):

- Comparable or superior ease of application,
- No formaldehyde release during application or service,
- Equivalent textile service-life features (specifically referring to durability, comfort and tensile properties),
- Similar cost-effectiveness to the already exploitable FR products (or even cheaper),
- Comparable or lower toxicological and environmental issues,

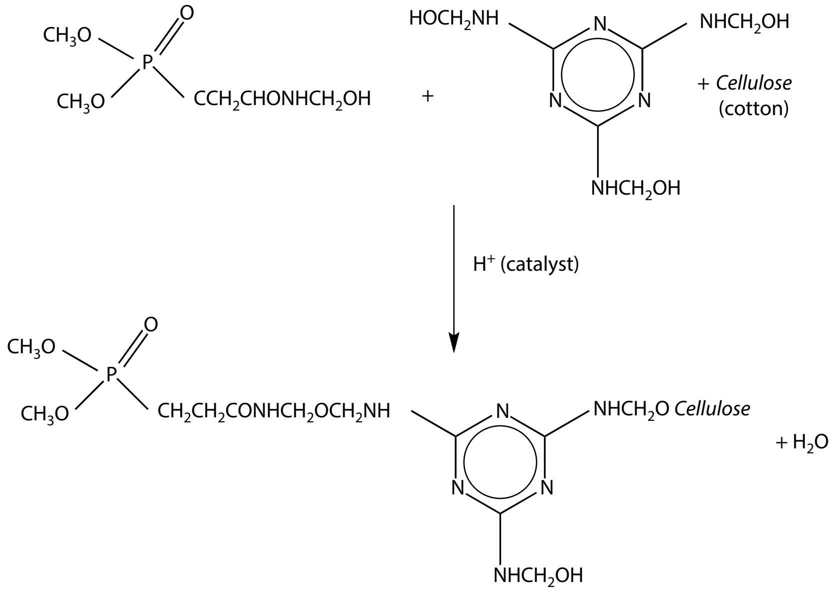

Figure 14.3 Scheme of the Pyrovatex® process.

- High air permeability of the treated fabric substrates,
- No changes as far as the outward appearance and aesthetics of the fabrics is concerned,
- No changes in the hue of the dye and/or dye ability of the fabrics.

At present, the scientific community is changing the approach toward the design of FR alternatives: in particular, the processes and technologies that have been proposed in the last decade are being focused on the development of low impact FRs, notwithstanding that washing fastness is still required for any new FR product.

In this context, the possibility of using bio-macromolecules (in particular some proteins and nucleic acids, even in combination with standard FRs) seems to pave the way toward the development of a new strategy fully addressed to the development of "green" and low environmental impact alternatives. In fact, when applied to fabric substrates, these selected bio-macromolecules, exhibiting a chemical composition that includes those elements (namely, phosphorus, nitrogen and/or sulphur) able to provide the treated fabrics with FR features, offer an improved resistance to flame spread as well as to a heat flux. Besides, some of them can be considered as by-products or wastes of the agro-food industry, so that their recovery and successive use as effective FRs may represent a new way for a further valorization, limiting and/or avoiding their landfill confinement. The bio-macromolecules can be applied to the fabric substrates by using different methods: apart from the impregnation/exhaustion technique, for which the already existing industrial plants could be directly utilized in large scale processes, layer by layer (LbL) treatments can be successfully used.

In the next paragraphs, the recent advances on the use of different bio-macromolecules as environmentally-friendly FRs systems will be thoroughly discussed, highlighting, at the same time, their current limitations and some possible outlooks concerning their future use in textile flame retardancy.

14.2 The Role of Bio-Macromolecules as Flame Retardant Systems: Structure-Property Relationships

The feasibility of using selected bio-macromolecules as potential FR alternatives to the current FR products is strictly determined by their structure and chemical composition. More specifically, the bio-macromolecules that show interesting FR features usually contain phosphorus, nitrogen and/or sulphur: in fact, all these elements, when opportunely organized within the bio-macromolecule structure, can provide interesting FR feature to the treated fabric substrates, as it will be shown in the next paragraphs.

14.2.1 Whey Proteins

These bio-macromolecules possess a globular structure with a considerable amount of α-helix structures, in which the acidic/basic and hydrophobic/hydrophilic aminoacids are fairly distributed along the polypeptide skeleton. The main constituents of whey proteins are β-lactoglobulin (β-LG), α-lactalbumin (α-LA), bovine serum albumin (BSA) and immunoglobulin (IG); these proteins are about 20% of the total protein content in milk (the remaining fraction comprises caseins).

They show a high nutritional value ascribable to their high essential amino acid content, specifically related to the sulfur-containing structures (i.e. cysteine and methionine; 5 and 8 cysteine residues are present in α-lactalbumin and β-lactoglobulin, respectively). Among the main functional features of whey proteins, it is worthy to mention their high water absorption, good solubility, gelatinization and emulsifying propensities, which are exploited in food applications [17].

Three main structures of whey protein products are obtainable: whey protein isolate (WPI), whey protein concentrate (WPC) and whey protein hydrolysate (WPH).

Among the different "traditional" uses, whey proteins have being utilized for obtaining edible and biodegradable films for food purposes, as food emulsifying agents, and for encapsulating bioactive elements in the design of functional foods [18–20].

Referring to FRs, quite recently cotton fabrics were treated with a WPI coating [21]: in particular, aqueous suspensions of both folded (WP) and unfolded/denatured (DWP) proteins (at 10 wt.%) were applied to the cellulosic substrate; the surplus of the suspension was then gently removed with a rotary drum and the impregnated fabrics were dried to constant weight in a climatic chamber (at 30 °C and 30% R.H.). The final dry add-on was about 20 and 25 wt.%, for WP and WPD whey proteins, respectively. Thermogravimetric analysis and horizontal flame spread tests were exploited for assessing the thermal and thermo-oxidative stability and fire behavior of the coated fabric substrates respectively.

First, it is worthy to examine the thermal and thermo-oxidative behavior of the treated fabrics, which is compared to that of untreated cotton in Table 14.1.

Table 14.1 Thermogravimetric data of neat and treated cotton fabrics.

Sample	$T_{10\%}$ (°C)	T_{max1*} (°C)	T_{max2*} (°C)	T_{max3*} (°C)	Residue @ T_{max1*} (%)	Residue @ T_{max2*} (%)	Residue @ T_{max3*} (%)	Residue @ 600 °C (%)
Nitrogen atmosphere								
COT	329	362			45.0			8.0
COT_WP	276	355			45.0			18.0
COT_WPD	294	366			45.5			17.0
Air atmosphere								
COT	323	343	489	–	48.0	2.0	–	<1.0
COT_WP	283	341	487	580	57.0	14.0	2.5	1.5
COT_WPD	292	345	496	575	56.0	13.0	3.0	2.5

In inert atmosphere (nitrogen flux), the thermal degradation of the cellulosic material occurs according to a single step, during which the maximum weight loss is reached (Table 14.1). This finding can be attributed to the pyrolysis of cellulose, which occurs following two competitive routes: the former involves the decomposition of the glycosyl units, which favors the formation of char at lower temperatures. The latter encompasses the depolymerization of glycosyl units toward the formation of volatile species at higher temperatures [22, 23]. The protein coating, irrespective of the bio-macromolecule structure (i.e., folded or unfolded), accounts for a strong sensitization of cellulose decomposition: this is indicated by the remarkable decrease of $T_{10\%}$ values (i.e., the temperature, at which the sample shows 10% weight loss) in the presence of the protein coatings.

The collected thermo-oxidative data are also presented in Table 14.1. In this environment, cotton generally shows three degradation steps. The first is located within 300–400 °C and comprises two competitive routes that favor the formation of volatile products together with an aliphatic carbonaceous residue. The second step, located in between 400 and 800 °C, is accompanied by the transformation of the aliphatic char into an aromatic counterpart, as well as by the formation of carbon monoxide and carbon dioxide species, which derive from the concurrent carbonization and char oxidation phenomena. Around 800 °C, the third and last thermo-oxidative step takes place: it involves the oxidation of the pre-formed char mainly to carbon monoxide and carbon dioxide.

Cotton fabrics treated with the whey proteins show two decomposition peaks at 343 and 489 °C, as shown in Table 14.1. As already discussed in nitrogen atmosphere, also in thermo-oxidative conditions the protein coating, regardless of the protein type, is accountable for the sensitization of cellulose decomposition (as confirmed by $T_{10\%}$ values); at the same time, it allows the formation of a thermally stable degradation product upon the first degradation stage (see the residues at T_{max1}). This degradation product, at high temperatures, undergoes other two degradation steps (referring to T_{max2} and T_{max3}), leading to the formation of slightly higher final residues as compared with untreated cotton.

The third and last weight loss can be detected for the protein-treated fabrics only (at 580 and 575 °C for COT_WP and COT_WPD, respectively): this phenomenon can be attributed to chemical or physical interactions occurring in between the protein coatings and the cellulosic substrate, which lead to an increase of the final residues at 600 °C.

The results of horizontal flame spread tests are collected in Table 14.2. Unlike untreated cotton, which burns very quickly without leaving any noticeable residue, the protein coating is responsible for a significant

Table 14.2 Flammability data of untreated and treated cotton fabrics.

Sample	Total burning time (s)	Burning rate (mm/s)	Residue (%)
COT	78	1.5	0
COT_WP	126	1.0	30
COT_WPD	133	1.1	5

increase of total burning time, as well as for the decrease of the burning rate; in addition, the bio-macromolecule treatment with WP favors the formation of a coherent and consistent residue. Conversely, the residue derived from WPD is brittle and not consistent. However, for both the protein coatings, despite the significant differences of final residues (30% vs. 5%, for COT_WP and COT_WPD, respectively), the fabric texture is maintained at the end of flame spread test, thus indicating that the bio-macromolecules are able to partially exert a protection effect on the underlying cellulosic substrate, possibly by limiting the oxygen diffusion and absorbing the heat evolved during the combustion process.

14.2.2 Caseins

Caseins are phosphorus-based proteins present in the main fraction of milk proteins (around 80%) and, maybe, the most extensively studied food proteins, obtained as co-products during the making of skim milk.

They are essentially made of α_{S1}, α_{S2}, β, and κ-caseins. α_{S1}-caseins bear 8 or 9 bound phosphate groups/mol and represent the major protein fraction of bovine milk; α_{S2}-caseins, which are analogous to α_{S1}counterparts, contain, according to their four different phosphorylated isoforms, from 10 to 13 phosphate groups/mol. β-caseins are less phosphorylated as compared to the α structures; furthermore, they include glutamines bearing amino groups and they have a single major phosphorylation site close to the N-terminus. Bovine β-caseins show a fully phosphorylated form only, bearing 5 phosphate groups/mol. Finally, κ-caseins show phosphorylated regions, present as single sites, located into the C-terminal region of the bio-macromolecule structure.

Notwithstanding the use of caseins in cheese industry, these proteins have been generally utilized as a food ingredient for improving some physical features, such as whipping, thickening, and foaming, and as emulsifying agents; furthermore, they turned out to fit applications including printing, papermaking, leather finishing, and manufacturing of synthetic fibers [24].

Their use as FRs is quite recent: in this context, casein aqueous suspensions (5 wt.%) were exploited for dip-treating cotton, polyester and cotton polyester blend (polyester content: 65 wt.%) fabrics in a climatic chamber (operating at 30 °C and 30% R.H.). Afterward, the excess of the suspensions was removed by gently pressing with a rotary drum; then the treated substrates were dried to constant weight (final dry add-on: 20 wt.%) [25, 26].

The thermal and thermo-oxidative data for the different fabrics treated with caseins are collected in Table 14.3. Alike cotton, in nitrogen polyester degrades according to a single step, during which the maximum weight loss is recorded at about 426 °C. More specifically, two competitive volatilization–charring processes may take place, involving either a heterolytic cleavage or a homolytic scission of ester bonds. Thus, the degradation favors the obtainment of vinyl- and carboxyl-terminated oligomers, which give rise to volatile species (like CO and CO_2, methane, ethylene, benzene, benzaldehyde, formaldehyde and acetaldehyde).These phenomena take place concurrently to the chain depolymerization due to intramolecular backbiting.

The polyester-cotton blend fabric displays a thermal degradation typical of a polymer blend, according two independent stages: the former takes place at ca. 351 °C and is attributable to cotton and the latter (at 423 °C) to the polyester component.

Once again, the casein coatings are responsible for a remarkable sensitization of both cellulose and polyester decomposition: in fact, $T_{10\%}$ values considerably decrease (−47 and −85 °C for COT Casein and PET Casein, respectively). This behavior can be attributed to the phosphate groups located on the shell of casein micelles, which, at high temperature, start releasing phosphoric acid that catalyzes the degradation of cellulose or polyester, favoring, at the same time, the formation of a thermally stable char.

The thermo-oxidation of polyester occurs according to a two-stage process, hence displaying two maxima weight losses (at 422 and 547 °C), attributable to concurrent β CH-transfer and chain depolymerization reactions, and to the further oxidation of both the residues formed during the first step and of the hydrocarbon species still present.

The thermo-oxidation of COT-PET blend shows a three-step process, with maxima weight losses at about 335, 416, and 525 °C.

Also in the case of caseins, a strong sensitization of the decomposition of the two fabric constituents is encountered, as shown by the $T_{10\%}$ decrease of about −76 and −82 °C for cellulose and polyester, respectively. Meanwhile, the first degradation step favors the development of a thermally stable product (see the residues at T_{max1}, Table 14.3), which evolves

Table 14.3 Thermogravimetric data of untreated and treated fabrics.

Nitrogen atmosphere								
Sample	$T_{10\%}$ (°C)	T_{max1}* (°C)	T_{max2}* (°C)	T_{max3}* (°C)	**Residue @** T_{max1}* (%)	**Residue @** T_{max2}* (%)	**Residue @** T_{max3}* (%)	**Residue @ 600 °C (%)**
COT	319	354	–	–	41.0	–	–	2.0
COT_Casein	272	337	–	–	49.0	–	–	21.0
PET	400	426	–	–	51.0	–	–	14.0
PET_Casein	315	397	–	–	53.0	–	–	22.0
COT-PET	332	351	423	–	73.0	37.0	–	15.0
COT-PET_Casein	304	334	405	–	75.0	42.0	–	22.0
Air atmosphere								
COT	318	339	478		48.0	4.0	–	<1
COT_Casein	242	327	482		51.0	10.0	–	<1
PET	392	422	547		47.5	1.5	–	0
PET_Casein	310	404	538		50.5	13.0	–	2
COT-PET	323	339	419	508	79.0	37.0	7.0	1
COT-PET_Casein	311	335	416	525	82.0	43.0	9.5	2

* From derivative curves.

Table 14.4 Horizontal flame spread and LOI data for untreated and casein-treated fabrics.

Sample	Total burning time (s)	Burning rate (mm/s)	Residue (%)	Dripping	LOI (%)
COT	78	1.3	–	No	18
COT_Casein	75	0.4	86	No	24
PET	57	1.8	43	Yes	21
PET_Casein	54	0.6	77	Yes	26
COT-PET	104	1.1	34	No	19
COT-PET_ Casein	171	0.7	55	No	21

at high temperatures (T_{max2}). The most important outcome is detected for treated PET between 425 and 525 °C: in fact, the formation of a stable and remarkable residue (i.e. 25 wt.%) is observed. It is worthy to note that, within the same temperature range, the untreated polyester achieves 10 wt.% residues only. Lastly, as far as COT-PET blends are considered, in addition to the first two peaks, a third weight loss takes place at about 508 °C; this value shifts to 525 °C when the blends are treated with the casein coating.

The FR features of the treated fabrics, evaluated by horizontal flame spread tests and Limiting Oxygen Index (LOI) measurements are presented in Table 14.4.

From an overall point of view, the casein coatings are responsible for a remarkable decrease of the total burning rate, as well as of a significant increase of the final residue, irrespective of the type of fabric considered. More specifically, caseins provide cotton fabrics with self-extinction, even after a second flame application. Casein-treated PET do not stop melt dripping, but remarkably decreases the burning rate (−67%), blocking the flame propagation within 30 mm and contributing to an important increase of the final residue. In addition, concerning the fabric blends, the presence of the casein coating reduces the burning rate by 36% with respect to the untreated counterparts, favoring, at the same time, the formation of a coherent final residue (see 4th column of Table 14.4). The measured LOI values of both cotton and polyester are also listed in Table 14.4: they remarkably increase (by 6 and 5%, for COT and PET, respectively, as compared to the untreated substrates).

Table 14.5 Cone calorimetry data for untreated and casein-treated fabrics.

Sample	TTI (s)	PkHRR* (kW/m^2)	ΔPkHRR (%)	Residue (%)
COT	18	52	–	1
COT_Casein	10	42	−19	3
PET	112	72	–	2
PET_Casein	62	70	−2.7	11
COT-PET	30	60	–	3
COT-PET_Casein	12	51	−15	5

* Experimental error: ±5%.

Lastly, the resistance to 35 kW/m^2 heat flux was assessed through cone calorimetry tests: the obtained results are shown in Table 14.5.

From the data of Table 14.5 it is noteworthy that the casein coatings, irrespective of the used fabric substrate, remarkably affect both time to ignition (TTI) and peak of heat release rate (PkHRR): in particular, the treated fabrics ignite earlier with respect to the untreated counterparts due to the activation of the protein coatings; in addition, PkHRR is considerably lowered for coated COT (-19%) and COT-PET blend (-15%). Finally, the char-forming behavior of caseins on PET fabrics is definitely shown by the significant increase of the residue after cone calorimetry tests.

14.2.3 Hydrophobins

Filamentous fungi produce hydrophobins that represent a wide family of small amphipathic bio-macromolecules having low molecular masses (ranging in between 7 and 9 kDa) [27].

Cysteine distribution and clustering of hydrophobic and hydrophilic amino acid residues allow classifying hydrophobins in two main groups, namely [28]:

- Class I (HFBI) proteins, which form hydrophobic aggregates, highly insoluble in aqueous media and with low wettability
- Class II (HFBII) proteins, which give rise to highly soluble hydrophilic aggregates.

Both these two classes have 8 cysteine residues that form 4 non-sequential disulphide bonds, hence stabilizing the protein tertiary structure. Hydrophobins are capable to self-assembly amphipathic monolayers at the hydrophobic–hydrophilic interfaces, hence acting as very surface-active bio-macromolecules [29].

Traditional applications of hydrophobins exploit the surfactant-like properties of these bio-macromolecules for the design of coating/protective agents, surface modifiers, adhesive systems, notwithstanding their quite recent utilization as surfactants and foaming agents, emulsifiers, for nanoencapsulation purposes, as nanovehicles in hydrophobic nutraceuticals for food and clear beverage enrichment, for biosensors, pharmaceuticals, and tissue engineering [30].

Their use in flame retardancy is quite new: recently, these proteins were applied to cotton fabrics, starting from a commercially-available 5 wt.% aqueous solution; the impregnation of the fabrics was carried out in a climatic chamber (30 °C and 30% R.H.) for 1 minute, then gently removing the solution excess with a rotary drum and drying the fabrics to constant weight in a climatic chamber. The final dry add-on was about 20 wt.% [25].

The thermogravimetric data in nitrogen and air for pristine (COT) and coated cotton (COT_H) fabrics are collected in Table 14.6.

As already assessed for all the afore-mentioned proteins, the hydrophobin coatings remarkably sensitize the cellulose decomposition (as confirmed by $T_{10\%}$ values of Table 14.6). In addition, notwithstanding that T_{max1} values are nearly unaffected by the presence of the protein coating, the residues left at 600 °C in both the atmospheres are significantly higher with respect to untreated cotton. This result can be attributed to the disulphide bonds of the protein, which start degrading at about 200 °C, releasing sulphidric acid that catalyzes cellulose dehydration toward the formation of a thermally stable carbonaceous residue.

Besides, the thermo-oxidative stability of the treated fabrics is similar to that of caseins: in fact, a thermally stable degradation product is obtained after the first degradation step (see the residue at T_{max1}); this product undergoes other two degradation stages (see T_{max2} and T_{max3}) at high temperatures and gives rise to a final residue slightly higher with respect to that of the untreated cellulosic substrate. The treated fabrics only show a further third and last weight loss at 620 °C, which can be attributed to chemical or physical interactions taking place among the degradation products of cotton and hydrophobins at high temperatures.

The results obtained after horizontal flame spread tests are listed in Table 14.7. Once again, the protein coating is accountable for a remarkable increase of the total burning time (+44%) and a decrease of the total

Table 14.6 Thermo gravimetric data of untreated and hydrophobins-treated cotton fabrics in nitrogen and air.

Nitrogen atmosphere								
Sample	**$T_{10\%}$ (°C)**	**T_{max1}* (°C)**	**T_{max2}* (°C)**	**T_{max3}* (°C)**	**Residue @ T_{max1}* (%)**	**Residue @ T_{max2}* (%)**	**Residue @ T_{max3}* (%)**	**Residue @ 600 °C (%)**
COT	329	362	–	–	48.0	–	–	8.0
COT_H	295	362	–	–	45.0	–	–	19.0
Air atmosphere								
COT	324	347	492	–	48.0	4.0	–	<1
COT_H	292	336	499	620	61.0	14.0	3.0	4.0

* From derivative curves.

Table 14.7 Flammability data of untreated and hydrophobin-treated cotton fabrics.

Sample	**Total burning time (s)**	**Burning rate (mm/s)**	**Residue (%)**
COT	72	1.5	0
COT_H	104	1.1	19

burning rate (–13%). In addition, the formation of a coherent final residue is observed at the end of the tests: SEM analyses performed on this letter clearly indicate the formation of several unblown pearl-like bubbles, ascribed to the cleavage of the disulphide bonds and to the crosslinking of amide groups.

The resistance to a heat flux was assessed through cone calorimetry tests: in particular, the HRR vs. time curves show a two-steps combustion process. As already found for the other proteins, the bio-macromolecular coating remarkably lowers time to ignition (–44%), but is also responsible for 45% decrease of peak of the heat release rate. The second and last combustion step can be ascribed to the formation of cracks within the irradiated surface, which create some preferential channels that further accelerate the combustion process.

14.2.4 Nucleic Acids

Deoxyribonucleic acid (DNA) is a very well known bio-macromolecule that comprises two long polymer chains of nitrogen-containing bases (i.e. adenine (A), guanine (G), cytosine (C), and thymine (T)), with backbones made of five-carbon sugars (i.e. the deoxyribose units) and of phosphate groups connected through ester bonds as well. These chains are rolled-up around the same axis and bonded together, thus forming a double helix. This latter takes advantage from the formation of hydrogen bonds between the bases that are placed side-by-side and combined in a specific 3D structure (i.e. adenine bases are paired with thymine ones, while cytosine bases are combined with guanine). As a result, the phosphoric residues and deoxyribose units are oriented toward the outside; conversely, the paired bases are positioned in the inner portion of the polymer and are stabilized by hydrophobic interactions.

In nature, both double helix and single chain DNA structures are present: the single chain can be also synthetically produced by exposing the double helix structure to thermal treatments above 80 °C or to extreme pH environments [31].

The aptitude of DNA to form double-stranded arrangements has been already utilized for producing several DNA-based nanomaterials, which can be exploited for several applications, comprising life science and even computing [32, 33].

The possible exploitation of DNA as a FR additive alternative to standard FR products is quite new and can be directly explained on the basis of its structure: in fact, it can be considered as an all-in-one intumescent system [34, 35], as it contains all the three components of an intumescent material in a single molecule:

- The phosphate groups, able to produce phosphoric acid that favors the dehydration of the fabric substrate, hence leading to the formation of a carbonaceous residue
- The deoxyribose units, which act as a carbon source and as blowing agents
- The nitrogen-containing bases (A, G, C, and T) that may release ammonia or nitrogen, hence contributing to the swelling of the system.

Generally speaking, when a heat flow or a flame are applied to intumescent materials, these latter give rise to the formation of a multicellular foamed carbonaceous shield on their surface, which behaves as a physical barrier able to limit the heat, fuel and oxygen transfer between flame and polymer, hence promoting flame extinction.

The first pioneering work, demonstrating the potentialities of DNA (extracted from herring sperm) as FR for cotton fabrics, dates back to 2013 [36]. It was found that, exploiting a standard impregnation/exhaustion method, the treated cotton fabrics were provided with self-extinction (bio-macromolecule final dry add-on: 19 wt.%). Among the most remarkable outcomes, an enhanced thermal and thermo-oxidative stability of the fabric in nitrogen and air, in terms of char residue formed at high temperatures was found. Furthermore, as assessed by horizontal flame spread tests, the combustion was stopped, reaching the flame out within 2 s, on the fabrics treated with the DNA coating. The FR properties of DNA were further confirmed by the measured LOI values (28 vs. 18% for DNA-treated fabrics and untreated cotton, respectively) and through cone calorimetry tests: for these latter, none of the treated specimens ignited upon exposure to 35 kW/m^2 heat flux.

The structure of the all-in-one intumescent additive clearly justified all the observed fire performances: in particular, the phosphoric acid released by the phosphate groups catalyzes the dehydration of cotton, favoring its auto-crosslinking toward the formation of a stable aromatic char (in combination with the deoxyribose units) and preventing the production of volatiles. This char behaves as a physical barrier, reducing the heat, fuel and oxygen transfer between the fabric substrate and the flame. Together, the decomposition of pyrimidine and purine bases results in the formation of azo-compounds, capable to further stimulate the char growth and the development of non-combustible swelling gases, such as nitrogen, carbon monoxide and carbon dioxide.

Then, the effect of different nucleic acids add-ons on cotton flammability was thoroughly investigated: in particular, three different add-ons (i.e. 5, 10 and 19 wt.%) were applied to cotton, by using the same impregnation/exhaustion method [37].

The thermogravimetric data in nitrogen and air for the treated fabrics are listed in Table 14.8. Once again, the bio-macromolecule coating remarkably sensitizes the cellulose decomposition, which is directly correlated to the DNA add-on: in particular, $T_{10\%}$ and T_{max1} values clearly indicate that, the higher is the bio-macromolecule add-on, the higher is the sensitization effect. This effect can be attributed to the phosphate groups

Table 14.8 Thermogravimetric data of pure and DNA-treated cotton fabrics in nitrogen and air.

Nitrogen atmosphere						
Sample	**$T_{10\%}$ (°C)**	**T_{max1}* (°C)**	**T_{max2}* (°C)**	**Residue @ T_{max1}* (%)**	**Residue @ T_{max2}* (%)**	**Residue @ 600 °C (%)**
COT	335	366	–	46.0	–	8.0
COT_DNA_5%	285	318	–	63.0	–	30.0
COT_DNA_10%	265	314	–	64.0	–	34.0
COT_DNA_19%	243	309	–	67.0	–	35.0
Air atmosphere						
COT	324	347	492	45.0	4.0	0
COT_DNA_5%	282	313	506	65.0	19.0	8.0
COT_DNA_10%	263	302	511	69.0	24.0	13.0
COT_DNA_19%	238	299	515	68.0	29.0	19.0

* From derivative curves

of DNA, which, upon decomposition, start releasing phosphoric acid at about 200 °C, hence favoring dehydration of the underlying cotton toward the formation of a char, thermally stable up to 600 °C. [38].

In air, the bio-macromolecule-treated fabrics show a decrease of both $T_{10\%}$ and T_{max1}, together with the development of a residue at T_{max1}, which is thermally stable beyond 500 °C (see T_{max2}, Table 14.8).

The results of horizontal flame spread tests are collected in Table 14.9. First of all, it is noteworthy that the fabrics treated with the lowest DNA add-on (i.e. 5 wt.%) burn completely.

At variance, the specimens treated with 10 wt.% DNA add-on reach the flame out after ignition and burn for 18 s, leaving a remarkable residue (67%) and a char length of 35 mm. Cotton fabrics treated with 19% DNA add-on show a very slow burning process and reach self-extinction within 2s after flame application: in this case, final residue is very high (i.e. 98%) and the char length is very short (just 6 mm). Furthermore, it is worthy to note that, after this short combustion process, it is not possible to ignite the specimen again, following the standard procedure.

Besides, SEM-EDS analyses were exploited in order to assess the morphology of the char in the burnt area: it was found that the texture of the fabrics is still preserved and the fibers appear almost intact and covered by small finely dispersed spherical structures, mainly comprising C, O and P elements: this finding confirms the intumescent character of the bio-macromolecule.

Finally, cone calorimetry tests were performed in order to assess the combustion behavior of the treated fabrics: the results collected at different heat fluxes (namely 35 and 50 kW/m^2) are listed in Table 14.10.

Table 14.9 Flammability data of untreated and DNA-treated cotton fabrics.

Sample	Total burning time (s)	Char length (mm)	Burning rate (mm/s)	Residue (%)	Note
COT	66	–	1.5	–	–
COT_DNA_5%	64	100	1.6	12.5	–
COT_DNA_10%	18	35	1.9	67.0	Flame out for 3/3 specimens
COT_DNA_19%	2	6	3.0	98.0	Flame out for 3/3 specimens

Table 14.10 Combustion data of untreated and DNA-treated cotton fabrics.

Sample	TTI (s)	PkHRR (kW/m^2)	DPkHRR (%)	Residue (%)
Heat Flux: 50 kW/m^2				
COT	16	128	–	<3
COT_DNA_19%	10	51	–60	17
Heat Flux: 35 kW/m^2				
COT	45	125		<3
COT_DNA_19%	No ignition			24
COT_DNA_10%*	19	62	–50	15
COT_DNA_5%	24	68	–56	15

* 2 specimens on 5 do not ignite.

Under 50 kW/m^2 heat flux, the untreated fabric quickly ignites and completely burns; conversely, the presence of the DNA coating (19 wt.% add-on), irrespective of an anticipation of TTI, turns out to significantly lower PkHRR (-60%) and to remarkably increase the final residue. When the heat flux is lowered at 35 kW/m^2, cotton burns vigorously and quite rapidly in 30 s; conversely, the specimens treated with 19% DNA add-on do not ignite at all, but undergo thermal-oxidation, leaving quite a high final residue (24%), which is still consistent. The lowering of the nucleic acid add-on from 19 to 10% still evidences a good combustion behavior of the treated fabrics, though just 2 specimens on 5 do not ignite during the exposure to the heat flux. The further reduction of the nucleic acid add-on from 10 to 5% does not block the ignition of the specimens under the heat flux, although a remarkable decrease of PkHRR and increase of the final residue are observed.

The high cost of commercially-available DNA has pushed the scientific community toward the design of cost-effective DNA-based FR systems. For this purpose, DNA was combined with chitosan [39], exploiting the LbL approach [40], for providing cotton fabrics with FR features.

Unlike the impregnation/exhaustion methods previously discussed, the LbL strategy allows minimizing the quantity of the bio-macromolecules necessary for reaching cotton self-extinction; in addition, this technique, which is usually based on the occurrence of electrostatic interactions in between the monomolecular deposited layers, is more effective in

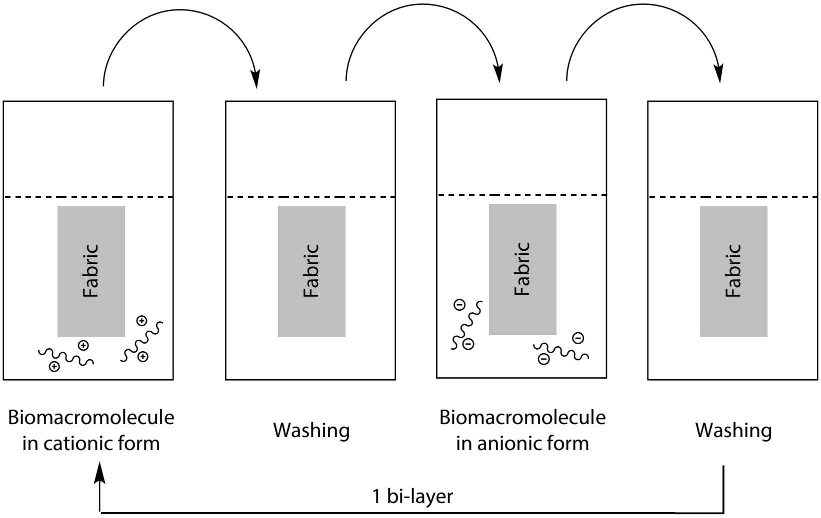

Figure 14.4 Scheme of the LbL method applied to fabrics.

protecting the very surface of the underlying substrate, without promoting any significant change in the bulk properties of the treated fabrics. A scheme of the LbL process is shown in Figure 14.4.

In particular, 5, 10, and 20 DNA/chitosan bi-layers (BL) were applied to cotton fabrics, achieving a final dry add-on of 2, 7 and 14 wt.%, respectively.

Table 14.11 shows the results from horizontal flame spread and LOI tests. First of all, it is noteworthy that the deposition of 5 BL does not affect either the burning time or the burning rate but is responsible for the increase of the final residue (8%). 10 BL assemblies significantly increase the final residue (48%), and decrease the burning rate (1.2 mm/s), increasing, at the same time, the burning time (125 s). The deposition of 20 BLs provides self-extinction to the treated cotton, leading to a very high final residue (88%). Furthermore, the LOI values of the treated cotton increase from 18 (untreated fabric) to 21, 23, and 24% for 5, 10, and 20 BL, respectively. Cone calorimetry tests (heat flux: 35 kW/m^2) were exploited for assessing the combustion behavior of the LbL-treated fabrics: the results are collected in Table 14.12.

First of all, TTI values of the LbL-treated cotton are significantly lower as compared to the untreated fabric: this result can be explained in terms of thermal activation, the bio-macromolecule has to undergo in order to release phosphoric acid, hence dehydrating the cellulosic substrate and favoring the char formation. Conversely, the presence of 20 BLs

Table 14.11 Flammability data of untreated and LbL-treated cotton fabrics.

Sample	Total burning time (s)	Burning rate (mm/s)	Residue (%)	Note	LOI (%)
COT	80	1.5	–	–	18
COT_5BL	78	1.5	8	–	21
COT_10BL	125	1.2	48	–	23
COT_20BL	30	1.0	88	Flame out for 3/3 specimens	24

Table 14.12 Cone calorimetry data of untreated and LbL-treated cotton fabrics.

Sample	TTI (s)	PkHRR (kW/m^2)	Residue (%)
COT	39	97	2
COT_5BL	17	73	11
COT_10BL	20	60	12
COT_20BL	23	57	13

is responsible for the most significant reduction of the peak of the heat release rate (around –40%).

14.2.5 Other Bio-Macromolecules: A Quick Recent Overview

Laufer and co-workers succeeded in conferring FR features to cotton fabrics by depositing 30 intumescent BLs of cationic chitosan and anionic phytic acid via LbL assembly [41]. In particular, the pH of the adopted aqueous deposition solutions changed the composition of the final nanocoatings: in fact, the LbL assemblies created at pH 6 were thicker and had 48 wt. % phytic acid in the coating, while the thinnest films (with a phytic acid content of 66 wt. %) were obtained at pH 4. As assessed in vertical flame spread tests, fabrics coated with high phytic acid content multilayers were found to achieve self-extinction, while the untreated fabric was entirely consumed. Microcombustion calorimetry tests showed a remarkable 50% reduction of peak heat release rate for all the coated fabrics as compared to the uncoated control. Furthermore, the fabrics treated with pH 4 solutions exhibited the greatest reduction in peak heat release rate and total heat release (about 60 and 76%, respectively).

Pan *et al.* deposited up to 20 BLs of chitosan and phosphorylated cellulose (PCL) on the surface of cotton fabrics, exploiting the LbL technique [42]. As assessed by vertical flame spread tests, the deposition of 20 BL allowed the cellulosic substrate achieving self-extinction. Furthermore, microcombustion calorimetry tests showed a reduction of peak of heat release rate and total heat release for all the treated cotton fabrics.

Very recently, Fang and co-workers [43] designed low impact LbL assemblies, coupling Potassium alginate, a green polymer extracted from seaweed, with polyhexamethylene guanidine phosphate: this way, it was possible to provide cotton fabrics not only with FR but also with antimicrobial features against *S. Aureus* and *E. Coli*. In particular, microcone calorimetry tests showed lower values of PkHRR and THR with respect to the untreated fabric, due to a limited release of volatile species. In flame spread tests, no afterglow phenomena were found; in addition, the fabric texture was maintained. Finally, as assessed by SEM microscopy, the residues after flame spread tests performed on 20 BLs-coated cotton fabrics showed the appearance of several bubbles, as a prove of the intumescent phenomena occurring in the coated substrate.

14.3 Current Limitations

Despite the high FR efficiency of the selected bio-macromolecules, their use is still under debate, as there are several issues that deserve further investigation.

First of all, till now the scientific research on these FR additives has been specifically focused on the assessment of their fire performances, rather than on the evaluation of their possible toxicity: this latter is a very important issue that should also be taken into consideration in the very next future.

In addition, the proposed bio-macromolecules have been exploited at the lab scale only: in fact, a possible scale-up at least to pre-industrialization plants is still under evaluation for several reasons. Among them, one of the key limiting factors refers to the cost-effectiveness of some of the proposed bio-macromolecules, specifically referring to commercially available nucleic acids, which are at present very expensive and therefore, currently out of the market. As a consequence, a significant cost reduction of these bio-macromolecules is required: in this context, some efforts related to the increase of the production capacity of the industrial extraction plants for these bio-macromolecules are being carried out and are expected to contribute to the development of high yield extraction methods and technologies, which should also maintain the purity of the recovered bio-macromolecules at a suitable level, necessary for their application in FR textiles.

Another important issue is related to the washing fastness (i.e. launderability) of the fabrics treated with the bio-macromolecules: in fact, almost all the proposed "green" additives do not fulfill this requirement, as they come off the fabric substrate even when subjected to mild washing cycles in hot water without any surfactant. Some recent attempts to overcome this problem were addressed to the exploitation of the photo-induced grafting of chitosan to cotton fabrics, when deposited either as a mixture or as an LbL assembly together with DNA [44]. In particular, the UV-cured treated fabrics showed enhanced water resistance, self-extinction in flammability tests and good antimicrobial activity. However, further research will have to be addressed to the evaluation of possible answers for this limitation, keeping in mind that the "green" character of the proposed FR treatments should require a green approach for fixing the bio-macromolecules to textiles.

14.4 Conclusions and Future Perspectives

This chapter has clearly described the significant potential provided by the utilization of bio-macromolecules (namely, proteins and nucleic acids) as sustainable FR alternatives for cotton, polyester and cotton-polyester fabric substrates. In particular, the structure and composition of these "green" additives seems to indicate their suitability for this specific use, notwithstanding that the toxicity of the selected bio-macromolecules has never been investigated yet. In addition, as mentioned in the previous paragraph, the current limitations comprise either the possible large-scale exploitation of the bio-macromolecules, or the launderability issues of the treated fabrics.

However, it seems quite reasonable to expect further growth of these novel FRs, which could represent a possible alternative to the current phosphorus-based synthetic products.

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Reference

1. Brushlinsky, N.N., Ahrens, M., Sokolov, S.V., Wagner, P. *World fire Statistics*, CTIF, n.21, 2016.
2. World Fire Statistics, *Information Bulletin of the World Fire Statistics Centre, Volume 29*, Geneva, Switzerland, April 2014
3. Bourbigot, S., Flame retardancy of textiles – new approaches, *Advances in fire retardant materials*, A.R. Horrocks, Price, D. (Eds.). pp. 9–40, Woodhead Publishing, Cambridge, 2008.
4. Weil, E.D., Levchik, S.V., Flame retardants in commercial use or development for textiles. *J. Fire Sci.*, 26 (3), 243–281, 2008.
5. Neisius, M., Stelzig, T., Liang, S., Gaan, S., Flame retardant finishes for textiles, in: *Functional Finishes for Textiles*, Paul, R. (Ed.),, Woodhead Publishing Series in Textiles, Amsterdam, pp. 429–461, 2015
6. Horrocks, A.R. and Price, D., *Fire retardant materials*. Woodhead Publishing Limited, Cambridge, 2000.
7. Horrocks, A.R., Flame retardant challenges for textiles and fibers: New chemistry versus innovatory solutions. *Polym. Degrad. Stab.*, 96 (3), 377, 2011.
8. Weijs, L., Dirtu, A.C., Malarvannan, G., Covaci, A., Bioaccumulation and Biotransformation of Brominated Flame Retardants, Compre. *Anal. Chem.*, 67, 433, 2015.
9. Howard, P.H., Muir, D.C.G., Identifying new persistent and bioaccumulative organics among chemicals in commerce. *Environ. Sci. Technol.*, 44, 2277, 2010.
10. Iqbal, M., Syed, J.H., Katsoyiannis, A., Malik, R.N., Farooqi, A., Butt, A., Li, J., Zhang, G., Cincinelli, A., Jones, K.C., Legacy and emerging flame retardants (FRs) in the freshwater ecosystem: A review. *Environ. Res.*, 152, 26, 2017.
11. Howard, G.J., Chemical alternatives assessment: The case of flame retardants. *Chemosphere*, 116, 112, 2014.
12. de Boer, J., Ballesteros-Gomez, A., Leslie, H.A., Brandsma, S.H., Leonards, P.E.G., Flame retardants: Dust – And not food – Might be the risk. *Chemosphere*, 150, 461, 2016.
13. Hull, T.R., Law, R.J., Environmental Drivers for Replacement of Halogenated Flame Retardants, in: *Polymer Green Flame Retardants*, C.D. Papaspyrides, P. Kiliaris (Eds.), pp. 119–179, Elsevier, Amsterdam, 2014.
14. Horold, S., Phosphorus-based and Intumescent Flame Retardants, in: *Polymer Green Flame Retardants*, C.D. Papaspyrides, P. Kiliaris (Eds.), pp. 221–254, Elsevier, Amsterdam, 2014.
15. Horrocks, A.R., Anand, S.C., *Handbook of Technical Textiles*, Woodhead Publishing Limited, Cambridge, 2000.
16. Muthu, S.S., *Handbook of sustainable apparel production*, CRC Press, Boca Raton, 2015.
17. Gunasekaran, S., Ko, S., Xiao, L.J., Use of whey proteins for encapsulation and controlled delivery applications. *Food Eng.*, 83, 31, 2007.

18. Lopez-Rubio, A., Lagaron, J.M., Whey protein capsules obtained through electrospraying for the encapsulation of bioactives. *Innov. Food Sci. Emerg. Technol.*, 13, 200, 2012.
19. Shen, Q., Quek, S.Y., Microencapsulation of astaxanthin with blends of milk protein and fiber by spray drying. *J. Food Eng.*, 123, 165, 2014.
20. Gounga, M.E., Xu, S., Wang, Z., Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. *J. Food Eng.* 4, 521, 2007.
21. Bosco, F., Carletto, R.A., Alongi, J., Marmo, L., Di Blasio, A., Malucelli, G., Thermal stability and flame resistance of cotton fabrics treated with whey proteins. *Carbohydr. Polym.*, 94, 372, 2013.
22. Alongi, J., Malucelli, G., Cotton flame retardancy: State of the art and future perspectives. *RSC Adv.*, 5, 24239, 2015.
23. Alongi, J., Malucelli, G., Thermal degradation of cellulose and cellulosic substrates, in: *Reactions and Mechanisms in Thermal Analysis of Advanced Materials*, A. Tiwari and B. Raj (Eds.), pp. 301–332, Wiley, Beverly, 2015.
24. Liu, Y., Liu, L., Yuan, M., Guo, R., Preparation and characterization of casein-stabilized gold nanoparticles for catalytic applications. *Colloids Surf. A*, 417, 18, 2013.
25. Alongi, J., Carletto, R.A., Bosco, F., Carosio, F., Di Blasio, A., Cuttica, F., Antonucci, V., Giordano, M., Malucelli, G, Caseins and hydrophobins as novel green flame retardants for cotton fabrics. *Polym. Degrad. Stab.* 99, 111, 2014.
26. Carosio, F., Di Blasio, A., Cuttica, F., Alongi, J., Malucelli, G., Flame retardancy of polyester and polyester-cotton blends treated with caseins. *Ind. Eng. Chem. Res.* 53, 3917, 2014.
27. Kwan, H.Y., Winefield, R.D., Sunde, M., Matthews, J.M., Haverkamp, R.G., Templeton, M.D., Mackay, J.P., Structural basis for rodlet assembly in fungal hydrophobins. *Proc. Natl. Acad. Sci.* USA, 103, 3621, 2006.
28. Linder, M., Szilvay, G.R., Nakari-Setala, T., Soderlund, H., Penttila, M., Surface adhesion of fusion proteins containing the hydrophobins HFBI and HFBII from Trichoderma reesei. *Protein Sci.*, 11, 2257, 2002.
29. Israeli-Lev, G., Livney, Y.D., Self-assembly of hydrophobin and its co-assembly with hydrophobic nutraceuticals in aqueous solutions: Towards application as delivery systems. *Food Hydrocolloids*, 35, 28, 2014.
30. Opwis, K., Gutmann, J.S., Surface modification of textile materials with hydrophobins. *Text. Res. J.* 81, 1594, 2011.
31. Fitzgerald-Hayes, M., Reichsman, F., *DNA and Biotechnology*, Academic Press, Burlington, 2010.
32. Sonmezoglu, S., Sonmezoglu, O.A., Optical and dielectric properties of double helix DNA thin films, Mater. *Sci. Eng. C,* 31, 1619, 2011.
33. Teles, F.R.R., Fonseca, L.P., Trends in DNA biosensors. *Talanta*, 77, 606, 2008.
34. Alongi, J., Di Blasio, A., Milnes, J., Malucelli, G., Bourbigot, S., Camino, G., Thermal degradation of DNA, an all-in-one natural intumescent flame retardant. *Polym. Degrad. Stab.*, 113, 189, 2015.

35. Alongi, J., Cuttica, F., Di Blasio, A., Carosio, F., Malucelli, G., Intumescent features of nucleic acids and proteins. *Thermochim. Acta*, 591, 31, 2014.
36. Alongi, J., Carletto, R.A., Di Blasio, A., Carosio, F., Bosco, F., Malucelli, G., DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem., A, 1*, 4779, 2013.
37. Alongi, J., Carletto, R.A., Di Blasio, A., Cuttica, F., Carosio, F., Bosco, F., Malucelli, G., Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics, Carbohydr. *Polym*., 96, 296, 2013.
38. Alongi, J., Milnes, J., Malucelli, G., Bourbigot, S., Kandola, B., Thermal degradation of DNA-treated cotton fabrics under different heating conditions. *J. Anal. Appl. Pyrol*., 18, 212, 2014.
39. Carosio, F., Di Blasio, A., Alongi, J., Malucelli, G., Green DNA-based flame retardant coatings assembled through Layer by Layer. *Polym*., 54, 5148, 2013.
40. Malucelli, G., Layer-by-Layer nanostructured assemblies for the fire protection of fabrics. *Mater. Lett*., 166, 339, 2016
41. Laufer, G., Kirkland, C., Morgan, A.B., Grunlan, J.C., Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton. *Biomacromolecules*, 13, 2843, 2012.
42. Pan, H., Song, L., Ma, L., Pan, Y., Liew, K.M., Hu, Y., Layer-by-layer assembled thin films based on fully biobased polysaccharides: Chitosan and phosphorylated cellulose for flame-retardant cotton fabric. *Cellulose*, 21, 2995, 2014.
43. Fang, F., Chen, X., Zhang, X., Cheng, C., Xiao, D., Meng, Y., Ding, X., Zhang, H., Tian, X., Environmentally friendly assembly multilayer coating for flame retardant and antimicrobial cotton fabric. *Prog. Org. Coat*., 90, 258, 2016.
44. Casale, A., Bosco, F., Malucelli, G., Mollea, C., Periolatto, M., DNA-chitosan cross-linking and photografting to cotton fabrics to improve washing fastness of the fire-resistant finishing. *Cellulose*, 23, 3963, 2016.

15

Significant Trends in Nano Finishes for Improvement of Functional Properties of Fabrics

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Abstract

Nano finishes on textile materials have been the area of interest over the world during the past two decades. As a result, a number of innovative approaches have been developed that promise wider areas of functional applications with improved properties. The chapter critically reviews some new concepts that are revolutionary. In one such work, extract from yellow papaya peel has been used in order to develop nano safe textile through extracellular synthesis of highly stable silver nano particles. The treated fabrics have been observed for antibacterial activity. The papaya peels derived nano particles can be coated on fabrics and could prove effective against microorganisms. The method is more eco-friendly as natural agent is used. In another interesting area of study, cotton denim fabrics have been treated with micro and nano encapsulated herbal extracts from three types of herbs. The finishing has been done with methanol extracts of these herbs. Very good antimicrobial efficiency has been observed with wash durability. An interesting attempt has been made to develop multifunctional cotton fabric. The fabric surface has been activated by atmospheric plasma treatment to facilitate deposition of nano silicon oxide, and nano titanium dioxide onto cotton fabric. The treated fabric has been studied for ultraviolet protection factor (UPF), antimicrobial activity, and flame retardancy. Also, surface morphology, thermogravimetric analysis, and mechanical properties are investigated. There has been improvement in the flame retardancy, UPF, antibacterial activity and thermal stability of the treated fabrics using helium-oxygen plasma. Hexamethylsiloxane plasma polymer has been deposited on the finished fabric to improve wash fastness and thereby

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improves durability. In yet another interesting work, silver nano particles that have been synthesized through biological approach using natural leaf extract have been applied on cotton fabrics and tested for antimicrobial efficiency. Outstanding antibacterial activity has been observed on the treated fabrics and holds the promise in medical and infection prevention applications. Thus the recent research studies highlighted herein prove more effective in improvement of functional properties of fabrics and have the potential for wider areas of applications.

Keywords: Denim, functional properties, green approach, herbal extract, nano finishes, scanning electron microscopy

15.1 Introduction

The present global scenario in the textile industry shows that the conventional textile business is going through a crisis period despite heavy capital investment, since there is drastic increase in competition. As a result, conventional textile products are cheaply available in the market at large quantities. This decreases the percentage of profit to a least. In order to sustain in such a tough competition, a high-tech industrial revolution is directly necessary [1]. The functional and high performance properties such as specialized coating, plasma based products, smart/technical technologies and nanotechnologies are being achieved by the textile industry at a global level by shifting towards new trends and most promising technologies [2]. Impact of nanotechnology on the textile industry and the application of nano-materials in textiles have dramatically improved the fiber and processing technology to fulfill the needs of society [3]. Drastic changes have been observed in the last five decades in the applications of textiles and there is no doubt that in the next few years nanotechnology will penetrate in every field of textile industry [4]. Nanotechnology is defined as the precise manipulation of individual atoms and molecules to create layered structures. One nanometer is defined as 1 billionth meter i.e., 1×10^{-9} m and involves developing materials or devices within that size [5, 6]. Nano size particles can exhibit unexpected properties different from those of the bulk material. The small size of nanoparticles leads to particle–particle aggregation thereby making physical handling of nanoparticles difficult in liquid and dry powder forms. The basic concept is that properties can dramatically change when a substance's size is reduced to the nanometer range. In bulk form, gold is inert; however, once broken down into small clusters of atoms it becomes highly reactive [7]. It is the application of functional systems in the sub-micro range. Nanotechnology is an interdisciplinary science which takes a role in the material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, textiles, optical coatings, antibacterial agents, physics, and biology. Decreasing the size of particles to nano scale dimensions fundamentally changes the properties of the material. For example, 50 kg of 1 mm-size Silicon dioxide particles, with a surface of 120 m^2, when decreased to 1 nm would have a surface area of 120,000,000 m^2. In addition, as the particle size decreases the number of molecules in the surface relative to the bulk increases, giving new and unexpected properties [8].

During the recent years, it has been shown that nanotechnology can be used to improve textile properties, like fabric softness, durability, and breathability, water repellency, fire retardancy, anti-microbial properties in fibers, yarns, and fabrics [9]. Fundamentals of nanotechnology lie in the fact that the properties of materials drastically change when their dimensions are reduced to nanometer scale. Textile exports, for instance, are using nanotechnology for self-cleaning properties of the leaves of the lotus-flower for textile applications. This is the domain of intelligent textiles.

15.2 Significance of Nanotechnology

Nanotechnology has shown promise as good commercial potential for the textile industry. It could mainly be attributed to the fact that conventional methods used to impart different properties to fabrics generally produce temporary effects, and will lose their functions after laundering or wearing. Whereas, nanotechnology can provide high durability for fabrics since the nanoparticles have a large surface area-to-volume ratio and high surface energy thereby contributing to better affinity for fabrics and resulting in an increase in durability of the function [10]. Also, the physical and mechanical properties like hand, strength, air permeability, and wetting are not affected by a coating of nanoparticles on fabrics [11]. The purposes of using nanotechnology in textile and apparel applications are low chemical usage and lower energy costs. Thus, nanotechnology is today's most preferred solution for the textile industry because of the techno-economic advantages.

15.3 Application of Nanotechnology in Textiles

It is necessary to consider the application of nanotechnology in the textile value chain so as to know the clear outline concept of the nanotechnology in the textile industry. Nano technology can be applied in two areas of the textile value chain. The first is for production of fibers and the second is in application of technology on the surface of yarn or fabric as coating at the finishing step. Techniques to incorporate nanotechnology in the manufacturing process include the integration of nanomaterials into fabrics (e.g., silver nanoparticle additives on fibers), use of nanosize fibers or use of various nano-coating processes to provide a particular surface resistance. The increased demand for textiles and fabrics that provide comfort with enhanced functionality and improved appearance is driving the demand for nanotechnology in this sector [12]. Moreover, natural textile fibers are also complex nano structures and ultimately, the natural world can only be understood by analysis at the molecular level [13]. Among the most interesting nanotechnology applications, their application in the textile industry offer the possibility of reducing the use of harsh chemical (such as in antimicrobial application), improve the long term performance and durability of textile generated products which are more eco-friendly and greener, as well as applications which deliver the following performance enhancing features.

- Antimicrobial and antibacterial applications with silver compound
- Nanoparticles to test the efficiency of protective textile and other materials.
- Nanomaterial to reduce the quantity of harmful chemicals in finishing recipes.
- Nanocoating for oil, flame and heat resistance.
- Use of nanotechnology for biomimics, such as recreating the surface of a lotus leaf on textiles at the nanoscale in order to reproduce its resistance to oil and water for potential use in self cleaning textile applications [14].

Some of the other applications of nanotechnology are:

a) Color fastness
b) Color changing
c) Water repellence
d) Abrasion
e) Fire retardancy
f) UV absorption
g) Energy storage
h) Data storage
i) Communications
j) Controlled release of additives [15].

Textile materials play a key role in automotive industry where nanotechnology is prominent. Their use includes interior panels for doors and pillars, seat coverings and padding, parts of the dashboard, cabin roof and boot carpets, headliner, safety belts, air bags, air filtration, tyre cord, and trimmings. Additionally, the use of textiles, specifically natural-based materials owing to their easier recyclability, contributes to reducing car weight by replacing many conventional hard-surface structures.

Advantages of nano enabled automotive textile include:

- Both in terms of passenger needs and environmental impact.
- Nano-enabled textiles provide new and innovative solutions for car upholstery with moisture wicking, self-cleaning, antimicrobial and antistatic properties, or tear/wear resistance and noise reduction features.
- Safety can also be enhanced with nano-enabled textiles possessing valuable flame retardant/ resistance properties.

Smart textiles hold future prospect in that they can monitor variables like the driver's condition. But there can be issues relating to privacy. The advantages arising out of increased use of textiles in the car are decrease in the car weight and therefore lesser fuel consumption and carbon dioxide emissions [16]. The necessity of improved protective apparel and accessories has arisen owing to increase in health and safety concerns for those exposed to dangerous environments or high risk professions. Protective textiles are part of the personal protective equipments (PPE) family and represent a specific area of the advanced technical textiles sector, a strongly growing market for the textile industry and satisfying an increasing demand for high performance requirements. Personal protective textiles are produced with the aim of eliminating or minimizing the risk of injuries, accidents and infections, acting as shields against chemical, biological and nuclear hazards, high temperatures and fire, sharp objects, and ballistic projectiles. Novel surface treatments and coatings, nanocomposite and nanoscale fibers, and functional nanoparticles offer textile products providing improved levels of protection together with a lower weight, higher comfort, new or multi-functionalities, or more environmentally friendly processes. Advantages offered by nano enabled technical textiles in the protective textiles sector.

1. PPE is increasingly important in the quest to eliminate or minimize the risk of injuries, accidents, and infections arising from a variety of threats and environments.

2. Protective textiles have been selected by the European commission as one of the areas of the lead market initiative for Europe, aimed to create an innovation-friendly market framework and to reinvigorate and increase competitiveness of traditional industries.
3. Nanotechnologies can play a fundamental role in the development of improved or novel multifunctional protective textiles by providing higher levels of protection, lower weight and bulkiness, and higher levels of comfort. Moreover, nanotechnologies, by facilitating the integration of electronics into garments, make possible development of smart/intelligent textiles that allow tracking, monitoring and control of physiological parameters, generation of energy for powering wearable equipment and communication functions [17].

15.4 Nanotechnology for Improved Fabric Finishing

In textile production there has been a good emphasis on finishing of fabrics made of natural and synthetic fibers to achieve required hand, surface texture, color, and other special aesthetic and functional properties. During the past decade, nanotechnology has emerged and has made good advances resulting in many innovations. Application of nano technology in fabric finishing has assumed a new dimension and demonstrated a great potential for significant improvements. The developments in the areas of surface engineering and fabric finishing have been highlighted in several papers [18–21]. There are many ways in which the surface properties of a fabric can be manipulated and enhanced by implementing appropriate surface finishing, coating, and/or altering techniques, using nanotechnology. Nanotechnology provides plenty of efficient tools and techniques to produce desirable fabric attributes, mainly by engineering modifications of the fabric surface. For example, the prevention of fluid wetting towards the development of water or stain-resistant fabrics has always been of great concern in textile manufacturing. The basic principles and theoretical background of “fluid-fabric” surface interaction are well described in a recent manuscript by Schrauth *et al.* [22]. They have demonstrated that by altering the micro-and nanoscale surface features on a fabric surface, a more robust control of wetting behavior can be attained. It has been proved that such a change in the surface properties of fabric can show the “Lotus-Effect” that signifies the inherent hydrophobic behavior of a leaf surface. Such type of surface technology that can mimic hydrophobic behavior is useful to develop special chemical finishes for producing water-and/or stain-resistant fabrics.

15.5 Problem Associated with Nanotechnology

There is a need to establish nano finished fabrics under hazardous category of wastes. They can be recycled or thermally utilized using conventional methods. Doubts arise about the mass land filling of nano finished fabrics (possible impairment of water and soil). Hence it becomes necessary to carry out research and rectification before commercializing so as to prevent any damage to humans and the environment. Upgradation of the recycling systems is required so as to keep pace with such scientific advances where pure nanomaterials are produced or there is the mass use of materials finished with nano particles [23].

15.6 Nano Safe Textile Finishes with Papaya Peel and Silver

15.6.1 Overview

The green technique of synthesis of nano particles holds advantageous over other techniques in that, it very effectively controls particle size and morphology effectively. It is also faster and more convenient than other conventional techniques [25]. Papaya peel derived silver nano particles, owing to their very good antibacterial activity, can be applied on fabrics and thereby offer protection from micro-organisms. The significant reduction in reaction time with fruit peel extract is an important result and will enable nanoparticle biosynthesis methods to compete with other routes for the formation of nanoparticles that are currently much more rapid and reproducible.

15.6.2 Related Aspects

Nanoparticles have been synthesized in an eco-friendly way by the combination of biotechnology and nanotechnology, jointly bio-nanotechnology or nano-biotechnology. Nanoparticles made from rich metals such as gold, silver, and platinum have been investigated extensively. Because of their broad range of applications in fields like electronics, catalysis, chemistry, energy and medicine, the commercial demand for them has increased [26].

Moreover, nanotechnology shows good promise in the textile industry for innovation of new materials. The application of nanotechnology can result in production textiles with very novel properties or combination of various functions, besides improving their functionality [27]. Some examples of such multifunctional textiles are antistatic textiles, reinforced textiles, antibacterial, self-cleaning textiles, bleaching resistant, and so on. They can open up possibilities for use of products outside the scope of traditional industries and opened the way for the use of its products in other fields outside the traditional industries [28–30].

Owing to the broad range of antimicrobial activities silver nanoparticles have gained special attention. Silver has been incorporated into various forms of plastics such as dental material, catheters, medical devices, implants and burn dressings to protect against microbial infection. The metal based nanoparticles have also been applied on fabrics for durable finish. Silver nanoparticles have very good antibacterial effect. In the synthesis of silver nanoparticles, a number of techniques have been used such as chemical, physical, and biological techniques, which are of recent origin [31]. In the development of metal nanoparticles, there has been a great focus on biological techniques as a feasible option. During the synthesis of silver nanoparticles, different types of bacterial and fungal species have been used [32, 33]. However, most of them have been found to accumulate silver nanoparticles intracellularly. Whereas, plant extract mediated synthesis i.e., green synthesis occurs extracellularly, and there action times are much shorter than microbial synthesis.

Many extracts of plants and weeds have proved their potential in decrease of silver nitrate and avoid chemical agents in the formation of silver nanoparticles [34, 35]. Papaya has its origin in northern India and has been cultivated widely, since many years and possesses medicinal properties. In the synthesis of silver nanoparticles, various parts of papaya plant such as flower and fruits have been used. Very few studies have been reported relating to the synthesis of silver nanoparticles using peel extracts. In the biosynthesis of green silver nanoparticles, the potential of yellow papaya peels as non toxic biological systems have been studied for the first time.

15.6.3 Analysis of UV Visible Spectra

The silver nanoparticles are known to show yellowish brown coloring aqueous solution because of excitation of surface plasmon vibrations in them. The UV–visible spectroscopy can be used to study the size and shape-controlled nanoparticles in aqueous suspensions. As can be seen

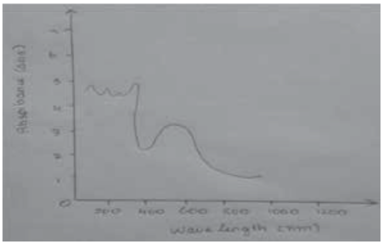

Figure 15.1 Visible UV-spectra of silver nanoparticles [25].

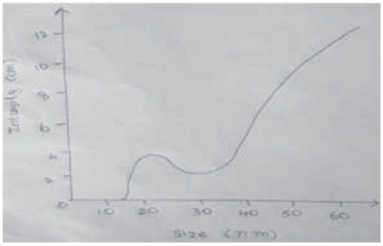

Figure 15.2 X-ray diffraction showing DLS pattern of papaya peel derived silver nanoparticles [25].

from Figure 15.1, the UV-visible spectra of silver nanoparticles show peak absorption and broadening of peak around 450 nm implying polydispersion of the particles. This finding agrees well with earlier ones [36].

15.6.4 Dynamic Light Scattering

Figure 15.2 depicts the representative dynamic light scattering (DLS) pattern which shows that silver nanoparticles so synthesized have a zeta average diameter between 20–140 nm. A particle size of 50 nm is the highest fraction of silver nanoparticles present in the solution. The DLS measured size has been found to be slightly bigger than the particle size measured by any other method since the DLS method measures the hydrodynamic radius.

As depicted in Figure 15.3, intense peaks in the entire spectrum of 2θ values between 20–75° are observed in the XRD (X–ray diffraction) pattern of the yellow papaya peel derived silver nanoparticles. From the XRD spectrum the precise nature of the silver particles formed can be understood. On comparison of the XRD spectrum obtained with the standard, it has been confirmed that the silver nanoparticles formed are in

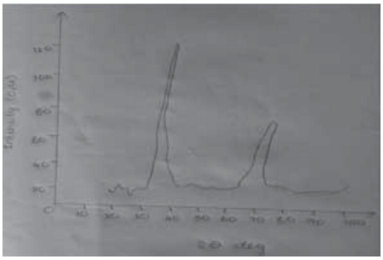

Figure 15.3 XRD of green silver nanoparticles [25].

the form of nanocrystals. The average estimated particle size of this sample is 20 nm derived from the FWHM (Full Width Half Maximum) of peak corresponding to (111) plane using Debye Scherrer formula.

15.6.5 Evaluation of Antibacterial Activity of Textile Material

The zone of inhibition is around 2.5 cms with finished fabric while with fabric washed with water in order to check the durability, it is found to be 1.5 cm. In the case of both controls, the zone of inhibition is found to be zero. It has not been possible to understand the mechanism behind the antimicrobial action of silver ions. But, there is a possibility that as the silver ions penetrate into the microbial cell the DNA molecule converts it into condensed form and loses its replication ability, resulting in death of cell. It has also been reported that heavy metals react with proteins by getting attached with the thiol (-SH) group and the proteins get inactivated [37]. Because of their very large surface area that enables better contact, the silver nanoparticles exhibit more efficient antimicrobial property than other metal nanoparticles and hence provide effective control of microorganisms like bacteria and fungi. Silver, basically possesses antimicrobial and antibacterial properties. Because of synergistic influence of secondary metabolites such as alkaloids, terpenoids, saponins, tannins, and flavonoids, the antimicrobial activity of silver nanoparticles derived from green papaya peels exhibit improvement in activity [38].

The green synthesis technique has proved effective in controlling particle size and morphology compared to the various techniques of synthesis of nanoparticles. The technique is also more convenient and faster than other conventional ones. As papaya peel derived silver nanoparticles possess high antibacterial activity, they can be incorporated into fabrics and thereby offer protection to textile materials from microbial attack. The considerable decrease in reaction time with fruit peel extract is a critical factor that will be useful in nanoparticles biosynthesis methods for compatibility with other methods of nanoparticle synthesis which are presently far more rapid and reproducible.

15.7 Plasma Induced Finishes for Multifunctional Properties

15.7.1 Overview

When titanium dioxide/silicon dioxide nanoparticles have been applied onto cotton fabrics, excellent UV protection, flame retardancy, and antibacterial properties have been observed. Fabrics treated with plasma showed better results than those without plasma. Titanium dioxide plays the role of a photo catalyst to improve UV protection ability. Titanium dioxide/silicon dioxide acts as a physical barrier (thermal insulator), with SHP as an active agent in the condensed and/or vapour phase to improve the flame retardancy [39]. Moreover, titanium dioxide/silicon dioxide and BTCA (ButanetetracarboxylicAcid) exhibit the best result with regard to wrinkle recovery as carboxylic acids would cause cross linking of cellulose. Ultimately, it can be concluded that there is improvement in durability of finish by the use of HMDSO plasma polymerization. Plasma technology proves economical over conventional finishing methods since it consumes fewer chemicals, and thereby reduces the environmental pollution.

15.7.2 Related Aspects

During the past few years, there has been growing demand for protective garments due to increasing concern over damage caused by exposure to microbes, chemicals, pesticides, UV light, and pollutants. In order to offer protection to the wearers from infection, UV light, chemical and biological agents, modern day clothing should be waterproof, flame resistant, self cleaning, insect repellent, and antimicrobial [40].

The apparel industry is dictated by cellulose fiber of which cotton, known as the king of fibers plays the lead role. Cotton has some unique properties such as soft-handle, breathability, strength, durability, and comfort, making it ideal for apparel purpose. But, because of its glucose content, it is susceptible to microbial attack, and is also attacked by fire. Hence, multifunctional textiles can satisfy the need of ultraviolet protection, antimicrobial functionality and anti flammable textiles.Plasma technologies on the one hand improve material properties while on the other hand can enable to sustain inherent advantages of the substrates [41, 42]. Plasma is partially ionised gas, and comprises of ions, electrons, and charged neutral particles. The etching or cleaning effect is caused by the high energy in plasma of the active species, which alters the fiber surface characteristics. The surface roughness of the materials is enhanced by the treatment and enables subsequent process to improve the effectiveness [43–46]. The atmospheric pressure plasma is the most popular among different types of plasma treatments, and is widely used in the textile industry to modify the fabric surface. It is an eco friendly process which aids in conserving chemicals and energy [43, 47, 48]. Plasma polymerization has great potential for sustainable innovation and value addition in the field of textile processing operations including finishing [49]. The films obtained through plasma polymerization are normally insoluble, pinhole free, highly cross-linked and adhere strongly to substrates [50]. Hence, in order to enhance the durability finish, effort has been taken to deposit a barrier film of plasma polymer on the finished fabric's surface. The experimental data on plasma treatment for multifunctional finishing of cotton to impart UV protection, flame retardancy, and antibacterial properties have been explained. The morphology changes in surface and surface chemistry of the fabric samples due to plasma finishing have been explained with regard to their performance properties.

15.7.3 Ultra Violet Protection

The effectiveness of textile fabrics in protecting the human skin from harmful ultraviolet radiations (UVR) is measured by the means of UPF. It is the ratio of time necessary for the skin to exhibit redness (erythema) with and without protection, under continuous exposure to solar radiation. Investigation has been carried out on the influence of plasma preactivation and plasma polymerization on UV protection. The UPF of the fabrics treated and subjected to washing cycles up to 20 washes is depicted in Figure 15.4.

The Figure 15.4 shows that the control fabric is not capable to protect from the UV radiations. But, all the fabrics treated with t titanium dioxide/silicon dioxide exhibit the UPF value above 50, which can be considered as excellent protection against the UV radiation. Such increase in the UPF is because of the natural attribute of titanium dioxide for UV radiation. The UV-absorption property can be explained by the solid band theory [51]. The fabrics have been washed as recommended by AATCC (AmericanAssociation of Textile ChemistsandColorists) standard test method. Only after 5 washes, there is significant decrease in the UPF of finished fabrics, and decreases after each wash. After 20 washes (with and without plasma treatment) the fabrics exhibit only good protection.

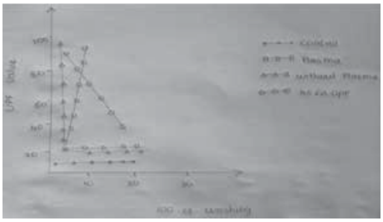

Figure 15.4 Effect of washing on UPF of finished fabric [39].

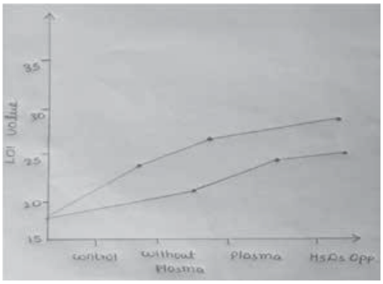

Figure 15.5 Effect of washing on LOI values of the finished samples [39].

Whereas, the fabric treated with HMDSO plasma polymer exhibits excellent UV protection even after 20 washes, which can be due to deposition of plasma polymer that is insoluble in water. The plasma polymer acts as a barrier to washing and thus the finish is not leached out.

15.7.4 Flame Retardant Properties

When exposed to external flame cotton undergoes combustion, ignites, and burns easily. Flame retardant systems are those that delay or stop the combustion process. They act physically/chemically and can interfere with different process involved in combustion [52]. Phosphorus-based flame retardant agents which are active in the condensed and/or vapour phase, can be supplemented [53]. The limiting oxygen index (LOI) has been used in assessment of flame retardancy of treated fabric and 45° inclined flammability measurements (Figure 15.5).

The LOI values of various finished fabrics before and after 20 washing cycles are depicted in Figure 15.5. There is considerable increase in the LOI values of fabrics treated with titanium dioxide/silicon dioxide nanocomposite. Further, the LOI value show considerable difference in the case of fabrics treated with and without plasma. As an instance, the control cotton shows the LOI value of 18.1 which is increased to 27.5 and further increased to 30.7 after plasma treatment. It can be due to the formation of reactive species on the surface of plasma treated fabrics or surface cleaning/etching effect of plasma treatment that renders fibers more accessible for the diffusion of chemicals inside the fibers. Further, there is a slight enhancement in the LOI value by treating with HMDSO polymer plasma [53]. Investigations on the influence of plasma treatment and titanium dioxide on the flame retardancy of cotton fabric reported that the flame-retardancy improves by plasma pre-treatment and by the addition of metal oxide as a co-catalyst. It has also been reported that there is enhancement in cross linking process between flame retardant and cotton fabric by plasma pre-treatment and metal oxide co-catalyst added in the flame-retardant finishing, minimizing the formation of free formaldehyde.

The flammability characteristics of a material are measured by the ease of ignition and the relative ability to sustain combustion. The flammability test at 45° has been carried out based on IS standard. The correlation between 45° flammability and LOI has been determined.

It has been found that the time necessary to burn specific length of fabrics drastically improved and further improvement in the effectiveness of the finish result from plasma treatment. The burning time also increases with the LOI values. Hence, the LOI values and time required to burn specified length of the fabric are directly proportional. The presence of phosphorous and silicon compounds on the treated fabrics that serve as a barrier, is responsible for such increase in the LOI.

15.7.5 Thermo-Gravimetric Analysis

Investigations have been carried out regarding the TGA of the untreated cotton fabric and fabric treated with plasma-silicon dioxide. The peak temperature, corresponding loss in weight, and the residue of untreated and treated samples have been determined. Such value shows that there is increase in thermal stability of the treated fabric because of the increase in residue followed by a significant reduction in the corresponding weight loss. There is considerable change in thermal behavior of cotton fabric due to treatment with plasma silicon dioxide. This change can be attributed to silicon dioxide as it significantly changes the thermal stability of cotton [54–57]. Silica protects cotton from heat and oxygen transfer and favoring the formation of a carbon aqueous residue, and thereby serves as a thermal insulator/physical barrier [58]. Test results of low oxygen index and 45° flammability show the increase in thermal stability of treated sample which is also reflected by the improved flame retardancy of cotton fabric as shown by the results of LOI and 45° flammability.

15.7.6 Morphology of Surface

SEM technique has been used to investigate the extent of deposition on the surface of finished cotton fabrics. SEM (ScanningElectronMicroscope) images of fibers treated with titanium dioxide/silicon dioxide have been depicted in the micrograph of untreated cotton fibers and it can be seen that there is no trace of deposition. SEM image so fall finished cotton samples exhibit the deposition of nanomaterial on the fiber surface. Furthermore, the fibrilar structure of the cotton is fully covered due to the deposition of the nanomaterial and cross linking agent on the surface. In addition, the samples treated with plasma show the higher deposition than that of the without plasma treatment. Moreover, the samples treated with HMDSO pp show the smooth coating on the surface. The deposition as seen in the SEM micrographs is responsible for conferring UV protective and flame retardant characteristics to the cotton sample.

15.7.7 Antibacterial Properties

The antibacterial properties of the fabric against Gram-positive *Staphylococcus aureus* and Gram-negative *Klebsiella pneumonia* negative have been evaluated using prescribed AATCC methods. The fabric treated with plasma and nano titanium dioxide/silicon dioxide exhibit an excellent antibacterial activity against both Gram-positive and Gram-negative bacteria, as pointed out by studies. Such improvement is due to plasma treatment since it cleans the surface and causes the penetration of the chemicals inside the material. HMDSO pp treated fabrics exhibit good durability to washing and more than 80% bacterial reduction for both the bacteria after 20 washes.

15.7.8 Crease Recovery Angle

In this study, BTCA has been used as a binder or crosslinker which is well known for its reactivity with cotton. It binds the free hydroxyl groups of cotton to impart the crease recovery [59, 60].It is observed that after plasma pre-activation, crease recovery angle (CRA) increases and further treatment with HMDSO decreases the CRA slightly (Figure 15.6), This may be due to the softening of the samples after HMDSO treatment. Moreover, it can be seen from figure that without plasma treatment, samples show

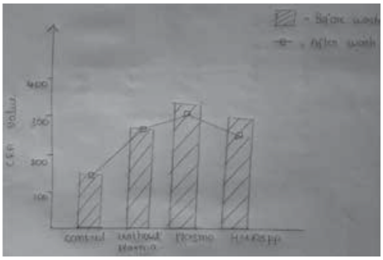

Figure 15.6 Crease recovery angle of control and finished samples [39].

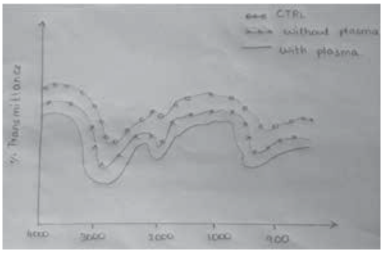

Figure 15.7 FTIR spectra of BTCA treated samples, control cotton, with and without plasma [39].

20% reduction in CRA after 20 washes. The reduction in CRA decreases after HMDSO treatment to 4%. These results can correlate well with the results of UPF, LOI and antibacterial properties. It can be inferred that with the use of HMDSO plasma treatment, the durability of the treatment is improved. This can be ascribed to the hydrophobic nature of the HMDSO polymer which restricts the leaching of finish during washing.

15.7.9 Surface Chemical Changes

The FTIR spectra of cotton fabric in Figure 15.7 shows strong absorption near 3433 cm^{-1} which is attributed to O-H stretching vibration. The peak at 2902 cm^{-1} is due to the presence of C–H bond of cellulose. The peak located at 1648 cm^{-1} is attributed to O-H bending of adsorbed water molecules. The peaks at 1432 cm^{-1} and 1372 cm^{-1} can be attributed to CH_2 scissoring and hydroxyl group bending. The spectra of treated samples shows the distinct peak at 1729 cm^{-1} which can be ascribed to C=O stretching vibration of the ester carboxyl band due to cross-linking of cotton with polycarboxylic acid (BTCA). The occurrence of the peak at 1729 cm^{-1} is prominent especially in the case of plasma treated sample. This infers that the higher cross-linking of the BTCA occurs due to the plasma pre-activation of cotton sample.

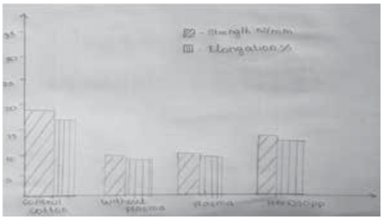

Figure 15.8 Tensile strength and elongation of finished samples [39].

15.7.10 Tensile Properties

Results of the tensile strength hand elongation study of the untreated cotton fabric and treated samples are shown in Figure 15.8. Significant strength loss is noticed due to functional finishing of the cotton samples, this loss may be due to cross-linking of cotton with BTCA. Cross-linking between cellulose molecules causes stiffening of the cellulosic macromolecular network and fiber embrittlement, thus reducing the mechanical strength of the treated cotton [61]. There is no change observed in the tensile properties of the plasma treated and untreated samples, as plasma only modifies the surface and does not change the bulk properties of the material.

15.8 Nano Finishes Adopting Green Approach

15.8.1 Overview

Cotton fabric has been treated and coated with silver nanoparticles that have been synthesized biologically with natural extracts of *Acalypa Indica*. The coating of the herbal extract is by means of insitu chemical reaction [62]. The nanoparticles obtained had a particle size of 100 nm. Scanning electron microscopy has been used to identify the structure and morphology of nanoparticles coated on cotton fabric. The findings reveal excellent antibacterial activity by the incorporation of 5% leaf extracts on cotton fibers. These fibers have also exhibited superior antibacterial activity indicating their usage for medical and infection prevention applications.

15.8.2 Related Aspects

The tremendous increase in microbial infections has prompted development of antibacterial coated textile materials during the recent years [63, 64]. Attempts have been directed towards the development of a non-toxic, cost effective and eco-friendly source of antimicrobial finishing textiles for healthcare application. The most common textile material used as raw material for medical and healthcare products is cotton fiber [65]. But owing to the very high moisture absorption capacity, cotton fibers are more susceptible to microbial attack under certain conditions of humidity and temperature. Cotton being a nutrient, it is conducive for the growth of bacteria and fungi [66]. Hence, in order to achieve textile materials having better antimicrobial properties, cotton fibers are treated with many chemicals [67–69]. Treatment based on nano-materials is found to be the most effective among the different antimicrobial treatments. Silver nanoparticles have shown strong inhibitory and antibacterial effects [70]. The strong toxicity of silver nanoparticle over a broad spectrum of microorganisms has gained popularity [71]. Moreover, the antimicrobial activity of silver nanoparticles against *Escherichia coli,* which is a Gram-negative bacterium, has been investigated. Chemical reducing technique which is related to environmental toxicity is one of the important techniques followed in synthesis of silver nanoparticles [72]. Hence, the development of silver nanoparticles through natural extract is considered as most important technique. The biosynthesis of silver nanoparticles using bacteria, fungi, plants has been reported. Literature is available on the biosynthesis of nanoparticles through plant leaf extracts and their

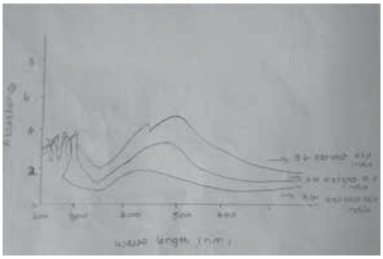

Figure 15.9 UV-spectra of nanoparticles form using 3, 4, & 5% *A. indica* leaves extract solutions [62].

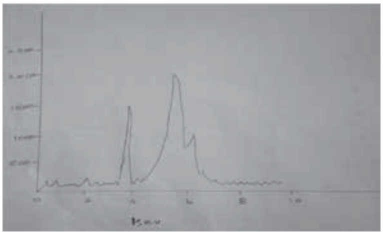

Figure 15.10 EDS analysis of silver nanoparticles [62].

potential application [73]. The use of extracts of germanium and neem leaf in bio-reduction of chloraurate ions and silver ions has been studied. Efforts have been directed towards the synthesis of silver nano particles using aqueous leaf extracts of *A. indica* and analyze its antibacterial activity against microbes like *E. coli* and *Vibrio cholera*.

15.8.3 Release of Silver Nano Particle

The release test has been used to determine the antimicrobial activity for certain duration and is considered as one of the important aspects. Silver nanoparticles are normally non reactive. However, they release silver ions in aqueous media that are responsible for the antimicrobial activity of that structure. For carrying out the test the coated textile structure has been immersed into the saline solution at 37 °C. UV spectra has been used to interpret the regular time intervals of the percentage of silver nano particle release. The pattern of the *in vitro* release pattern of silver nanoparticles by varying the percentage of *A. indica* extract is depicted in Figure 15.11. In comparison with all the combinations, 5 g extract based coating yields faster release compared with other nano particles loaded cotton fabrics. The release has been studied for duration of 200 hrs. The cumulative average release of silver nanoparticles has been found to be 42.13 % during the entire release study period. The prolonged release of silver nanoparticles helps to produce the cure, the wound for long period of time.

15.8.4 Anti-Microbial Activity

Disc diffusion technique has been used for assessment of the antibacterial activity of *A. indica*. Silver nanoparticles against both Gram positive and Gram negative (*Bacillus cereus, Klebsiella pneumonia, Candida albicans, Pseudomonas aeruginosa, Candida glabrata*) pathogenic microorganisms. Figure 15.12 depicts the zone of inhibition relating to the antimicrobial activity of the coated silver nano particles on cotton fabrics.

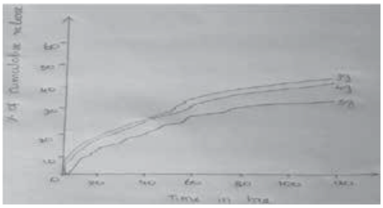

Figure 15.11 *In-vitro* release of Ag nanoparticles coated on cotton fabric [62].

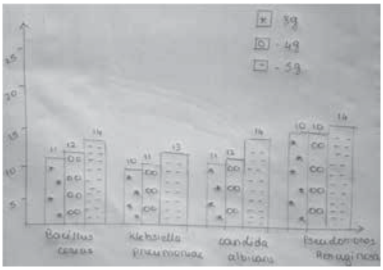

Figure 15.12 Zone of inhibition (mm) of silver nanocoated cotton sample against various bacterial species [62].

The diameter of inhibition zone has been studied to understand the antimicrobial activity of silver nanoparticles that covered an almost similar range against pathogens investigated. The zone of inhibition ranged between 12–14 mm. Many investigations have indicated the biocidal properties of silver nanoparticles against microorganisms. It is suggested that the silver nanoparticles probably get attached to the negatively charged cell surface and alter its physical and chemical properties and also affect the permeability, regulation, electron transport and respiration [74]. Also the silver nanoparticle causes further damage by permeating into the cell, and interacts with the DNA [75]. The silver nanoparticle then releases the silver ions producing higher biocidal effect on the microorganisms. Among the chosen herbal extracts higher bactericidal activity is achieved through *A. indica* extract. It could be attributed to higher activity resulting from the greater amount of silver nanoparticles on the cotton fabric surface. No further enhancement has been reached by increasing more than 5 g *A. indica* extract. This has been due to the optimum loading of silver nanoparticles that has been achieved through 5 g *A. indica* extract itself.

15.9 Multi Functional Nano Finish on Denim Fabrics

15.9.1 Overview

Titanium dioxide nanoparticles have been synthesized adopting reversible reaction in semi batch mixed technique. The nanoparticles have been almost spherical with size that covered a narrow range. SEM technique has been used to study the nanoparticles. The synthesized titanium dioxide nanoparticles have been applied on denim fabric adopting three methods

a) Direct exhaustion of the nanoparticles
b) Microencapsulation of the nanoparticles, and
c) Nanoencapsulation of the nanoparticles

The efficacy of the titanium dioxide nanoparticles have been tested and evaluated with regard to multifunctional properties such as antimicrobial, UV protection, and stain repellency. The fabrics treated with nano titanium dioxide have shown considerable increase in stain release property, and also protects the body against solar radiation and microbes. The finding shows that the multifunctional effect can be imparted to 100% cotton "denim" fabric treated with nano titanium dioxide without altering their fundamental textile property [76]. Various effects can be obtained on denim garments such as fading, vintage, streaks, and so on by washing with enzymes and different chemicals. Such an investigation provides the possibility to the denim industry for value addition on denim products.

15.9.2 Related Aspects

Even though denim is considered to be the oldest fabric in the world, it still continues to enjoy popularity. Indigo has been done in the most significant natural dye till the introduction of the synthetic dyes [77]. Denim has been considered as both fashion and performance driven [78]. Attempt has been made through use of nanoparticle synthesis. Plasma treatment of fabrics using titanium dioxide nanoparticles to impart some functional effect in denim material. Nanotechnology is related to materials that have structure which show considerable novel and improved physical, chemical consumption and biological properties, phenomena and functionality owing to their nano scaled size [79]. The developments in textile finishes create an unprecedented level of performances of stain resistant, hydrophilic, antistatic, wrinkle resistant, and shrink proof abilities [80]. As the surface area of silver nanoparticles is larger, their efficiency is better than larger size particles [81]. Recently, there has been an increase in demand of bioactive textiles due to increasing awareness of health and hygiene [82]. The emergence of nano science and technology has ushered in a new era in textile finishing [83]. The UV blocking property of a fabric is enhanced when a dye, pigment, delustrant, or UV absorber finish is present in the fabric that absorbs UV radiation and blocks its transmission through the fabric to the skin [84]. Since nanoparticles possess large surface area-to-volume ratio and high surface energy, nanotechnology enables high durability of silk fabrics. Nanoparticles thus have better affinity to fabrics and result in an increase in the durability of the function [85]. Also, the breathability, or hand feel of the fabric will not be affected by coating of nanoparticles on the fabric [86]. There is a need in standardization in the application protocol in imparting functional finishes to textile materials, since there have been developments in the synthesis and characterization of different types of nano-materials [87]. Attempt has been made to convert titanium dioxide into nano form. In order to impart multifunctional effects, the synthesized nano titanium dioxide has been applied on denim fabrics. Investigation has been done on the treated material for UV protection ability, antimicrobial ability, and stain repellent properties, and few essential physical properties, to find the effect of treatment on the fabric.

15.9.3 Characterization of Nanoparticles

SEM technique has been used to study the nanoparticles between the magnification ranges of 20,000–37,000. The particles of titanium dioxide have been found to be of nano size. The nano particle size is found to be about 100 nm.

15.9.4 Characterization of Treated Fabric

Studies have been carried out using SEM for fabric finished by exhaustion, micro encapsulate coated and nano encapsulate coated fabrics. A magnification of 5000 has been used. The presence of nanoparticles in the fabric has been observed. Compared to the other two techniques, uptake of nanoparticles is found to be more uniform in the case of nano encapsulation. In the case of both techniques, the presence of nano particle on fabric surface is revealed by SEM. The deposits in the fabric after the finishing process are confirmed.

It has been found that there is very good bacterial resistance against gram positive as well as gram negative bacteria in the case of denim fabric finished with titanium dioxide. The denim fabric treated with titanium dioxide has been compared with control denim fabric using direct exhaustion method. It has revealed highest degree of bacterial resistance against *Staphylococcus aureus*. The fabric treated with micro encapsulation and nano encapsulation technique against *S. aureus* has been studied. The microencapsulation and nano encapsulation process holds the titanium dioxide nano particle inside the wall material. Thus compared to the direct method the potential of microbial resistance is less. However, the leach ability of the nanoparticles is improved by subsequent wash [88].

The inhibition zone of treated fabric against *E. coli* has been studied. The findings reveal that the zone of inhibition is less against *E. coli*. The zone of inhibition of *E. coli* is more complex in comparison with *S. aureus*, since the former has multi-cellular wall structure in the outer structure, and also has the potential to survive in mild antibodies. The highest zone of inhibition is observed in direct exhaust method.

The effectiveness of fabrics in protecting human skin from UV radiations is measured by means of UPF. It is the ratio of the extent of time necessary for the skin to exhibit redness (erythema) with and without protection, under continuous exposure to solar radiation [89]. Erythemal effectiveness of light is thus proportional to harmfulness. Figure 15.13 depicts the erythemal effectiveness of ultraviolet light. From the figure it is evident that wavelength of 280–300 nm is 1000 times more harmful than wavelength 30 nm [90]. The percentage of transmission of fabric treated with titanium dioxide by different methods has been determined. The UPF values for two ranges have been calculated. Fabrics treated with titanium dioxide have been provided higher protection from UV radiation. The calculated value of UPF is approximated to the nearest of five to give the UPF rating, in the case of calculation of UPFR. One effect of this is that materials actually need to achieve a calculated UPF value of 55 or higher in order to be classified as UPF 50+. The effectiveness of UPFR value has been based upon sun protective clothing-evaluation and classification [91].

The findings confirm that cotton fabric treated with nano titanium dioxide UV blocking capability of 96–97.4%. The treated fabric blocks the radiation to very good level. Hence the findings prove that application of nano titanium dioxide on denim fabrics holds great promise as UV protection material.

The stained fabrics have been washed and dried according to prescribed AATCC standards. The chosen types of stains include vegetable, soil, pickle, saffron, and oil. Stained denim fabrics as well as washed denim fabrics have been independently compared with the residual stain on the test specimen with the stains on the stain release replica and each test specimen has been rated to the nearest 0.5 grade based on prescribed AATCC standard [92]. The various grading made by judgment for different stains have been

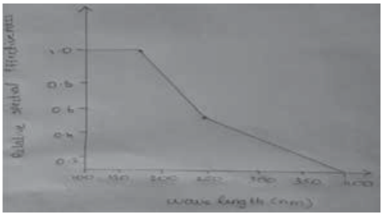

Figure 15.13 Relationship between wave length and relative spectral effectiveness [76].

Table 15.1 Standard grades of UPF and its classification based on AATCC 183 [76].

S. No.	UPF rating	Percentage of UV blocking	UV protection category
1	15–24	93–96%	Good
2	25–39	96–97%	Very good
3	40–50+	97–99%	Excellent

determined. Irrespective of the treatment method, all the three methods showed more or less the same repellency towards the stains. Pickle and oil stains had the poor rating among the chosen stains.

It has been found that treatment with nano titanium dioxide produces very small effect on the basic physical properties of fabric. Experimental study shows that the decrease in air permeability of the finished fabric is very negligible. It arises due to the finishing treatment wherein titanium dioxide coating on the fabric surface blocks the inter fiber pores and intra fiber pores. Also there has been insignificant decrease in the values of tearing strength. The stiffness of the fabric is also affected considerably in the warp direction. There is considerable increase in the drapeability of the fabric as indicated by the drape coefficient value due to treatment with titanium dioxide. There is a slight variation in abrasion resistance in warp (increase) as well as weft (decrease) direction. But, it has been suggested that treatment with nano titanium dioxide in different methods has very small effect on the physical property of the denim fabric. Investigations have thus made it evident that the treatment with titanium dioxide can impart multifunctional properties on denim fabric without affecting its physical properties.

15.10 Role of Silk Sericin in Nano Finishing with Silver Particles

15.10.1 Overview

During the preparation of silver nanoparticles, sericin extracted from silk worm cocoons has been effectively utilized as capping agent. The coagulation of silver nano particles is prevented by sericin, which maintains them in an aqueous medium in moderately stabilized condition. The spherical particles of nanosilver have an average particle size of 15 nm and are fairly monodispersed [93]. Also, antibacterial properties are imparted to silk fabric by application of sericin capped silver nanoparticles.

15.10.2 Related Aspects

Silver nanoparticles can be synthesized in an aqueous medium by the reduction of silver nitrate. As the nanoparticles are very small in size, they have high surface energy and are inherently unstable. Hence, surfactants, also known as capping or stabilizing agents, should be used at early stage to capture the nano particles, and make them float in the solvent by controlling their growth and agglomeration. A number of materials have been used as capping agents such as PVP, gelatin, polyglutamic acid, sophorolipids, PVA and mixtures of different agents [94–99]. Earlier, during the preparation of silver nano particles, the silk protein fibrion has been used as capping and reducing agent [100]. There are two types of proteins in silk, namely, fibrion and sericin. The sericin surrounds fibroin which is silk filament. It constitutes about 25% of raw silk. During the processing of silk, sericin is removed as waste. But, since it possesses useful properties and can be used in different areas of applications, it has attracted research interest [101, 102]. Fibroin is insoluble in water and preparation of its solution is a tedious process involving the use of chemicals, whereas sericin which is readily soluble in water can be extracted by a simple process, *i.e.* by boiling [103]. Earlier, during the green synthesis of silver nano particles the sericin has been used as a reducing and capping agent, and the average nano particle size was 25 nm [104]. A method has been developed wherein the size of the silver nanoparticle is 15 nm, and sericin has been used as the capping agent. Also, evaluation of the antimicrobial efficacy of the nanoparticles that has been applied on silk fabrics has been done. This is an improvement in the previous method since even though the solution was yellow in color and, there has been no significant change in color of the treated silk fabric [105].

15.10.3 Characterization of Silver Nanoparticles

Studies using travelling electron microscope has revealed that the shape of the silver nano particles is spherical and their average diameter is about 15 nm. Studies through scanning electron microscope reveal that the silver nano particles are of fairly uniform size. As depicted in Figure 15.14, the peak width at half maximum calculated from the spectrum is about 60 nm, which also shows a fairly uniform size distribution. The zeta potential

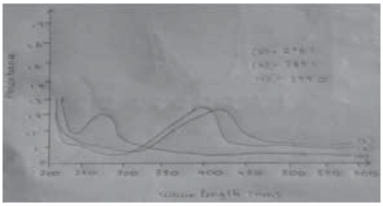

Figure 15.14 UV Spectra of (i) sericin, (ii) AGNP before capping and (iii) sericin capped AGNP [93].

measures indicate a moderate stability. Studies have been done relating to the dependence of particle size on the concentrations of metallic salts [106]. In previous studies, a higher concentration solution of silver nitrate has been used. The finer size of nanoparticle could possibly have arisen from the lower concentration of the silver nitrate solution. The UV-Vis peaks show a shift in absorption peaks from 415 nm in the previous method to 398 nm in the method concerned, which also points to decrease of particle size.

15.10.4 Importance of Sericin asCapping Agent

The silver nitrate reduced by sodium borohydride yield silver ions, which by accepting an electron are further reduced to silver ion. The silver nanoparticles are formed by aggregation of a group of neighboring atoms. These are capped by the sericin micelle and result in a solution that is yellow in color due to the formation of colloidal particles. The sericin micelle is known to have a negative charge. Hence, owing to repulsive forces, the silver nanoparticles capped by sericin which carry negative charges would remain suspended in water. The electrostatic repulsion is also created by the repulsive forces arising from the positive charges of the nuclei. Thus, it can be inferred that the stability is due to electrostatic means. Steric means can also influence stabilization. During steric stabilization, the coagulation of suspensions is inhibited by some additives like hydrophilic polymers. As this polymer is hydrophilic, it would remain associated with water rather than interact with any other surface, except that they are attached at one end to a particle. Hydrophilic repulsion specifically takes place in aqueous solutions between polar molecules to maximize the formation of hydrogen bonds with water. Besides being attached to silver nanoparticles, the amino acids of sericin possess a high content of about 80% of hydrophilic lateral groups. Hence, owing to the effects of electrostatic repulsion coupled with steric stabilization the sericin capped silver nanoparticles form a moderately stable colloidal suspension in the aqueous medium.

15.10.5 Application of Silver Nano Particles as Antibacterial Agent

Studies have shown that silver nanoparticles exhibit antibacterial properties when applied on silk fabrics. However, the fabric has been permanently stained in yellowish green color due to the treatment. In the study considered the silk fabric is not significantly stained by the color even though silver nanoparticles exhibit antimicrobial properties.

SEM images of filaments removed from one of the silk yarns unraveled from the untreated and treated fabrics have revealed that silver nanoparticles are present on the treated filaments but not on the untreated filament. The treated as well as untreated fabrics have been evaluated for antibacterial activity as per prescribed AATCC test method. This method demonstrates bacteriostatic activity and provides evidence of antibacterial activity against both Gram positive and Gram negative bacteria, viz. *S. aureus* and *K. pneumonae*. While bacterial growth has been observed in the untreated fabric, it has not been seen beneath the treated fabric. Also, there has been no inhibition zone, which indicates that the silver nanoparticles do not leach out of the fabric but effectively inhibit bacteria which come in contact with the fabric. The nanoparticles that have been prepared are found to be about 15 nm in size and possibly too small to impart any color to the fiber and fabric significantly. But owing to their small size, they have high surface to volume ratio, and the surface atoms play role in reactions and are thus highly effective against microbes.

15.11 Improvement in Coloration and Antimicrobial Properties in Silk Fabrics with Aqueous Binders

15.11.1 Overview

Isophorondi-isocyanate, polyethylene glycol 6000 and hydroxyl ethyl acrylate have been used to prepare an aqueous binder of polyurethane acrylate using the catalyst as dibutyltin dilaurate. The findings reveal that the binder can be used safely with titanium dioxide nanoparticles in the preparation of ink for pigment dyeing or printing pastes for coloration of silk fabrics and the binder improves the UV protection, antibacterial, and wrinkle resistance properties of silk fabrics. The color strength of the fabric increases with the increase in concentration of polyurethane acrylate and PEG 6000 binder. Higher color strength than that obtained in printing paste can be obtained by the use of polyurethane acrylate and PEG 6000 [108]. There is increase in color strength and ultraviolet protection of fabrics, particularly in case of printing with the increase in titanium dioxide nanoparticles. Using titanium dioxide in either printing paste or in ink preparation shows antibacterial properties good for *E. coli* (G-) and *S. aureus* (G+). The results obtained in case of printing are found to be better than those obtained in case of dyeing. When titanium dioxide nanoparticles are used in printing paste or ink preparation there is overall improvement in fastness properties.

15.11.2 Related Aspects

Among the various printing techniques, the pigment printing is the oldest and simplest considering simplicity of application [109, 110]. As pigment printing has definite advantages like versatility and ease of near final print at the printing stage itself majority of the printed goods are based on this method. During the printing process it is necessary to consider formaldehyde emissions and clogging on the screens and these setbacks are related to the binders used [111–113]. The pioneering work on nanotechnology has been done by Nano-tex [114]. Nanoparticles are generally applied on textile materials by coating technique. The coating compositions that can modify the surface of textiles usually include nanoparticles, surfactant, ingredients, and carrier medium [115]. A number of techniques for application of coating onto fabrics have been studied. These include spraying, transfer printing, washing, rinsing and padding [116–118]. Padding is the most commonly adopted technique. Application of nanoparticles on textile materials imparts various properties like water repellency, soil resistance, wrinkle resistance, antibacterial, anti static, UV protection, flame retardation, and improvement in dyeability. An aqueous UV curable binder of polyurethane acrylate based on polyethylene glycol 6000 has been synthesized, with titanium dioxide nanoparticles either in ink preparation for pigment dyeing or in printing paste for coloration of silk fabrics in order to improve their UV protection, anti-bacterial and wrinkle resistant properties.

15.11.3 Analysis of Polyurethane Acrylate

Most of the acrylated oligomers are based on polyester, polyether, and epoxy resins. It is due to the functionality of such condensation resins that can be precisely controlled to 2 or 3 to prevent gelling and to maintain low viscosity. Isocyanato-terminated polyurethane prepolymer can be formed by reaction of diisocyanate with polyethylene glycol. The polyethylene glycol reacts with the primary isocyanate group of IPDI, under controlled reaction conditions and catalyst concentrations, leaving the secondary isocyanate group intact for subsequent reaction with hydroxyl ethyl acrylate. Infra-red spectra reveals that the emergence of strong absorption bands at certain band widths proves the formation of the polyurethane acrylate oligomer. The spectra also show that there is no absorption band that relates to NCO group [119]. It shows that the entire amount of isophorone-diisocyanate enters in the reaction but the end product is free from isocyanate. All of this confirms the occurrence of the addition reaction to get on the aqueous binder of PUA based on PEG 6000.

15.11.4 Influence of PUA Concentration on K/S Value

The influence of PUA binder concentration on the color strength (K/S) of screen or pigment dyed silk fabrics have been studied. It has been found that the color strength of the fabrics increases with increase in the concentration of PUA and PEG 6000 binder. Moreover, the color strength results are higher than those obtained using this binder on printing paste as compared to that in ink preparation.

15.11.5 Influence of Titanium Dioxide Concentration on K/S Value

The influence of concentration of titanium dioxide nanoparticles on the color strength (K/S) of screen printed or pigment dyed silk fabric with and without use of PUA and PEG binder has been studied. It has been found that the color strength of the colored fabrics increases, particularly with printing, as the concentration of the titanium dioxide nanoparticle increases. The increase in K/S value may be due to the increase in titanium dioxide nanoparticles which catalyzes the rate of polymerization reaction of the binder through the unsaturated bonds. It results in increase of color strength and more fixation of the pigment. Moreover, higher results of color strength are achieved in the case of using the binder in ink preparation than that of printing paste.

15.11.6 UV Protection

Since the inorganic UV blockers are non toxic and chemically stable under exposure to UV radiations as well as high temperatures, they are preferable over organic ones. Some semiconductor oxides like titanium dioxide, silicon dioxide, and aluminium oxide are good examples of inorganic UV blockers. Of these, zinc oxide and titanium dioxide are mostly used

[120–124]. Nano-sized zinc and titanium dioxide are considered better UV blockers since they are more effective absorbers and scatterers of UV radiation, as compared with conventional size. Nanotechnology has been used to carry out a number of investigations on the UV protection treatment to fabric. Sol-gel technique has been used to investigate the UV protection treatment for cotton fabrics [125]. A thin layer of titanium dioxide has been applied on the surface of treated cotton fabric which provides excellent UV protection. It is possible to sustain the effect even after 50 home launderings. The influence of concentration of titanium dioxide nano particles on UPF of screen printed or pigment dyed silk fabric has been determined with and without PUA binder. It has been found that the UPF of the fabrics increases with the increase in the concentration of titanium dioxide nanoparticles. This is more particularly so with the printing of silk fabrics. The use of PUA and PEG 6000 binder alone also gives an UPF due to the presence of unsaturation bonds in this compound. In addition, there is an increase in UPF owing to the presence of titanium dioxide nanoparticles in printing paste or the ink used for dyeing. Since the nanoparticles have a larger surface area per unit mass and volume compared to conventional materials, an excellent UPF rating is achieved. It results in the increase in effectiveness of blocking UV radiation. In the case of small particles, light scattering predominates at about 1/10th of the wavelength of scattered light. The scattering is found to be strongly dependent on wavelength and inversely proportional to the wavelength to the fourth power.

15.11.7 Antimicrobial Property

Nano sized zinc oxide, titanium dioxide, and silver oxide has been used for imparting antibacterial properties [126–129]. A certain level of sterilizing effect is exhibited by metallic ions and compounds. The oxygen present in air or water is partially converted into oxygen because of the catalysis with the metallic ion, and thus dissolves the organic substance to produce a sterilizing effect. The influence of concentration of titanium dioxide nanoparticles on antimicrobial properties of screen printed or pigment dyed silk fabric with and without PUA binder has been determined. It has been found that the use of PUA binder alone does not influence the antimicrobial property. However, use of titanium dioxide in either printing paste or ink preparation shows good results against Gram positive as well as Gram negative bacteria. Also printing gives better results than dyeing. It may be due to the fact that the titanium dioxide is a photo catalyst, once it is illuminated by light with energy higher than its band gaps the electrons in titanium dioxide jump from the valence band to the conduction band

and the electron electric whole pairs will be formed on the surface of the photo catalyst. The negative electrons and oxygen combine into oxygen the positive electric holes and water generates hydroxyl radicals. As the two chemical substances are unstable, when the organic compound falls on the surface of the photo catalyst it combines with the oxygen and hydroxyl groups and turns into carbon dioxide and water. Such a reaction is known as oxidation reduction. The commonly found organic matters in the air like odor molecules, bacteria and viruses are decomposed by the photo catalyst by means of the reaction.

15.11.8 Wrinkle Resistance

The influence of the concentrations of titanium dioxide nano particles on crease recovery of screen printed or pigment dyed silk fabric with and without the use of PUA binder has been determined. As the concentration of titanium dioxide increases there is improvement in crease recovery.

15.11.9 Fiber Surface

SEM studies have been carried out on silk fabric, printed silk fabric, with PUA and PEG 6000 binder and the nanoparticles with PUA, PEG6000 and titanium dioxide nanoparticles. A smooth surface of silk fiber is revealed by the micrograph. The printed silk fabric with PUA, PEG6000 and titanium dioxide nanoparticles appears to be covered by a layer of titanium dioxide. But, only a thin coating is seen with PUA and PEG6000 binder. Such difference arises from titanium dioxide nanoparticles, which is coated on the surface of silk fabrics.

15.11.10 Fastness Properties

The color strength and fastness properties of silk fabrics with PUA and PEG 6000 aqueous binder in screen printed or pigment dyed silk has been determined. All the colored fabrics are characterized by soft handle. The long chain hydrocarbon in PUA and PEG 6000 binder can be an attributing factor. The K/S (color strength) value depends on both the nature of binder used and the concentration of titanium dioxide particle. It has been found that when titanium dioxide nanoparticles are used in either ink preparation or printing paste there is an improvement in the overall fastness properties. It can be because of the fact that titanium dioxide enhances the unsaturation site of the vinyl site of the vinyl group which is responsible for the fixation of dispersed pigment during thermo fixation through the polymerization process. The PUA and PEG 6000 binder is found to give good fastness properties. But the color fastness to washing, rubbing and perspiration ranges from good to very good by use of titanium dioxide nano particles.

15.12 Nanoparticles for Improving Flame Retardant Properties of Fabrics

Presently, the flame retardancy of fibers and fabrics has gained much interest in the academics as well as industry. One of the fatalities in domestic dwelling fires as pointed out by recent fire statistics is domestic accidents involving a small flame in the presence of natural and synthetic fibers [130, 131]. Hence, the standards and norms to produce flame-retardant fibers and fabrics for numerous application sectors, such as protective garments, upholstery, furniture, mattresses and bed linens, have become very strict, especially in the UK. Within this scenario, common industrial and academic practices often rely on flammability tests, such as LOI or vertical/horizontal flame spread tests, as useful methods to completely describe how a fabric may behave in a realistic fire scenario. These tests are not completely reliable, however, and as already shown in the literature [132–134], these tests are only able to describe the ignitability of a material (both textile and plastic) when subjected to a direct small flame application; furthermore, they do not provide any additional helpful information about the combustion behavior of the same material when irradiated by the heat flux developed by flame. To this aim, more sophisticated instrumentation like the oxygen consumption cone calorimeter can be considered a very useful tool [135, 136]. Sometimes a commercial product sold as being made of a flame-retardant material can have surprising results in these flammability tests, as they are not efficient in delaying or blocking the combustion of a polymer under a certain heat flux [137, 138]. In fact, the LOI values and combustion data collected by cone calorimetry are often not in agreement. In the past, high LOI values have been accepted as an indication of flame retardancy for a product; at present, however, this standard is not yet sufficient in order to guarantee a high safety level and has never been used as an official test standard for textiles. Indeed, the new standards for transportation, automotive, furniture and protective garments require high performances of the fabrics to the radiating panel or cone calorimetry, in addition to high LOI values [139–141].

Together with the optimization of the characterization techniques available to describe a realistic fire scenario, great attention has also been focused recently on the chemical nature of the employed flame retardant.

As it is well known, the need to find halogen-free additives for synthetic fibers is becoming urgent, as well as the necessity to replace formaldehyde-based additives for cotton [142, 143]. In this contest, flame retardants containing phosphorus compounds seem to be the most promising and suitable, although their efficiency is low if compared with that of halogens and their derivatives. On the other hand, some of the latter have been found to be toxic, bio-accumulative, and even carcinogenic [144]. Over the last few years, the use of nanoparticles in the flame-retardancy field has shown encouraging results and seems to be a valid alternative, in particular when applied as coatings on fabric surfaces [145–147]. In addition, the low amount of nanoparticles normally employed (<1–2 wt%) can be seen as a great advantage. Nevertheless, not all the nanoparticles available in the market are able to act as flame retardants for all substrates. Their chemical nature plays a key role in the combustion behavior of the polymer. Furthermore, the procedure by which the nanoparticles can be deposited onto textile fibers or fabrics must be considered fundamental and pivotal for a possible industrial application. With this purpose, different approaches can be used indeed, nanoparticles can be directly synthesized *insitu* on the fibers and fabric surfaces through techniques such as sol–gel processes, or alternatively, preformed nanoparticles can be deposited on the fabric surface by using new approaches like Layer-by-layer assembly or nanoparticles adsorption [143, 147, 148]. In the latter case, both natural and synthetic fabrics are initially impregnated with stable aqueous suspensions of nanoparticles and subsequently thermally treated; this process mimicking the typical impregnation/exhaustion procedure currently employed in the wet processing textile industries for conferring numerous properties to fabrics.

The use of nanoparticles bearing different chemical structures and aspect ratios, as potential flame retardants have been compared for polyester, cotton and two of their blends. The flame-retardant properties achieved have been investigated by cone calorimetry. Particular attention has been paid to the application procedure, and the use of dispersing agents or binders has been taken into consideration in order to increase the nanoparticle dispersion level, as well.

This analytical comparison deals with new results as well as preliminary data already published and collected [139, 147].

The potential for commercially available nanoparticles for enhancing the flame-retardant properties of synthetic and natural fabrics and their corresponding blends have been critically studied. Each nanoparticle has been applied to the fabric through a finishing-like process (namely impregnation/exhausting or, more simply, nanoparticle adsorption) in aqueous media and the resulting properties of these fabrics have been assessed in terms of combustion behavior by use of a cone calorimeter under a heat flux of 35 kW/m2. The influence of these nanoparticles on the main combustion parameters of polyester, cotton, and some of their blends has been thoroughly discussed. As a result of this discussion, a flame-retardant efficiency ranking of the nanoparticles under review has been established.

15.13 Application of Herbal Synthesized Silver Nano Particles on Cotton Fabric

Owing to their size, distribution and morphology, nanoparticles exhibit unique properties. Silver nanoparticles enjoy a wide range of end users due to their well-known antimicrobial activity which can be used in microbial protective textiles, wound dressing and drug delivery, coating for medical implants and dental material, food storage container and packaging, water filters, dyeing, finishing and cosmetics [150–154]. The emerging infectious diseases all around are a matter of serious concern for the development of textiles with resistance to the pathogenic bacteria. Although AgNPs has potential antimicrobial efficacy against a broad spectrum of bacteria, still they have negligible toxicity to human cells and hence their applicability becomes quite promising [155]. Several mechanisms have been proposed to explain the inhibitory effect of silver nanoparticles on bacteria. It is assumed that the high affinity of silver towards sulfur and phosphorus is the key element of the antimicrobial effect. Due to the abundance of sulfur-containing proteins on the bacterial cell membrane, silver nanoparticles can react with sulfur-containing amino acids inside or outside the cell membrane, which in turn affects bacterial cell viability [156–157]. It was also suggested that silver ions (particularly Ag+) released from silver nanoparticles can interact with phosphorus moieties in DNA, resulting in inactivation of DNA replication, or can react with sulfur-containing proteins, leading to the inhibition of enzyme functions [158–160]. Again, it is suggested that the bacterial DNA molecules are in relaxed state replicates DNA effectively. If DNA molecules are in condensed form they lose their replicability. AgNPs goes inside the microbial cell, and DNA molecules turn into condensed form by losing their replicability leading to bacterial death [161, 162]. Similarly, it is also becoming now a day's necessary to build up a UV protective textile once, as in these days UV radiation is found to be reaching earth surface. The UVR ranges from 40 nm to 400 nm with further classified into UV-A (320 to 400 nm), UV-B (290 to 320 nm), and UV-C (200 to 290 nm) regions. UV-C is totally absorbed by the upper atmospheric ozone layer and does not reach the earth [163]. UV-A weaken the immunological response of skin cells and UV-B creates dangerous skin cancer. UV protective textile can be made by coloration and natural polyphenols deposition in textile, silver nanoparticles are found to give coloration, if it is herbal synthesized [164, 165].

Having a huge area of applications, its path of synthesis by chemical root is creating a bottleneck situation, as it is toxic one where NaBH4, Aniline, Sodium citrate,etc. and a polymeric compound such as poly (vinylpyrrolidone) (PVP), poly (ethylene glycol) (PEG), and some surfactants are used as stabilizers to prevent nanoparticles agglomeration and precipitation. These chemicals are toxic and hazardous to the environment [166–172]. There of stems a desire for developing an economic, eco-friendly and easily scalable process for large scale synthesis of AgNPs. The researchers have been thus focusing on the green synthesis of nanoparticles using microorganisms, enzymes, and herbal extracts which could offer several benefits over conventional physical and chemical methods. Herbal synthesis pathways don't need to use toxic chemicals, high pressure, temperature, and energy like microwave-assisted method with enhanced applicability [166, 173]. Among these eco-friendly methods, the usage of plant materials i.e., the herbs is more advantageous than other biological processes as it eliminates the risk as well as the elaborate process preparation.

Since a few years, green synthesis of AgNPs has been reported using Olive leaf, *Aloe vera Averrhoa carambola* fruit, Marigold flower, *Lantana camara* leaf, *Catharanthus roseus* leaf, *Eucalyptus chapmaniana* leaves, etc [174–180]. The important plant metabolites such as terpenoids, polyphenols, sugars, alkaloids and phenolic acids are responsible for the bio reduction of metal ions into nanoparticles [181–184]. *Cocos nucifera*, *Artocarpus heterophyllus* and *Phyllanthus emblica* are commonly known as Coconut, Jackfruit and Indian goose berry in English language and in India known as Narikel, Panasa, and Amalika in the Sanskrit language. These plants well known for their medicinal application as their body parts like leaves and fruits are rich in several polyphenols, flavonoid and ascorbic acid also contain amino acids and antioxidant [185, 186]. Therefore, their aqueous extract can be used as both reducing and capping agents for the preparation of AgNPs. The herbal synthesis of silver nanoparticle (H-AgNPs) using mentioned herbal extract (Narikel leaf, Panasa leaf, and Amalika fruit) have been considered, and the performance properties of the fabric carrying such nanoparticles have been reported.

Exploitation three herbal reducing and stabilizing agents such as Narikel leaf, Panasa leaf and of Amalaki fruit for the synthesis of Ag nanoparticles and Characteristic functional groups of these herbs were proved by FTIR analysis of herbal synthesized silver nanoparticle. Reduction of Ag^+ ion into Ag° was confirmed by Surface Plasmon Resonance study. The further size of particles was measured by particle size analyzer testing which yielding 18 nm in P-AgNPs. Synthesized silver nanoparticles were deposited on cotton fabric by two different process pad cure multilayer and polyelectrolyte multilayer to fabricate durable protective textile in terms of Antibacterial and UV-Protective [187]. Deposition of silver nanoparticles was proven by XRD, EDX and SEM analysis. SEM analysis ravels the same with the data of particle size analyzer. Change in thermal behavior due to deposition of silver nanoparticles was noticed in TGA. Also, herbal synthesized silver nanoparticles give coloration effect to the cotton fabric. The color difference was accessed by CIE Lab. Colored Cotton fabric, because of silver nanoparticle gives good to excellent UV protection and antibacterial activity was outstand even after 10th wash against both Gram Positive, i.e. *S. aureus* as well as Gram-Negative, i.e. *E. coli* bacterial isolates.

15.14 Conclusion

Over the past two decades, a good deal of research has been done in the area of nano textile finishing. Of these, there are some significant and noteworthy contributions that open up new avenues aimed towards achieving safer and superior finishes. It has become easier to control the nanoparticle size. One of the interesting areas is the use of papaya peel extract with silver nanoparticles. It has shown that biosynthesis method of producing nanoparticles accelerates the reaction rate and thereby offers an option to other methods of nanoparticle synthesis. Plasma treatment of fabrics using titanium dioxide/silicon oxide nanoparticles reduces chemical consumption and proves ecologically advantageous. Application of titanium dioxide nanoparticles on denim fabrics using different methods imparts multifunctional properties. Moreover, various effects can be obtained thereby increasing value addition and becomes a boon to the denim industry. The green approach in the synthesis of silver nanoparticles imparts excellent antimicrobial property to cotton fabrics. Use of sericin obtained from silk has been used as capping agent on silver nanoparticles and prevents agglomeration of the nanoparticles. The finish on fabrics imparted excellent resistance to microbes. Use of aqueous binders with titanium dioxide nanoparticles improved coloration and antibacterial properties of silk fabrics. Such treated fabrics show better results in printing than dyeing. Thus from the aforesaid discussions, it is clear that the newer methods of nano textile finishes hold promise for the future since they offer advantages like better synthesis of nanoparticles, improvement in functional properties, economical and ecologically good. The treated fabrics can be used over a wide range of applications.

References

1. How to catch up with latest textile market trends Pakistan.. https://www.dawn.com/news/201711/how-to-catch-up-with-latest-textile-market-trends (Accessed on 28.08.2017). Dawn News, July 17, 2009.
2. Hussain, T., Textile Education in Pakistan. *Pakistan Text. J.*, 4, 43–44, 2008.
3. Qian, L., Hinestroza J.P., Application of nanotechnology for high performance textiles. *J. Text. Apparel Technol. Management*, 4, 1–7, 2004.
4. Sinha, A.N.V.T., Kelvin Y., Textile Industry review and outlook. Adsale ATA Text. Online – *J. Asia Text. Apparel*, Feb, 2011.
5. Vijaya, S., Mrudula, T., Naga Deepth, C.H., Sree, V., Novel applications of nanotechnology in life sciences. *J. Bioanal. Biomed.*, 11, 2011.
6. Menaa, B., The importance of nanotechnology in biomedical sciences. *J. Biotechnol. Biomater.*, 1(5), 105e, 2011.
7. Liu, Y.C., Lin, L.H., Chiu, W.H., Size-controlled of gold nanoparticles from bulk gold substrates by sonoelectrochemical methods. *J. Phys. Chem.*, 108, 1923 -1924, 2004.
8. Kathirvelu, D., Souza, L., Bhaarathi, D., Nanotechnology applications in textiles. *Indian J. Sci. Technol.*, 1(5), 1–10, 2008.
9. Sawhney, A.P.S., Condon, B., Pang, S.S., Li, G., Modern Applications of Nanotechnology in Textile. *Textile Res. J.*, 78, 731–739, 2008.
10. Wong, Y.W.H., Yuen, C.W.M., Leung, M.Y.S., Ku, S. K. A., Lam, H.L.I. Selected applications of nanotechnology in textiles. *Autex Res. J.*, 6(1), 1–8, 2006.
11. Carfagna, C., *Nanomaterials in fibres and textiles. Nanotechnology for the Italian Textile*, Milano, Italy, July, 2005.
12. Anon, Nanotechnologies and the textile sector, http://webarchive.nationalarchives.gov.uk/+/interactive.bis.gov.uk/nano//sections/nanotechnologies-and-the-textiles-sector_(Accessed on 10.08.2017).
13. Tayler, D.J., Report on Present Status and Future Potential of Nanotechnologies in the. http://www.hollings.mmu.ac.uk/~dtyler/Nanotechnology1.html. Textile Industry TechniTex Conference. 30th April 2004.
14. Texman, *Application of nanotechnology in developing technical textile*, New cloth market, June, 2010.
15. Van Heeren, H., *Nanotechnology and Lifestyle. Nanotechnology Aerospace Applications*, pp. 1–4.
16. Anon, Nanoenabled automotive textiles, http://ebookbrowse.com/observatorynano-briefing-no-24-nano-enabled-automotive textiles-pdf-d26784083., Dec, 2011.

17. Anon, Nano-enabled protective textiles. http://www.nanotec.it/public/wp-content/uploads/2014/04/ObservatoryNano_BRIEFING_No7_-Nano-EnabledProtectiveTextiles.pdf Dec., 2010.
18. Chinta S.K., Landage S.M., Swapnal, J., Water repellency of textiles through nanotechnology. *Int. J. Adv. Res. IT Eng.*, 2(1), 36–57, 2013.
19. Sudarshan, T.S., New horizons in surface engineering of textiles. *Surface Eng.*, 19(1), 1–3, 2003.
20. Kathiervelu, S. S., Synth. Fib.,Vol. 32, 2003.
21. Harper, T. F., Ind. Fahr Prod., Vol. 89, 2004.
22. Amberg, S., Weber, U., Mt. Text. Bull., 2004.
23. Schrauth, A. J., Saka. N., Sub, N. P., Nano Ma, IF. (Daejeon, Korea). *Proc. of the Second International Symposium*, 2004.
24. Anon, Consumer Conference on Nanotechnology in Foods, Cosmetics and Textiles. BFR., Nov, pp. 1–11, 2006.
25. Agarwal, R., Neelam, G., Kashyap, S.R., and Chauhan,R.P., Antibacterial finish of textile using papaya peels derived silver nanoparticles. *Indian J. Fibre Text. Res.*, 40, 105–107, 2015.
26. Salata, O.V., 2004. Applications of nanoparticles in biology and medicine. *J. Nanobiotechnol.*, 2(1), 1–6, 2004.
27. Raghunandan, D., Mahesh, B.D., Basavaraja, S., Balaji, S.D., Manjunath, S.Y. and Venkataraman, A., Microwave-assisted rapid extracellular synthesis of stable bio-functionalized silver nanoparticles from guava (*Psidium guajava*) leaf extract. *J. Nanopart. Res.*, 13(5), 2021–2028, 2011.
28. Gupta, D., Bhaumik, S., Antimicrobial treatments for textiles. *Indian J. Fibre Text. Res.*, 32, 254–263, 2007.
29. Sivakumar, A., Murugan, R., Sundaresan, K., Periyasamy, S., UV protection and self-cleaning finish for cotton fabric using metal oxide nanoparticles. *Indian J. Fibre Text. Res.*, 38(3), 285–292, 2013.
30. Kathirvelu, S., D'Souza, L., Bhaarathi, D., UV protection finishing of textiles using ZnO nanoparticles. *Indian J. Fibre Text. Res.*, 34, 267–273, 2009.
31. Bhat, N.V., Bharati, R.N., Gore, A.V., Patil, A.J., Effect of atmospheric pressure air plasma treatment on desizing and wettability of cotton fabrics. *Indian J. Fibre Text. Res.*, 36(1), 42–46, 2011.
32. Durán, N., Marcato, P.D., Alves, O.L., De Souza, G.I. and Esposito, E., Mechanistic aspects of biosynthesis of silver nanoparticles by several Fusarium oxysporum strains. *J. Nanobiotechnol.*, 3, 1–7, 2005.
33. Zhou, Y., Kong, Y., Kundu, S., Cirillo, J.D. and Liang, H., Antibacterial activities of gold and silver nanoparticles against Escherichia coli and bacillus Calmette-Guérin. *J. Nanobiotechnol.*, 10, 1–9, 2012.
34. Zhang, Y., Yang, D., Kong, Y., Wang, X., Pandoli, O. and Gao, G., Synergetic antibacterial effects of silver nanoparticles@ aloe vera prepared via a green method. *Nano Biomed. Eng.*, 2(4), 252–257, 2010.
35. Satyavani, K., Gurudeeban, S., Ramanathan, T. and Balasubramanian, T., Biomedical potential of silver nanoparticles synthesized from calli cells of Citrullus colocynthis (L.) Schrad. *J. Nanobiotechnol.*, 9, 1–8, 2011.

36. Chaudhari, P.R.,Masurkar, S.A., Kamble, S.P., *MicroNanolett.*,7, 646, 2012.
37. Feng, Q. L., Wu, J., Chen, G. Q., Cui, F. Z., Kim, T.N., Kim, J.O., A mechanistic study of the antimicrobial effect of silver ion nano-silver on *Escherichia coli* and *Staphylococcus aureus. J. Biomed. Mater. Res.,* 52, 662–668, 2000.
38. Imaga, N.A., Gbenle, G. O., *Sci. Res. Essays*, 52201, 2010.
39. Palaskar, S.S., Desai, A.N., and Shukla, S.R., Plasma Induced Nano – Finish for Multifunctional Properties on Cotton Fabric. *Indian J. Fibre Text. Res.*., 41, 325–330, 2016.
40. Onar, N., Aksit, A.C., Sen, Y. and Mutlu, M., Antimicrobial, UV-protective and self-cleaning properties of cotton fabrics coated by dip-coating and solvothermal coating methods. *Fibers Polym.*, 12(4), 461–470, 2011.
41. Radetić, M., Ilić, V., Vodnik, V., Dimitrijević, S., Jovančić, P., Šaponjić, Z. and Nedeljković, J.M., Antibacterial effect of silver nanoparticles deposited on corona-treated polyester and polyamide fabrics. *Polym. Adv. Technol.*, 19(12), 1816–1821, 2008.
42. Lam, Y.L., Kan, C.W. and Yuen, C.W.M., Effect of plasma pretreatment on enhancing wrinkle resistant property of cotton fiber treated with BTCA and TiO2 System. *J. Appl. Polym. Sci.*, 124(4), 3341–3347, 2012.
43. Hwang, Y.J., Mccord, M.G., An, J.S., Kang, B.C. and Park, S.W., Effects of helium atmospheric pressure plasma treatment on low-stress mechanical properties of polypropylene nonwoven fabrics. *Text. Res. J.,* 75(11), 771–778, 2005.
44. Wang, C.X., Liu, Y., Xu, H.L., Ren, Y. and Qiu, Y.P., Influence of atmospheric pressure plasma treatment time on penetration depth of surface modification into fabric. *Appl. Surf. Sci.*, 254(8), 2499–2505, 2008.
45. Kaplan, S., Plasma processes for wide fabric, film and non-wovens. *Surf. Coat. Technol.* 186(1), 214–217, 2004.
46. Virk, R.K., Ramaswamy, G.N., Bourham, M. and Bures, B.L., Plasma and antimicrobial treatment of nonwoven fabrics for surgical gowns. *Text. Res. J.*, 74(12), 1073–1079, 2004.
47. Bourbigot, S. and Duquesne, S., Fire retardant polymers: recent developments and opportunities. *J. Mater. Chem.*, 17(22), 2283–2300, 2007.
48. Wang, C.X. and Qiu, Y.P., Two sided modification of wool fabrics by atmospheric pressure plasma jet: Influence of processing parameters on plasma penetration. *Surf. Coat. Technol.*, 201(14), 6273–6277, 2007.
49. Kale, K.H. and Palaskar, S., Atmospheric pressure plasma polymerization of hexamethyldisiloxane for imparting water repellency to cotton fabric. *Text. Res. J.*, 81(6), 608–620, 2011.
50. Kale, K.H. and Palaskar, S.S., Structural studies of plasma polymers obtained in pulsed dielectric barrier discharge of TEOS and HMDSO on nylon 66 fabrics. *J. Text. Inst.*, 103(10), 1088–1098, 2012.
51. Yang, H., Zhu, S. and Pan, N., Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme. *J. Appl. Polym. Sci.*, 92(5), 3201–3210, 2004.

52. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J. M., Dubois, P. H., New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Mater. Sci. Eng. R:Reports*, 63(3), 100–125, 2009.
53. Lam, Y.L., Kan, C.W., Yuen, C.W., Effects of oxygen plasma pre-treatment and titanium finished cotton fabrics. *Bioresouses.*,6(2), 1454–1474, 2011.
54. Alongi, J., Ciobanu, M. and Malucelli, G., Cotton fabrics treated with hybrid organic–inorganic coatings obtained through dual-cure processes. *Cellulose*, 18(5), 1335–1348, 2011.
55. Alongi, J., Ciobanu, M. and Malucelli, G., Sol–gel treatments for enhancing flame retardancy and thermal stability of cotton fabrics: optimisation of the process and evaluation of the durability. *Cellulose*, 18(1), 167–177, 2011.
56. Alongi, J., Ciobanu, M. and Malucelli, G., Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol–gel processes. *Carbohydrate Polym.*, 85(3), 599–608.
57. Alongi, J., Ciobanu, M., Tata, J., Carosio, F. and Malucelli, G., Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol–gel treatments. *J. Appl. Polym. Sci.*, 119(4), 1961–1969, 2011.
58. Alongi, J., Ciobanu, M. and Malucelli, G., Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol–gel processes. *Carbohydrate Polym.*, 87(3), 2093–2099, 2012.
59. Welch, C.M. and Peters, J.G., Curing Agents Having Low or Zero Phosphorus Content for Formaldehyde Free DP Finishing with Polycarboxylic Acids. *Text. Chem. Colorist*, 25(10), 25–29, 1993.
60. Yang, Y. and Li, S., Crease Resistant Finishing of Silk Fabric with BTCA. *Text. Chem. Colorist*, 26(5), 25–29, 1994.
61. Yang, C.Q., Wei, W. and Lickfield, G.C., Mechanical strength of durable press finished cotton fabric: Part III: Change in cellulose molecular weight. *Text. Res. J.*, 70(10), 910–915, 2000.
62. Senthil Kumar, B., Study on Antimicrobial Effectiveness of Silver Nano Coating Over Cotton Fabric Through Green Approach. *Int. J. Pharma Sci. Res.*, 7, 363–368, 2016.
63. Danese, P.N., Antibio film approaches: prevention of catheter colonization. *Chem. Biol.*, 9(8), 873–880, 2002.
64. Lewis, K., Klibanov, A. M., Surpassing nature: rational design of sterile-surface materials. *Trends Biotechnol.*, 23, 343–348, 2005.
65. Czajka, R., Development of medical textiles. *Fib. Text. East. Eur.*, 13, 13–15, 2005.
66. Gao, Y., Cranston, R., Recent advances in antimicrobial treatments of textiles. *Text. Res. J.*, 78, 60–72, 2008.
67. Duran, N., Marcato, P., DeSouza, G. I. H., Alves, O. L., Esposito, E.,Antibacterial effect of silver nanoparticles produced by fungal process on

textile fabrics and their effluent treatment. *Biomed. Nanotechnol.*, 3, 203–208, 2007.

68. Son, Y.A., Kim, B.S., Ravikumar, K., and Lee, S.G., Imparting durable antimicrobial properties to cotton fabric susing quaternary ammonium salts through 4-aminobenzenessulfonicacid-chloro-triazineadduct. *Eur. Polym. J.*, 42, 3059–3067, 2006.
69. Lim, S.H., Hudson, S.M., Application of a fibre-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish. *Carbohydrate Polym.*, 56, 227–234, 2004.
70. Uchida, M., Antimicrobial zeolite and its application. *Chem. Ind.*, 46, 48–54, 1995.
71. Sondi, I. and Salopek-Sondi, B., Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria. *J. Colloid Interface Sci.*, 275(1), 177–182, 2004.
72. Chen, M., Wang, L.Y., Han, J.T., Zhang, J.Y., Li, Z.Y., Qian, D.J. Preparation and study of polyacryamide-stabilized silver nanoparticles through a one-pot process. *J. Phys. Chem.*, B110, 11224–11231, 2006.
73. Sastry, M., Ahmad, A., Khan, M., I., Kumar, R., *Curr. Sci.* 85., 162–170, 2003.
74. Marambio-Jones, C., Hoek, E.M.V., A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *J. Nanoparticle Res.*, 12, 1531–1551, 2010.
75. AshaRani, P.V., Mun, G. L. K., Hande, M. P., Valiyaveettil, S., Cytotoxicity and genotoxicityof silver nanoparticles in human cells. *ACS Nano.*, 3, 279–290, 2009.
76. Vijayalakshm, D., Rathinamoorth, R., and Ramachandran, T., An Experimental Study on the Multi -Functional Efficacy of Nano Tio^2 Treated Denim Fabrics. *JTATM.*, 7(4), 1–12, 2012.
77. http://www.denver fabrics.com/content/denim/denim.aspx
78. Virginia, S., Borland, It 39s in the Jeans. *Textile world*, 2002.
79. Wang, Z. L., *Characterization of Nano Phase Material*, Wiley-VCH Verlag GmbH, Germany, 2001.
80. Wong, Y. W. H., Yuen, C. W. M., Leung, M. Y. S., Ku, M. Y. S., and Lam, H. L. I., Selected applications of nano technology in textiles. *Autex Res. Journal.*, 6(1), 1–10, 2006.
81. http://www.nano-tex.com
82. Purwar, R. and Joshi, M., Recent developments in antimicrobial finishing of textiles – a review. *AATCC Review*, 4, 22–26, 2004.
83. Vigneshwaran, N., SampathkumarKathe, A. A., Varadarajan, P.V., and Virendra Prasad, Functional finishing of cotton fabric using zinc oxide-soluble starch nanocomposites. *Nanotechnol.*, 17, 5087–5095, 2006.
84. Hustved, C., and Crews, P., Cultra-violet protection factor of naturally pigmented cotton. *J. Cotton Sci.*, 9, 47–55, 2005.
85. Jeevani, T., Nanotechnology in Agriculture. *J. Nanomed. Nanotechnol.*, 2, 124–130, 2011.

86. Frederick, A., Smart Nanotextiles: Inherently Conducting Polymers in Healthcare. Da Vinci's Notebook, 3, 1–2, 2011.
87. Kathirvelu, S., Nanotechnology applications in textiles. *Indian J. Sci. Technol.*, 1(5), 1–10, 2008.
88. Thilagavathi, G., Krishnabala, S., and Kannaian, T., Microencapsulation of herbal extracts for microbial resistance in healthcare textile. *Indian J. Fiber Text. Res.*, 32, 351–354, 2007.
89. Perenich, T.A., Textiles as preventive measures for skin cancer. *Colourage*, 45, 71–73, 1998.
90. Das, B. R., UV Radiation Protective Clothing. *The Open Text. J.*, 3, 14–21, 2010.
91. Gies, P., and Roy, C., Ultraviolet radiation, ozone thinning, the environment and UPF testing. Proceedings SDCANZ Textiles and Sun Protection Conference, UNSW, 6–24.
92. AATCC Test Method 130–2000, (2005) AATCC Technical Manual 217–219, 1993.
93. Prakash, N., Nivedita, S., and Roy, S., Use of Sericin of Bombyx Mori in the Synthesis of Silver Nano Particles their Characterization and Application. *Indian J. Fiber Text. Res.*, 36, 168–171, 2011.
94. Li, Z., Wang, Y. and Yu, Q., Significant parameters in the optimization of synthesis of silver nanoparticles by chemical reduction method. *J. Mater. Eng. Perform.*, 19(2), 252–256, 2010.
95. Mock, J.J., Barbic, M., Smith, D.R., Schultz, D.A. and Schultz, S., Shape effects in plasmon resonance of individual colloidal silver nanoparticles. *J. Chem. Phys.*, 116(15), 6755–6759, 2002.
96. Yu, D.G., Formation of colloidal silver nanoparticles stabilized by Na^+–poly (γ-glutamic acid)–silver nitrate complex via chemical reduction process. *Colloids Surfaces B: Biointerfaces*, 59(2), 171–178, 2007.
97. Kasture, M.B., Patel, P., Prabhune, A.A., Ramana, C.V., Kulkarni, A.A. and Prasad, B.L., Synthesis of silver nanoparticles by sophorolipids: effect of temperature and sophorolipid structure on the size of particles. *J. Chem. Sci.*, 120(6), 515–520, 2008.
98. Petica, A., Gavriliu, S., Lungu, M., Buruntea, N. and Panzaru, C., Colloidal silver solutions with antimicrobial properties. *Mater. Sci. Eng.: B*, 152(1), 22–27, 2008.
99. Filippo, E., Serra, A. and Manno, D., Poly (vinyl alcohol) capped silver nanoparticles as localized surface plasmon resonance-based hydrogen peroxide sensor. *Sensors Actuators B: Chem.*, 138(2), 625–630, 2009.
100. Chen, W., Wu, W., Chen, H. and Shen, Z., Preparation and characterization of noble metal nanocolloids by silk fibroin *in situ* reduction. *Sci. China Series B: Chem.*, 46(4), 330–338, 2003.
101. Mondal, M., The silk proteins, sericin and fibroin in silkworm, Bombyx mori Linn.,-a review. *Caspian J. Environ. Sci.*, 5(2), 63–76, 2007.

102. Mase, K., Iizuka, T., Okada, E., Miyajima, T. and Yamamoto, T., A new silkworm race for sericin production,"SERICIN HOPE" and its product,"VIRGIN SERICIN". *J. Insect Biotechnol. Sericol.*, 75(2), 85–88, 2006.
103. Kaneko, H., The colloidal behaviour of sericin. III. Bull. Chem. Soc. Japan, 9(7), 283–302, 1934.
104. Nivedita, S., Bhat, P.N. and Roy, S., Sericin of *Bombyx mori* as a reducing and capping agent in the preparation of silver nanoparticles. *Séricologia*, 50(3), 351–357, 2010.
105. Gulrajani, M.L., Gupta, D., Periyasamy, S. and Muthu, S.G., Preparation and application of silver nanoparticles on silk for imparting antimicrobial properties. *J. Appl. Polym. Sci.*, 108(1), 614–623, 2008.
106. Sarathy, K.V., Raina, G., Yadav, R.T., Kulkarni, G.U. and Rao, C.N.R., Thiol-derivatized nanocrystalline arrays of gold, silver, and platinum. *J. Phys. Chem. B*, 101(48), 9876–9880, 1997.
107. Solomon, S. D., Bahadory, M., Jayarajasingam, A. V., Rutkowsky, S. A., Synthesis and Study of Silver Nanoparticles. *J. Chem. Edu.*, 84(2), 322–330, 2007.
108. Molla, M. M., Ei-Khatib, E. M., Ei-Gammel, M. S., and Abdel- Fattah, Nanotechnology to Improve Coloration and Antimicrobial Properties of Silk Fabrics. *Indian J. Fiber Text. Res.*, 36, 266–271, 2011.
109. Schwindt, W., Melliand, *Textilber*. 71, 693, 1990.
110. Holme, I., Market development: challenge to dyeing and finishing. *Color. Technol.*, 22(1), 1–13, 1992.
111. Smith, H. G., Hiatt, J. D., & Bruce, J. E., U S Pat 6, 196, 126. (toIntex Corporation, NC), 2001.
112. Shah, K. P., Panchmatia, P. R., U S Pat 5, 969, 018. (to The B F Goodrich Company, USA), 1999.
113 Hotton, W. T., & Ronald, W. N., U S Pat 5,143,954. (to Rohm and Haas Company, USA), 1990.
114. Russell, E., Nanotechnologies and the shrinking world of textiles. *Text. Horizons*, 9/10, 7–9, 2002.
115. Cramer, R.D., Ponomarenko, E.A. and St, J.C.T.R.B., Method of applying nanoparticles. U.S. Patent 6,645,569 The Procter & Gamble Company, 2003.
116. Ward, D., Small-scale technology with the promise of big rewards. *Technical Text. Int.*, 12, 13–15, 2003.
117. Xin, J. H., Daoud, W. A., Kong, Y. Y., A new approach to UV-blocking treatment for cotton fabrics. *Text. Res. J.*, 74, 97–100, 2004.
118. Yeo, S. Y., Lee, H. J., Jeong, S. H., Preparation of nanocomposite fibers for permanent antibacterial effect. *J. Mater. Sci.*, 38, 2143–2147, 2003.
119. Lee, J.J., Chi, Z.K., Kuo, Y.M. and Chao, D.Y., Effect of the concentration of dye on the physical property of dye-based polyurethane ionomer. *J. Appl. Polym. Sci.*, 57(8), 1005–1011, 1995.

120. Burniston, N., Bygott, C. and Stratton, J., Nano technoology meets titanium dioxide. Surface coatings international. Part A, *Coatings J.,* 87(4), 179–184, 2004.
121. Sherman, J., Jonathan, A., Nanoparticulate titanium dioxide coatings, and processes for the production and use. thereof, U S Pat 6653356, Fuess and Davidness, 2003.
122. Yang, H. Y., Zhu, S. K., Pan, N., Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme. *J. Appl. Polym. Sci.*, 92, 3201–3210, 2003.
123. Saito, M., Antibacterial, deodorizing, and UV absorbing materials obtained with zinc oxide (ZnO) coated fabrics. *J. Coated Fab.*, 23, 150–164, 1993.
124. Xiong, M. N., Gu, G. X., You, B., Wu, L. M., Preparation and characterization of poly(styrenebutylacrylate) latex/nano-ZnO nanocomposites. *J. Appl. Polym. Sci.*, 90, 1923–1931, 2003.
125. Daoud, W. A., Xin, J. H., Low temperature sol-gel processed photocatalytic titania coating. *J. Sol-Gel Sci. Technol.*, 29, 25–29, 2004.
126 Wong, Y. W. H., Yuen, C. W. M., Leung, M. Y. S., Ku, S. K. A., Lam, H. L. I., Selected applications of nanotechnology in textiles. *Autex Res. J.,* 6(1)., 1–8, 2006.
127. Lee, H.J., Yeo, S. Y., Jeong, S. H., Antibacterial effect of nanosized silver colloidal solution on textile fabrics. *J. Mater. Sci.*, 38, 2199–2204, 2003.
128. Yeo, S, Y., Jeong, S. H., Preparation and characterization of polypropylene/silver nanocomposite fibers. *Polym. Int.*, 52, 1053–1057, 2003.
129. Daoud, W. A., Xin, J. H., Nucleation and growth of anatase crystallites on cotton fabrics at low temperatures. *J. Am. Ceramic Soc.*, 87, 953–955, 2004.
130. Brushlinsky, N.N.; Sokolov, S.V.; Wagner, P.; Hall, J.R. *World Fire Statistics. Report No. 10*; Centre of Fire Statistics, International Association of Fire and Rescue Service: Geneva, Switzerland, 2006.
131. Kobes, M.; Groenewegen, K. *Consumer Fire: European Statistics and Potential Fire Safety Measures*; Austrian Federal Ministry Labor, Social Affairs and Consumer Protection: Wien, Austria, 2009.
132. Babrauskas, V. Upholstered furniture heat release Rates: Measurements and estimation. *J. Fire Sci.*, 1, 9–32, 1983.
133. Babrauskas, V. The cone calorimeter. In Heat Release in Fires; Babrauskas, V., Grayson, S. J., (Eds.), pp. 61–91, Chapman & Hall: London, UK, 1995.
134. Babrauskas, V.; Baroudi, D.; Myllymaki, J.; Kokkala, M. The cone calorimeter used for predictions of the full-scale burning behaviour of upholstered furniture. *Fire Mater.*, 21, 5–105, 1997.
135. Standard Test Method for Determining the Heat Release Rate of Upholstered Furniture and Mattress Components or Composites Using a Bench Scale Oxygen Consumption Calorimeter 2004; ASTM E1474; ASTM International: West Conshohocken, PA, USA, 2004.
136. Standard Test Method for Determining the Heat Release Rate and Other Fire-Test-Response Characteristics of Wallcovering Composites Using a Cone

Calorimeter 2002; ASTM E1740; ASTM International: West Conshohocken, PA, USA, 2002.

137. Tata, J.; Alongi, J.; Carosio, F.; Frache, A., Optimization of the procedure to burn textile fabrics by cone calorimeter: Part I. Combustion behavior of polyester. *Fire Mater.*, 35, 397–409, 2011.
138. Tata, J.; Alongi, J.; Frache A. Optimization of the procedure to burn textile fabrics by cone calorimeter: Part II. Results and discussion on nanoparticle finished polyester. *Fire Mater.*, *36*, 527–536, 2012.
139. *Plastics—Smoke Generation—Part 1: Guidance on Optical-Density Testing 1996 + Part 2: Determination of Optical Density by a Single-Chamber Test 2002; ISO 5659*; International Organization for Standardization: Geneva, Switzerland, 2002. *Fire Test, Reaction to Fire—Part 1: Rate of Heat Release (Cone Calorimeter Method) + Part 2: Smoke Production Rate (Dynamic Measurement) + Part 3: Guidance on Measurement*; *ISO 5660*; International Organization for Standardization: Geneva, Switzerland, 2002 and 2003.
140. *Reaction to Fire Tests for Floorings—Part 1: Determination of the Burning Behaviour Using a Radiant Heat Source + Part 2: Determination of Flame Spread at a Heat Flux Level of 25 kW/m2*; *ISO 9239*; International Organization for Standardization: Geneva, Switzerland, 2002.
141. Horrocks, A.R., Flame retardant challenges for textiles and fibres: New chemistry *versus* innovatory solutions. *Polym. Degrad. Stab.*, 96, 377–392, 2011.
142. Alongi, J.; Carosio, F.; Horrocks, A.R.; Malucelli, G. *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions*; Smithers RAPRA Publishing: Shawbury, UK, 2013.
143. Van der Veen, I.; De Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, *88*, 1119–1153, 2012.
144. Alongi, J., Frache, A., Malucelli, G., Camino, G. Multi-component flame retardant coatings. in: *Handbook of Fire Resistant Textiles*, F. Selcen Kilinc, (Ed.), Woodhead Publishing, Cambridge, UK; pp.68–93, 2013.
145. Alongi, J., Carosio, F., Malucelli, G. Current emerging techniques to impart flame retardancy to fabrics. *Polym. Degrad. Stab.*,106, 138–149, 2014.
146. Malucelli, G., Carosio, F., Alongi, J., Fina, A.; Frache, A.; Camino, G. Materials engineering for surface-confined flame retardancy. *Mater. Sci. Eng. R Rep.*, 84, 1–20, 2014.
147. Alongi, J., Malucelli, G. State of the art and perspectives on sol-gel derived hybrid architectures for flame retardancy of textiles. *J. Mater. Chem.*, 22, 21805–21809, 2012.
148. Schartel, B., Bartholmai, M., Knoll, U. Some comments on the main fire retardancy mechanisms in polymer nanocomposites. *Polym. Adv. Technol.*, 17, 772–776, 2006.
149. Jenny, A., Jennifer, T., Federico, C., Giuseppe, R., Alberto, F., and Giovanni, C., A Comparative Analysis of Nanoparticle Adsorption as Fire-Protection Approach for Fabrics. *Polym.*, 7, 47–68, 2015.

150. Boris lldusovich Kharisov, Oxana Vasilievna Kharissova, Ubaldo Oritz Mendez; CRC Concise *Encyclopedia of Nanotechnology*, 1–8, 2016.
151. Teli, M. D., Samanta, K. K., Pandit, P., Basak, S., & Chattopadhyay, S. K., Low Temperature Dyeing of Silk using Atmospheric Plasma Treatment. *Indian J. Natural Fibres:* v, 1(1),1–7, 2014.
152. Teli, M. D., Samanta, K. K., Pandit, P., Basak, S., & Gayatri, T. N. Hydrophobic silk fabric using atmospheric pressure plasma. *Int. J. Biores. Sci.,* 2(1), 15–19, 2015.
153. Teli, M. D., Samanta, K. K., Pandit, P., Basak, S., & Chattopadhyay, S.K., Low-temperature dyeing of silk fabric using atmospheric pressure helium/nitrogen plasma. *Fibers Polym.*, 16(11), 2375, 2015.
154. Das, D., Pandit, P., Maiti, S., Dalapati, K.K., *Development of Protective Clothing for Pesticide Operation.*, 3(8), 851–855, 2016.
155. Ornelas-Megiatto, C., Shah, P.N., Wich, P.R., Cohen, J.L., Tagaev, J.A., Smolen, J.A., Wright, B.D., Panzner, M.J., Youngs, W.J., Fréchet, J.M. and Cannon, C.L., Aerosolized antimicrobial agents based on degradable dextran nanoparticles loaded with silver carbene complexes. *Mol. Pharmaceut.*, 9(11), 3012–3022, 2012.
156. Prabhu, S. and Poulose, E.K., Silver nanoparticles: mechanism of antimicrobial action,synthesis, medical applications, and toxicity effects. *Int. Nano Lett.*, 2, 32, 2012.
157. Jung, W.K., Koo, H.C., Kim, K.W., Shin, S., Kim, S.H. and Park, Y.H., Antibacterial Activity and Mechanism of Action of the Silver Ion in *Staphylococcus aureus* and *Escherichia coli*. *Appl. Environ. Microbiol.*, 74(7), 2171–2178, 2008.
158. Gupta A, Silver S., Silver as a biocide: will resistance become a problem? *Nat. Biotechnol.* 16, 888–890, 1998.
159. Matsumura, Y., Yoshikata, K., Kunisaki, S., Tsuchido, T., Mode of bactericidal action of silver zeolite and its comparison with that of silver nitrate. *Appl. Environ. Microbiol.*, 69, 4278–4281, 2003.
160. Vankar, P.S., Shukla, D., Biosynthesis of silver nanoparticles using lemon leaves extract and its application for antimicrobial finish on fabric. *Appl. Nanosci.*, 2, 163–168, 2012.
161. Chen, M., Yang, Z., Wu, H., Pan, X., Xie, X. and Wu, C., Antimicrobial activity and the mechanism of silver nanoparticles thermosensitive gel. *Int. J. Nanomed.*, 6, 2873–2877, 2011.
162. Saravanan, D., UV protection textile materials. *AUTEX Res. J.*, 7(1), 53–62, 2007.
163. Sarkar, A.K., An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants. *BMC Dermatol.*, 4, 15, 2004.
164 Grifoni, D., Bacci, L., Zipoli, G., Albanese, L. and Sabatini, F., The role of natural dyes in the UV protection of fabrics made of vegetable fibres. *Dyes Pigm.*, 91(3), 279–285, 2011.
165. Davidović, S., Miljković, M., Lazić, V., Jović, D., Jokić, B., Dimitrijević, S. and Radetić, M., Impregnation of cotton fabric with silver nanoparticles

synthesized by dextran isolated from bacterial species *Leuconostoc mesenteroides* T3. *Carbohydrate Polym.*, 131, 331–336, 2015.

166. Zielińska, A., Skwarek, E., Zaleska, A., Gazda, M. and Hupka, J., Preparation of silver nanoparticles with controlled particle size. *Procedia Chem.*, 1(2), 1560–1566, 2009.
167. Ai, L., Liu, X. and Jiang, J., Synthesis of loofah sponge carbon supported bimetallic silver–cobalt nanoparticles with enhanced catalytic activity towards hydrogen generation from sodium borohydride hydrolysis. *J. Alloys Comp.*, 625, 164–170, 2015.
168. Hussain, J.I., Kumar, S., Hashmi, A.D., Khan, Z., Silver nanoparticles: preparation, characterization, and kinetics. *Adv. Mat. Lett.*, 2(3), 188–194, 2011.
169. Aashritha, S., synthesis of silver nanoparticles by chemical reduction method and their antifungal activity. *Int. Res. J. Pharm.*, 4(10), 209, 2013.
170. Slistan-Grijalva, A., Herrera-Urbina, R., Rivas-Silva, J.F., Avalos-Borja, M., Castillón-Barraza, F.F. and Posada-Amarillas, A., Synthesis of silver nanoparticles in a polyvinylpyrrolidone (PVP) paste, and their optical properties in a film and in ethylene glycol. *Mater. Res. Bull.*, 43, 90–96, 2008.
171. Shkilnyy, A., Soucé, M., Dubois, P., Warmont, F., Saboungi, M.L. and Chourpa, I., Poly (ethylene glycol)-stabilized silver nanoparticles for bioanalytical applications of SERS spectroscopy. *Analyst*, 134(9), 1868–1872, 2009.
172. Zhao, X., Xia, Y., Li, Q., Ma, X., Quan, F., Geng, C. and Han, Z., Microwave-assisted synthesis of silver nanoparticles using sodium alginate and their antibacterial activity, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 444, 180–188, 2014.
173. Khalil, M.M., Ismail, E.H., El-Baghdady, K.Z. and Mohamed, D., Green synthesis of silver nanoparticles using olive leaf extract and its antibacterial activity. *Arabian J. Chemistry*, 7(6), 1131–1139, 2014.
174. Chandran, S.P., Chaudhary, M., Pasricha, R. Ahmad, A., Sastry, M., Synthesis of gold Nanotriangles and silver nanoparticles using Aloe vera plant extract. *Biotechnol.* Prog. 22, 577–588, 2006.
175. Chowdhury, I.H., Ghosh, S., Roy, M. and Naskar, M.K.,Green synthesis of water-dispersible silver nanoparticles at room temperature using green carambola (star fruit) extract. *J. Sol-Gel Sci. Technol.*, 73(1), 199–207.
176. Padalia, H., Moteriya, P. and Chanda, S., 2015. Green synthesis of silver nanoparticles from marigold flower and its synergistic antimicrobial potential. *Arabian J. Chem.*, 8(5), 732–741, 2015.
177. Ajitha, B., Reddy, Y.A.K. and Reddy, P.S., Green synthesis and characterization of silver nanoparticles using Lantana camara leaf extract, *Mater. Sci. Eng. C*, 49 373–381, 2015.
178. Ponarulselvam, S., Panneerselvam, C., Murugan, K., Aarthi, N., Kalimuthu, K. and Thangamani, S., Synthesis of silver nanoparticles using leaves of Catharanthus roseus Linn. G. Don and their Antiplasmodial activities, Asian Pac. *J. Trop. Biomed,* 2(7): 574–580, 2012.
179. Sulaiman, G.M., Mohammed, W.H., Marzoog, T.R., Al-Amiery, A.A.A., Kadhum, A.A.H. and Mohamad, A.B., Green synthesis, antimicrobial and

cytotoxic effects of silver nanoparticles using *Eucalyptus chapmaniana* leaves extract, Asian Pac. *J. Trop. Biomed.*, 3(1), 58–63, 2013.

180. Makarov, V.V., Love, A.J., Sinitsyna, O.V., Makarova, S.S., Yaminsky, I.V., Taliansky, M.E. and Kalinina, N.O., Green nanotechnologies: synthesis of metal nanoparticles using plants. *Acta Naturae*, 6(1/20) 35–44, 2014.
181. Teli, M.D. and Pandit, P., A Novel Natural Source Sterculia Foetida Fruit Shell Waste as Colorant and Antibacterial Agent for cotton. *J. Text. Association*, 76(5), 293–297, 2016.
182. Teli, M.D., Pandit, P., & Basak, S., Coconut shell extract imparting multifunction properties to ligno-cellulosic material. *J. Ind. Text.*, 2017. https://doi.org/10.1177/1528083716686937
183. Basak, S., Samanta, K.K., Chattopadhyay, S.K., Pandit, P., Maiti, S. Green fire retardant finishing and combined dyeing of proteinous wool fabric. *Color. Technol.*, 132(2), 135–143, 2016.
184. Singh, M.K., Yadav, S.S., Yadav, R.S., Singh, U.S., Shukla, Y., Pant, K.K. and Khattri, S., Efficacy of crude extract of Emblica officinalis (amla) in arsenic-induced oxidative damage and apoptosis in splenocytes of mice. *Toxicol. Int.*, 21(1), 8–17, 2014.
185. Singh, E., Sharma, S., Pareek, A., Dwivedi, J., Yadav, S. and Sharma, S., Phytochemistry, traditional uses and cancer chemopreventive activity of Amla (Phyllanthus emblica): The Sustainer. *J. Appl. Pharmaceut., Sci.*, 2(1), 176–183, 2011.

186 Hebeish, A., El-Naggar, M.E., Fouda, M.M., Ramadan, M.A., Al-Deyab, S.S. and El-Rafie, M.H., Highly effective antibacterial textiles containing green synthesized silver nanoparticles. *Carbohydrate Polym.*, 86(2), 936–940, 2011.

187. Teli, M.D., Sahoo, M.R. and Pandit, P., Antibacterial and UV- Protective Cotton fabric made by Herbal Synthesized Silver Nanoparticles. *Int. Res. J. Eng. Technol.*, 4(1), 1310–1321, 2017.

16

Rot Resistance and Antimicrobial Finish of Cotton Khadi Fabrics

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Abstract

In rising trend of use of eco-friendly chemicals, Cotton Khadi fabric may be treated with eco-friendly anti-microbial agents like Polyethylene Glycol (PEG-200), Potassium salt of Hydroxyl Amino Methyl Siliconate (PHAMS) and citric acid (CA) individually and in their blends as compared to treatment with Epoxy-Propyl-Trimethyl-Ammonium Chloride (EPTAC) in presence of CA and sodium hydrogen phosphate (SHP) as mixed catalyst system by low tensioned padding, drying at 100 °C for 10 minutes, followed by curing at 120 °C for 4 minutes, to investigate the effect of such treatment on key textile related properties and microbial resistance. PEG, PHAMS, and EPTAC have ability to react with –OH groups of cellulose under acidic catalyst to bound to cellulose macromolecules forming ether linkage which produce a modified cationized cotton attaching $-NR_3^+$ groups of EPTAC and $-NHR_2^+$or $-NH_3^+$groups of PHAMS. Treatment with Polyethylene Glycol (PEG 200), Cetrimide and Chitosan individually and in their blends, in presence of same catalyst may also be investigated for the desired effect. It may be observed that treatment with a mixture of Chitosan and PEG (in 1:1 ratio) or by combined treatment of PEG and PHAMS (in 3:1 ratio) shows reasonable rot resistance performance with optimum balance in other textile-related properties. FTIR, XPS, and TGA studies indicate the nature of reaction to support the modifications occur, and the effectiveness of the antimicrobial properties may be assessed by measuring the loss of tensile strength by soil burial test and by testing as per AATCC-100 and AATCC-147 standards.

Keywords: Cellulose, cotton, khadi, rot resistance finish, antimicrobial finish

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16.1 Introduction

Cotton Khadi fabric is an ancient heritage of India and out of 10.98 lakh persons employed in Khadi (hand spun and hand woven) sector in India, approx. 80% are women [1]. With substantially low capital investment, Khadi (hand spun and hand woven) cotton fabrics play a pivotal role in socio-economic empowerment of rural artisans in India. Major advantages of this fabric are its eco-friendliness and hand woven structure. Major disadvantages are lower strength, easy creasing, easy microbial attack, less dimensional stability and often nonuniform dyeing. Tensile strength of such woven cotton Khadi fabric is not only on lower side, but further reduced drastically during the chemical processing, storage and during its use due to washing. Khadi fabric being made of cotton is susceptible to easy microbial attack/rotting if remained in moist and humid condition for a prolonged period. Antimicrobial treatment for Khadi material is necessary to fulfill the objectives of prevention of damages of this textile due to microbial attack, i.e. rotting, cross infection by pathogenic microorganisms, control of infestation by microbes, arresting metabolism in microbes in order to reduce the formation odor, safeguarding this product from staining, discoloration and quality deterioration.

One of the major problems of cotton Khadi fabric is microbial susceptibility and that is again pronounced in finer cotton fabric like muslin as it has low strength and durability. Hence there is an essential need of some antimicrobial and rot resistant finish for such delicate cotton fabric with some specific agent that doesn't cause any/much deterioration of fabric strength and should be eco-friendly too. The degree of activity of the antimicrobial agent is denoted by either biocidal agent that kill microorganisms or bio-static agents that inhibits micro-organisms' growth. The latter is preferred in antimicrobial finish of textiles. There are many reports on antimicrobial finish/rot resistance finish on cotton and lingo-cellulosic fabrics [2–8] available in literature. Antimicrobial finish on cotton fabric has been studied earlier on Chitosan and/or PEG, etc. and recently it has been tried in fine variety of cotton Khadi fabric [4] wherein citric acid (CA) and sodium hydrogen phosphate (SHP) may be used as a mixed catalyst system for treating cotton with PEG and Chitosan with or without use of cetrimide. Antibacterial activities of cotton and polyester/cotton fabrics treated with chitosan or chitosan/DMDHEU have also been investigated earlier [9].

Treatment of cotton Khadi fabric with polyethylene glycol (PEG-200), Cetrimide (a quaternary ammonium compound), Chitosan (a natural amino polysaccharide) individually or in binary mixture may yield the required rot resistance/antimicrobial properties from these agents as single compound or in binary mixture application. Their effectiveness can also be compared with commercially available epoxy-propyl trimethylammonium chloride (EPTAC), an antimicrobial agent. Along with the test performance of rot resistance and antimicrobial activities, the change in other important properties like tenacity, bending length, crease recovery and surface appearance properties should also be investigated. Generally, cellulosic fabrics like cotton and its blends are conventionally treated with some metallic salts (copper sulfate, copper naphthenate) or quaternary ammonium compound like (cetyl trimethyl ammonium bromide, cetrimide or EPTAC, etc.) [10] which are some way or other not fully eco-friendly in nature. But the fabric can't become sufficiently wash fast and has some objectionable smell preventing its use in apparel sector.

Hence, it is imperative to treat such cellulosic fabrics with suitable eco-friendly antimicrobial as well as rot resistant chemicals which also should not impair its dyeability rather in turn facilitate eco-friendly dyeing, if the situation demands. Recent studies on use of flex carding waste as absorbent core and eco-friendly aloe-gel extract on filling mat and service site of sanitary napkin have found to give satisfactory antimicrobial and antifungal potential [11]. Extracts from plants (e.g., aromatic compounds, essential oils, and dyes), antimicrobial peptides (AMPs) and chitosan were also considered among natural-based biocides [12]. Influence of different preparation procedures of polypyrrole (PPy) on action of resulting antibacterial composite against *Escherichia coli*, *Staphylococcus aureus* and *Klebsiella pneumoniae* has been studied recently [13]. Use of state-of-the-art engineering of antimicrobial materials based on the use of nonthermal plasmas at low and atmospheric pressure was also recently studied [14]. *Ocimum sanctum* leaf extract as a natural bioactive agent has been applied on cotton and polyester/cotton blended fabrics for imparting antibacterial properties to the textile product for healthcare applications [15]. Antimicrobial agents and treatments that can be performed to produce antimicrobial textiles, using chemical or physical approaches, which are under development or already commercially available in the form of isolated agents or textile fibers or fabrics have been recently overviewed [16]. Use of microcapsules containing *Psidium guajava* Linn leaf extract for imparting antibacterial property on cotton fabric has been reported earlier [17]. Regenerablity and Stability of Antibacterial Cellulose Containing Triazine N-halamine have been reported earlier and found out to be an attractive candidate for broad range of application fields [18]. Effect of eco-friendly natural coloring matter such as pomegranate, curcumin, cutch, red onion peel and a mixture of red onion peel/curcumin on the cotton, silk and wool fabrics dyed with natural dyes has also been studied earlier for imparting antimicrobial and UV protection properties [19].

But limited and scanty work has been carried out for rot resistance and antimicrobial finishes on finer variety of cotton Khadi fabric and also on Jute fabrics [2–9]. Potassium salt of Hydroxyl Amino Methyl Siliconate (PHAMS) having methyl array on the surface of modified/treated cotton substrate reduces water absorption and thus reduces water imbibition, spalling due to freeze-thaw and efflorescence, hence, increases the life of the cellulosic substrate.

Moreover, PEG, CA, etc. also have been proved to possess a reasonable antimicrobial effect when applied on cellulosic and lingo-cellulosic fiber base/fabrics, as nontoxic antimicrobial agents [2–9]. Use of mixture of citric acid and PEG as rot resistant treatment on jute fabrics where citric acid acts as a cross-linking agent has been earlier reported [8]. There are silicone derivatives also known to be water repellent as well as rot resistant chemical [20]. Focuses on application of the above said selected chemicals individually or in combination on such cotton Khadi fabric in presence of CA+SHP as a catalyst system can also influence the tensile strength, other associated textile related mechanical/surface properties as well as its rot resistance/antimicrobial properties. After application of these chemicals by pad-dry-cure method at specific concentration as well as treatment conditions, the results of above said treatment can also be compared with the results of treatment with commercially available EPTAC.

Treatment of cotton Khadi fabrics with PHAMS (highly water repellent type and not allowing moisture to absorb for growth of microbes), PEG (highly desiccating properties, thermal adoptability and surfactant type preventing attachment of microbes) and citric acid (a cross linker with cellulose for its poly carboxylic nature and thus prevents microbes by forming the cross linking structure of CA) or their mixtures in different ratios in presence of mixture of CA and SHP as catalyst system under heating may expectedly render cellulose with a good level of antimicrobial/rot resistant properties with a balance in other textile related properties. The effectiveness of the antimicrobial properties to be developed by the said treatments may be quantified by measuring the loss of tensile strength by soil burial test for both treated and untreated cotton Khadi fabric and then be compared against a sample treated under same conditions with a commercially available rot resistant chemical like EPTAC. Most of the earlier invented antimicrobial finishes for cellulosic were not eco-friendly and involves objectionable chemical hazards in product stage and in their preparatory/manufacturing stage. To make green processing of cotton Khadi textiles assured, one may apply eco-safe chemicals on such cotton fabrics to impart eco-friendly antimicrobial finish for its application for surgical gown, medical apron, medicate bed linen and other such applications. Another way to fulfill the same objective, Khadi (hand spun and hand-loom woven) cotton fabric can be alternatively treated with eco-friendly antimicrobial agents like Polyethylene Glycol (PEG-200), PHAMS and CA individually and also in their blends, in presence of CA and SHP as mild acidic catalyst system, by low tensioned padding followed by drying at 100 °C for 10 minutes. The fabric may then be cured at 120 °C for 4 minutes in order to observe the effect of such eco-safe chemical treatment/finish on important textile related properties as discussed above. FTIR and TGA studies should also be carried out to understand the nature of chemical changes by such treatments.

The effectiveness of the antimicrobial properties after the said treatments can be assessed by measuring the loss of tensile strength by soil burial test and antimicrobial test as per AATCC-100 and AATCC-147 standards for treated and untreated cotton Khadi fabric sample and may be compared against EPTAC treated sample. The surface appearance properties such as brightness index (BI), yellowness index (YI) and whiteness index (WI) can also be evaluated and compared. XPS study may be carried out for treated and untreated samples to understand the elements present and changes in functional groups/type of chemical interactions, etc. between the fiber (cotton) and the applied chemicals (PEG, PHAMS, Chitosan, etc.). This can be compared with such effects on the same fabrics for a conventional treatment with a quaternary ammonium compound known as EPTAC (2,3-epoxy-propyl trimethyl ammonium chloride) which is prepared from CHPTAC (3-chloro-2-hydroxy-propyl tri methyl ammonium chloride) in presence of alkali or acid (reaction conditions).

Scanning electron micrograms can be carried out for untreated and treated cotton Khadi fabrics to visualize the surface characters.

16.2 Anti Microbial Treatment

Bleached cotton Khadi fabric may be initially treated with 2% aqueous solution by 100% exhaustion by pad-dry-cure process (so that application percentage on weight of the fabric is also 2%) for each of PHAMS, PEG and citric acid in one experiment and Cetrimide, Chitosan, PEG in another experiment and a binary mixture of two such agents in different combinations in presence of mixed catalyst system using CA and sodium di-hydrogen phosphate (SHP) (0.4% on weight of fabric) to investigate their effect on different textile related properties. The pH may be maintained at 5 to 5.5

by addition of sodium acetate and acetic acid as buffer (controlling the pH by soda ash and acetic acid), wherever applicable.

The same bleached cotton (control) Khadi fabrics for both the experiments may be padded in a lab padding mangle with 1.5 kg/cm^2 nip pressure to maintain 100% exhaustion for 2% on weight of fabric application of each of these chemicals individually and also for application of overall 2% on weight mixture of PEG and Cetrimide (1:1 initially), Cetrimide and Chitosan (1:1 initially) and PEG and Chitosan (1:1 initially), PEG and PHAMS (1:1 initially), PHAMS and citric acid (1:1 initially) and PEG and citric acid (1:1 initially) to get 100% wet pick up. It should be followed by drying at 100 °C for 10 minutes and then curing at 140 °C for 4 minutes. The ratio of mixture of chemicals may also be varied at later stage to determine the optimum ratio for use of such mixture to obtain the desired effect. In all the cases, a mixed catalyst (using 0.2% citric acid and 0.2% SHP) system may be used (0.4% on the weight of the fabric) to obtain the better washfast treatment of the selected chemicals on cotton Khadi fabrics.

For comparison of both antimicrobial and rot resistance properties, the control cotton fabric may be additionally padded with a solution of 60 g/l CHPTAC and 24 g/l NaOH (hydrated) mixture (after keeping the mixture for 10 minutes in room temperature) to form EPTAC [21] followed by drying and curing in the same manner described above.

Unless otherwise indicated, all the cured fabrics may be washed thoroughly, dried in air at ambient conditions.

16.3 Some Important Study on Eco-Friendly Antimicrobial Finishing of Cotton Khadi Fabric

16.3.1 Effect on Tensile Properties

Table 16.1 indicates data of tenacity, rot resistance (percentage retention of strength after soil burial test as per IS-1623-1992), dry crease recovery, bending length and surface appearance properties like WI, YI, BI and color strength value (*K/S* value) of untreated bleached cotton Khadi fabric and the same fabric after treatment with single and 1:1 mixture of chitosan, PEG and cetrimide under specific condition of treatment under CA and SHP mixed catalyst (1:1) –1/5th of the treatment agents in g/l system.

The relevant data in Table 16.1 indicate that Cetrimide (a quaternary ammonium compound in amide form) treatment alone or its mixture with Polyethylene glycol –DP 200 (PEG) and/or Chitosan, show some initial loss of strength, which is higher than the corresponding strength loss for

Table 16.1 Effect of treatment with Cetrimide, PEG-200, Chitosan and PEG, PHAMS and their mixtures on properties of cotton Khadi fabric.

Treatment	**Tenacity (cN/tex)**	**Retention of strength after specific treatment (%)**	**% Retention of strength after soil burial of 21 days**	**Dry Crease recovery angle in deg (warp +weft)**	**Bending length (cm)**	**Whiteness index (WI) (CIE scale)**	**Brightness index (BI) (TAPPI-452 scale)**	**Yellowness index (YI) ASTM E 313-00**	***K/S* Value**
Untreated Fabric	1.70	100	52.8	75.99	1.6	69.35	56.91	−0.10	0.526
2% Chitosan	1.37	80.6	70.4	146.5	3.25	73.90	57.87	−2.05	0.672
2% Cetrimide	1.33	78.2	64.0	136.1	1.72	68.37	56.44	0.67	0.423
2% PEG-200	1.54	90.5	73.7	148.2	1.84	75.03	58.52	−2.24	0.553
2% Chitosan+2% PEG-200	1.70	100	98.8	127.8	3.43	71.0	57.03	−0.74	0.632
2% PEG-200+2% Cetrimide	1.49	87.6	66.7	122.5	1.43	67.36	56.49	1.05	0.377
2% Chitosan+2% Cetrimide	1.40	82.3	68.7	148.4	3.31	62.32	54.01	2.73	0.440
2% PHAMS	1.60	94.5	72.0	106.1	1.26	9.97	54.84	23.70	0.301
2% Citric Acid	1.47	86.74	53.0	96.1	1.32	15.62	57.96	22.70	0.251
2% PHAMS+2% PEG-200	1.57	92.7	73.1	102.4	1.34	4.07	49.97	28.21	0.400
2% PEG-200+2% CA	1.36	80.1	64.1	95.9	1.30	12.7	56.1	23.20	2.76
2% PHAMS+2% CA	1.46	86.1	67.4	95	1.23	13.0	56.30	23.32	0.272

the treatment with either PEG or PEG and Chitosan mixture. Chitosan (a natural amino polysaccharide) is crystalline, brittle and less ductile (hard polymer), when treated alone onto fine and high drape soft bleached cotton Khadi fabric followed by pad-dry-curing at 140° for 4 minutes. The Chitosan polymer due to its partial immobility because of its high agglomerated structure, creates a nonuniform application and imparts partial brittleness in the fabric causing higher strength loss, particularly after curing as the Chitosan film dries out to become more hard and brittle. When Chitosan is applied on fabric in presence of CA and SHP as a mixed catalyst, CA may play an important role by chemically interacting with Chitosan. Free carboxylic acid group of citric acid may react with amino group of Chitosan and results in a salt linkage [22] which may then converts to ammonium salt in presence of dilute acid/Lewis acid (SHP acts here as Lewis acid) and hence, the mobility of the Chitosan film may be improved, hardness and brittleness may be reduced and probably a more uniform ductile film is formed over the surface of the cotton Khadi fabric.

Simultaneously, citric acid alone (even though in low percentage) causes ester cross-linking with cotton cellulose in presence of acidic catalyst and hence, impairs cross-linking brittleness and nonuniform rigidity in the structure of cellulose indicating higher strength loss in treated cotton Khadi fabric.

While treatment of cotton Khadi fabric with chitosan and PEG (1:1, 2% each) in presence of 1/5th of CA and SHP shows no strength loss under the same treatment condition, PEG improves flexibility and helps in reducing brittleness of chitosan in its mixture, being a good plasticizer and swelling agent. Although PEG and Chitosan are not highly compatible to each other, there is little chance of intermolecular chemical interaction between them except hydrogen bonding and decrease in the crystallization of Chitosan micro molecule [23] making chitosan more mobile and uniformly distributed along with PEG in a homogeneous manner. In presence of CA and SHP mixed catalyst, formation of ester between PEG and CA may take place, reducing the possibility of cross-linking of CA with cotton cellulose and hence, reduces the crosslinking brittleness, reducing the strength loss of cotton fiber. Thus, a better balance of tensile strength and other properties to a desirable level may be achieved by application of 2% PEG and 2% Chitosan in presence of 1/5th part of CA and SHP under the same condition of treatment. Application of Cetrimide alone or in mixture with either PEG or Chitosan causes yellowing of the fabric to a higher extent after curing, results in both higher strength loss and reduction in rot resistance property. Thus, it may not be considered as a suitable finishing treatment for cotton Khadi fabric.

Amongst 2% PEG, 2% PHAMS and 2% CA treatment separately on cotton Khadi fabrics, CA treatment shows higher strength loss (about 13.2% loss) than PHAMS (5.5% loss) and PEG (9.5% loss) treatments, while the mixture of 2% PHAMS and 2% CA treatment show almost 13.9% drop in tensile strength, mixture of 2% PEG and 2% CA treatment gives 19.9% loss indicating that PEG in presence of CA forms more cross linking brittleness in cotton and loss of strength due to the treatment is higher than the corresponding 2% mixture of each CA and PHAMS. Strength loss in 2% PEG and 2% PHAMS mixture treated fabric is lowest, i.e. around 7.3% which appears to be superior, provided its rot resistance and antimicrobial properties are found satisfactory. Hence, rot resistance properties of all these treatments tested can be arranged in the following order.

2% PEG+2% PHAMS > 2% CA+2% PHAMS > 2% PEG+2% CA

The surface appearance properties and bending/crease recovery properties may also be compared and it may be observed that when CA is present in the mixture of PEG+CA or PHAMS+CA, the CRA is somewhat lower than the corresponding treatment with mixture of PEG and PHAMS. This unexpected result, despite higher cross-linking potential of CA for cellulose may be explained by the fact that some degree of chain scission by CA at 120 °C during curing creates more free acidity, which supports the higher strength loss due to treatments wherein presence of CA was there in the mixture. Due to these said treatments, whiteness and BI of all samples enhances up to a noticeable extent, which however, is less reduced in treatments with any combination, where CA is present due to acidic leaching/salt cleaning of surface by CA itself. Same trend is observed for the BI of the samples. Hence, further experiments (Table 16.2) may be carried out with varying proportion of PEG and PHAMS treatment for finding their suitability.

Rot resistance of treated cotton Khadi fabric in presence of mixed catalyst was measured by soil burial test where the extent of fabric damage by micro-organism is indicated by percentage of strength loss. The fabric treated with mixture of PEG and chitosan with CA and SHP mixed catalyst system performs well followed by PEG, yielding minimum loss of strength in the fabric after 21 days of soil burial, whereas the untreated fabric almost deteriorates in soil burial test and retained only 52.8% tensile strength. Rot resistance property imparted is attributed to chemical modification which converts the cellulose polymer which in turn becomes detrimental to micro-organism. Cross-linking protects from microbial degradation by making cotton Khadi fabric inaccessible to cellulose degradable enzymes. The polycationic character of chitosan immobilize micro-organism and further its protonized amino group blocks the protein sequences of micro-organism, thus inhibits further proliferation. But this method does not create any firm chemical bond between chitosan and cellulose and may not show durability to repeated washing [22]. Hence, PEG being another

Table 16.2 Effect of varying concentration level of Chitosan and PEG for application of mixture of Chitosan and PEG on microbial and other properties Cotton Khadi fabric with CA and SHP as mixed catalyst.

Treatment	Tenacity (cN/tex)	% retention of strength due to treatment	% Retention of strength after soil burial of 21 days	Crease recovery angle in deg (warp +weft)	Bending length in cm	Whiteness index (WI) (CIE scale)	Brightness index (BI) (TAPPI-452 scale)	Yellowness index (YI) ASTM E 313-00	*K/S* Value
Untreated Fabric	1.70	100	52.8	75.99	1.6	69.35	56.91	−1.0	0.526
2% Chitosan+1% PEG	1.54	90.5	88.3	74.5	2.05	70.3	57.71	−0.18	0.451
2% Chitosan+3% PEG	1.35	79.4	80.7	56.5	1.83	74.35	58.91	−1.92	0.440
2% Chitosan+4% PEG	1.71	100.5	86.0	55.2	1.72	74.2	58.24	−1.93	0.491
2% PEG+1% Chitosan	1.57	92.3	81.9	55.1	1.63	76.1	58.57	−2.83	0.50
2% PEG+3% Chitosan	1.62	95.3	59.7	73.1	1.81	70.1	56.84	−0.32	0.479
2% PEG+4% Chitosan	1.51	88.8	66.1	76.2	2.10	76.48	59.27	−2.60	0.457
1% PHAMS+1% PEG	1.48	87.0	68.7	107.3	1.31	9.5	54.13	23.2	0.284
1% PHAMS+2% PEG	1.43	84.1	66	108.2	1.30	9.3	54.27	23.92	0.307
2% PHAMS+1% PEG	1.48	87.0	61.7	109.3	1.28	9.79	54.75	23.7	0.301
2% PHAMS+4% PEG-200	1.46	85.8	71.0	53.1	1.32	1.61	52.61	26.85	0.354
2% PHAMS+6% PEG	1.60	94.1	78.9	54.1	1.33	0.92	51.30	26.56	0.373
2% PHAMS+8% PEG	1.43	84.11	71.0	58.6	1.36	3.67	52.63	26.07	0.345
2% PEG+4% PHAMS	1.53	90.0	75.2	52.2	1.31	−0.509	50.17	29.15	0.408
2% PEG+6% PHAMS	1.38	81.1	71.0	53.8	1.30	−15.15	47.15	32.55	0.492
2% PEG+8% PHAMS	1.44	84.7	71.0	55.5	1.29	6.47	54.69	25.81	0.312
4%PEG+4%PHAMS	1.58	92.9	76.5	54.2	1.33	0.34	48.7	28.7	0.47

good antimicrobial agent has been admixed with Chitosan in presence of CA and SHP as a mixed catalyst system so that it can react with cotton and impart additional rot resistance properties. Due to intermolecular interaction between chitosan and PEG by Hydrogen bonding, the fabric becomes wash-fast to some extent. PEG acts as an antimicrobial agent in three ways, i.e. i) thermal adaptability of the treated fabric in a unique way because of latent heat provided by the mount polyols (Reaction Scheme 2) and hence, many other related properties may improve as well [22]; ii) highly hydrophilic properties of PEG desiccate microbes by depriving them of moisture and iii) its surfactant nature prevents the bacteria or fungi from becoming attached permanently. In presence of citric acid, the carboxylate group of citric acid and OH group of chitosan may form ester and carboxylate group of citric acid reacts with amino group of chitosan forming salt linkage, which converts hard and stiff chitosan to become more ductile, mobile and easy flow less crystalline chitosan micro molecules, relatively easier to spread and its polycationic character imparts better rot resistance properties.

The fabric treated with mixture of PEG and PHAMS results are shown in Table 16.2. The results in Table 16.2 indicate that with increase of PEG content in the mixture of PEG and PHAMS, the retention of tenacity values after soil burial test increases and highest tenacity retention value is obtained either by 4% PHAMS and 4% PEG (tenacity retention 76.3%) or 2% PHAMS and 6% PEG (tenacity retention 78.7%). Only Citric acid or combination of Citric acid with either Polyethylene Glycol (PEG-200), and/or Potassium salt of Hydroxyl Amino Methyl Siliconate (PHAMS) have not shown desirable resistance to microbial attack though invariably it is better than the untreated cotton fabric. The possible reactions for these chemicals on cotton (cellulose) may be depicted as reaction Schemes 1 to 10.

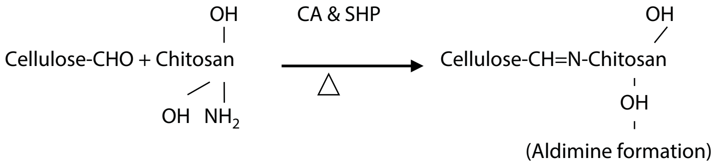
The mixture of PHAMS and PEG with 3:1 ratio (i.e. 6% PEG and 2% PHAMS) also yields the comparable strength of the fabric as addition of such a low mol wt PEG causes less phase separation with compared to higher mol wt PEG and with higher number of terminal hydroxyl groups per unit mass expected to interact more intensely due to higher extent of hydrogen bonding with PHAMS by adduct formation as suggested in the Reaction Scheme 10.

16.3.2 Reaction Scheme

The possible reaction Schemes (1 to 10) for chemical interaction amongst/between cellulose of Cotton and antimicrobial agents and additives taken are shown below to understand the true interaction there.

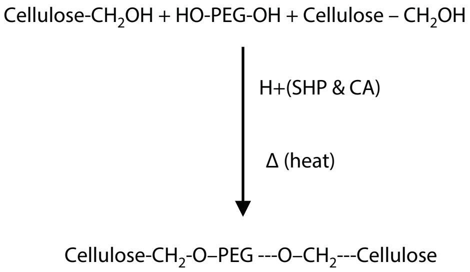
Reaction Scheme 1

OH CA & SHP OH



(Aldimine Formation)

Reaction Scheme 2

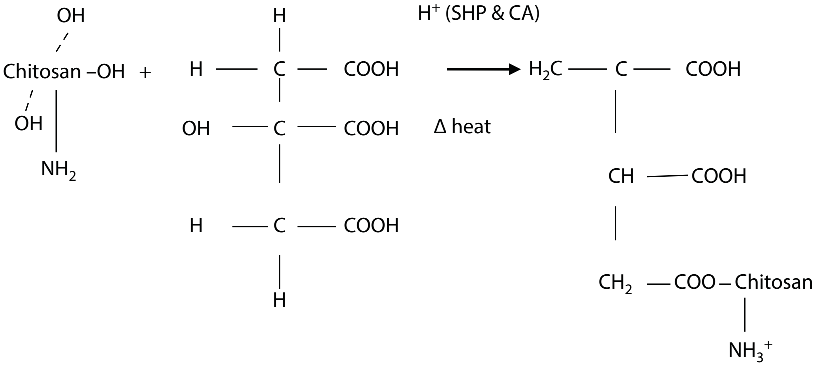


$$\text{Cellulose-CH}_2\text{OH} + \text{HO-PEG-OH} + \text{Cellulose} - \text{CH}_2\text{OH} \xrightarrow[\Delta\ \text{(heat)}]{\text{H+(SHP \& CA)}} \text{Cellulose-CH}_2\text{-O–PEG ---O–CH}_2\text{---Cellulose}$$

(Cross linking of cotton cellulose with PEG)

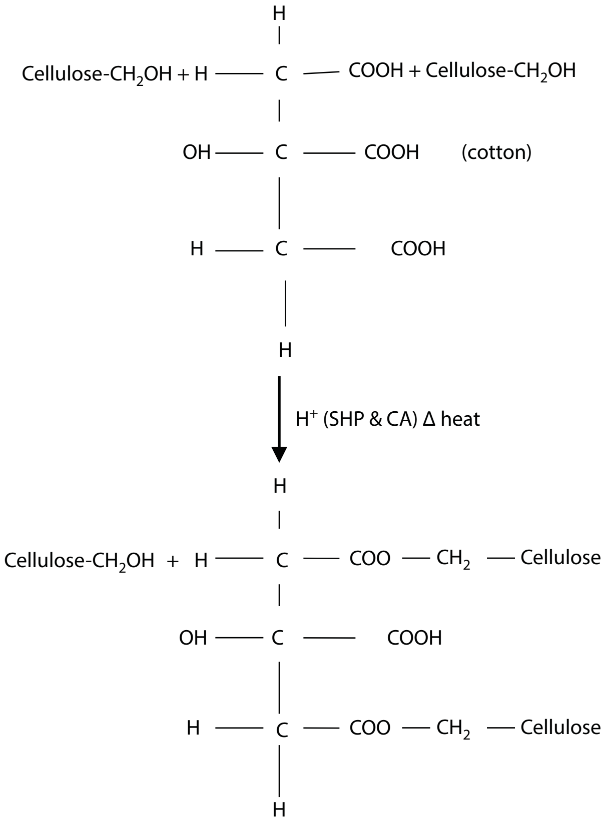
Reaction Scheme 3

OH H H$^+$ (SHP &CA)



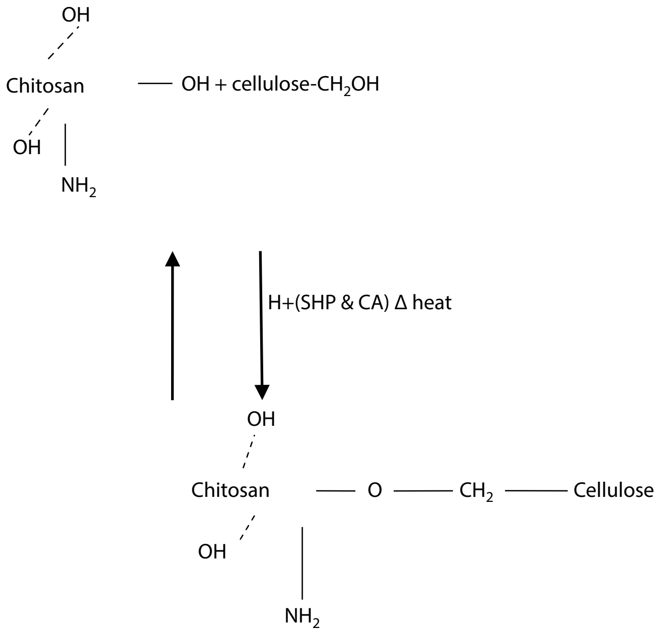
(Chitosan reacts with CA forming cationized chitosan)

Reaction Scheme 4



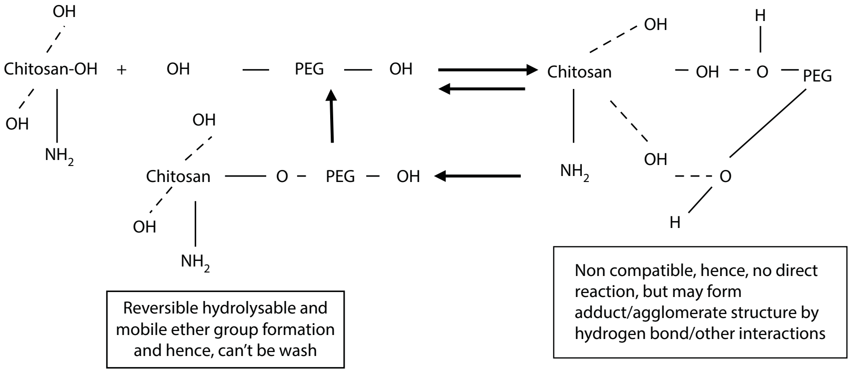
(Cross linking of cotton with critic acid)

Reaction Scheme 5



(Formation of mobile/hydrolysable ether group which may not make it wash fast)

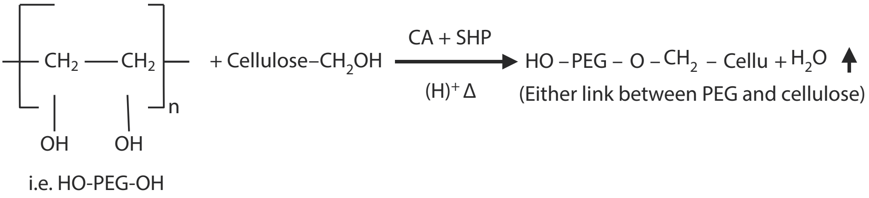
Reaction Scheme 6



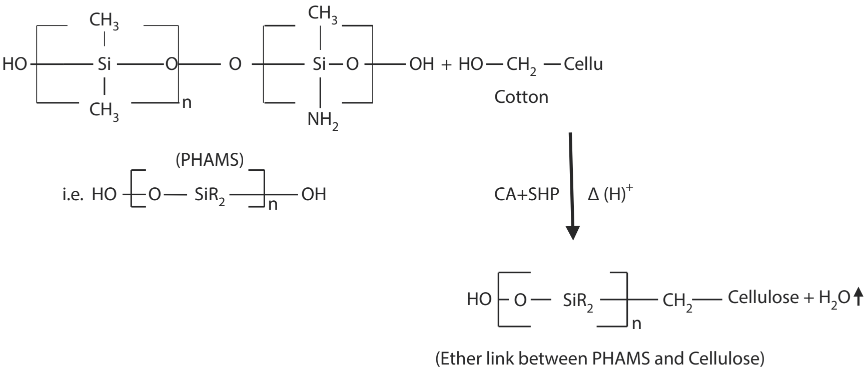
Reversible hydrolysable and mobile ether group formation and hence, can't be wash

Non compatible, hence, no direct reaction, but may form adduct/agglomerate structure by hydrogen bond/other interactions

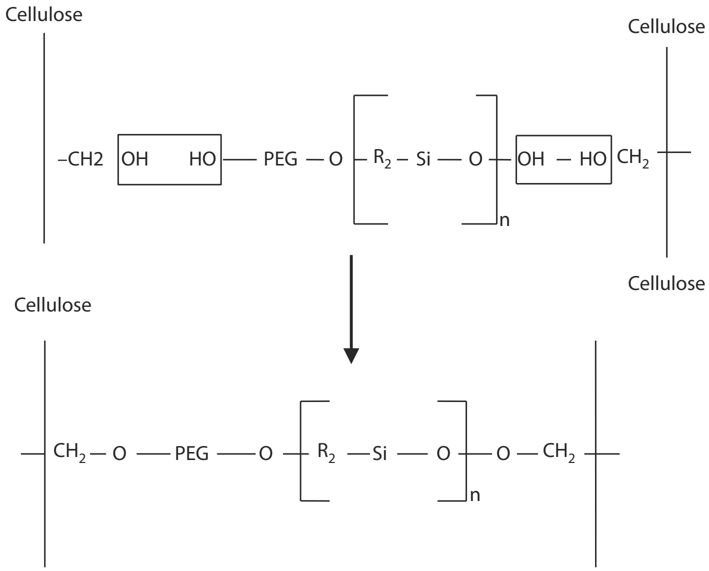
Reaction Scheme 7



Reaction Scheme 8

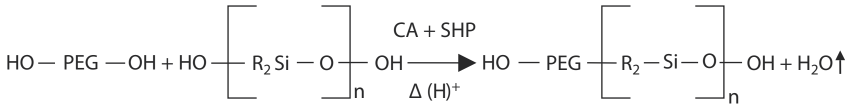


Reaction Scheme 9



(Cross Linking of Cotton with adduct of PEG+PHAMS)

Reaction Scheme 10



$$HO-PEG-OH + HO-\left[R_2Si-O\right]_n-OH \xrightarrow[\Delta\ (H)^+]{CA + SHP} HO-PEG-\left[R_2-Si-O\right]_n-OH + H_2O\uparrow$$

(Adduct of PEG + PHAMS)

(Adduct of PEG and PHAMS)

The Reaction Schemes 1 to 6 for fabric treated with PEG and Chitosan are supported by the C1s, N1s and O1s XPS [23], where the presence of C–N, C=O, C=N and COOH groups are evident in C1s as depicted in Figure 16.1 for derivatized cotton Khadi fabric treated with PEG and mixture of PEG and Chitosan under CA and SHP mixed catalyst system. The peak of 287.7 eV (C=O) of control fabric (a) has been shifted to 282.5 eV in treated fabric with lesser intensity indicates the presence of Si–C in PHAMS and

PEG-treated fabric as in Figure 16.1 (d) which supports Reaction Schemes 7 to 10. The presence of COOH group may be observed at 289.3 binding energy (eV) of C1s in case of both PEG treated and fabric treated with mixture of Chitosan and PEG as shown in Figure 16.1 (b) and (c). The presence of NH_3^+ group may be observed in N1s in Figure 16.2 (a), (b), and (c) for the control fabric, fabric treated with 2% PEG and fabric treated with mixture of PEG and Chitosan at 400.9 binding energy (eV) due to cationization, although the intensity of the peak is lesser in case of Figure 16.2 (a) and (b) due to presence of lesser inherent nitrogen content in control and 2% PEG-treated fabric. The additional peaks at 406.8 and 407.7 binding energy (eV) in Figure 16.2 (c) may be attributed to formation of nitrates (NO_3^-) due to oxidation of ammonia [24] in the case of fabric treated mixture of PEG and Chitosan. The peak at 533.7 binding energy (eV) in O1s is attributed to formation of ester in 2% PEG-treated fabric as shown in Figure 16.3 (b). In Figure 16.3 (c) and (a) in case of the peaks at 533.2 and 533.4 binding energy (eV) of fabric treated with mixture of PEG and Chitosan and control sample respectively, the binding energy for both of them drops down from very oxygen and hydrogen covalent bond in neutral water (534 eV)

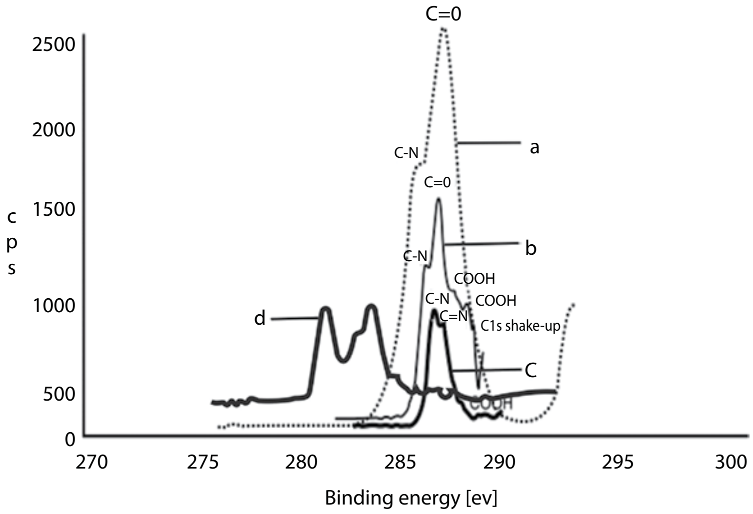


Figure 16.1 XP C1s of (a) control fabric, (b) fabric treated with 2% PEG under CA and SHP mixed catalyst system, (c) fabric treated with 2% PEG and 2% Chitosan mixture under CA and SHP mixed catalyst system, and (d) fabric treated with PEG and PHAMS under CA+SHP catalyst.

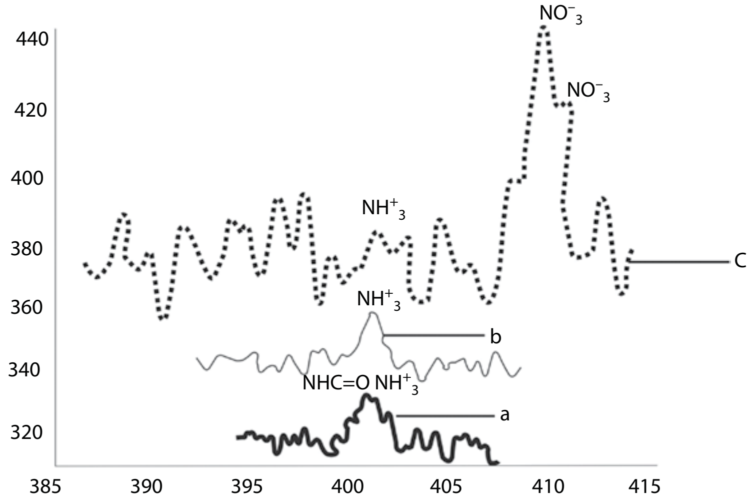


Figure 16.2 XP N1s of (a) control fabric, (b) fabric treated with 2% PEG under CA and SHP mixed Catalyst system, and (c) fabric treated with 2% PEG and Chitosan under CA and SHP mixed catalyst system.

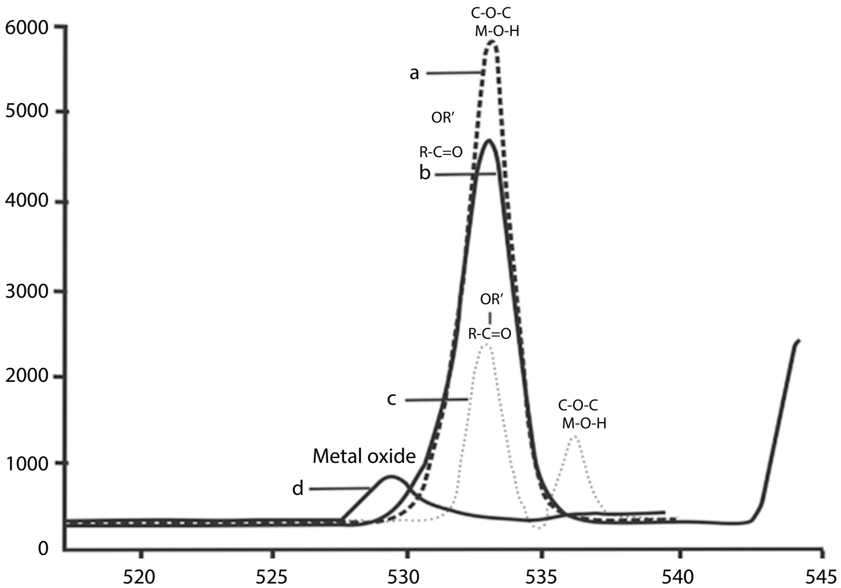


Figure 16.3 XP O1s of (a) control fabric (b) fabric treated with 2% PEG under CA and SHP mixed Catalyst system and (c) fabric treated with 2% PEG and Chitosan under CA and SHP mixed catalyst system, and (d) fabric treated with 6% PEG and 2% PHAMS under CA+SHP Catalyst.

and may be attributed to alcohol (C–O–H) and mixed metal hydroxides (M–O–H) due to presence of various metals in the chemical processing water [25]. A peak at 529.5 eV in PEG and PHAMS treated fabric in O1s (Figure 16.3 (d)) is due to metal oxides formed with Si and K elements supporting Reaction Schemes 7 to 10.

The quantification data for both derivatized and un-derivatized sample for fabric treated with mixture of PEG and PHAMS has been depicted in Table 16.3.

16.3.3 Crease Recovery and Stiffness

It is observed from the relevant data in Table 16.1 that CR value of untreated cotton Khadi fabric which is around 76° (warp+weft) has improved to 146.5° and 148.2° by application of 2% chitosan, 2% PEG alone respectively with the presence of CA and SHP mixed catalyst. The improvement of crease recovery for chitosan is believed to be due to its inherent stiff character film produced on cotton Khadi fabric as well as some degree of cross-linking between cellulose and polyol and/or with citric acid. But with the use of mixture of chitosan and PEG, improvement of crease recovery is found to be reduced to some extent due to less cross-linking between cellulose and PEG or cellulose and citric acid. This may be attributed to consumption of part polyol and part citric acid by chemical interaction with chitosan and thus they are less available to the cellulose. However, higher amount of polyol (more than 2% not reported here) produces more incompatibility between PEG and Chitosan, hence, the effect of individual component is reduced. The same trend is true for application of cetrimide alone in presence of CA and SHP mixed catalyst or cetrimide with mixture of PEG and Chitosan separately.

The bending length of treated cotton Khadi fabric increases, with addition of chitosan alone or in mixture due to its inherent stiffness. Application of PEG, a very soft hydrophilic plasticizing material reduces the stiffness by imparting its ductile and pliable feel on the surface of the cotton Khadi fabric. Cetrimide being a mid between the two chemicals (chitosan and PEG) in nature, indicates moderate results. However, this must be mentioned here that the elegant look and feel of the fabric may be changed to a stiffer transparent cotton Khadi fabric which appears to be more attractive and useful for some other purposes which was missing in such a fabric. Somewhat reduction in drape is converted to an advantageous stiffer fabric of unique nature, which may find application in newer area like smart apron, transparent cover design of readymade garments, fancy stiff skirts, etc.

Table 16.3 Derivatization of the functional elements present in the treated and control cotton Khadi fabric by area percentage.

Sample/Peak	**C1s**							**O1s**											**Si 2p**					**K 2p**				
	Position BE (eV)	**FWHM (eV)**	**Raw area (cps eV)**	**RSF**	**Atomic Mass**	**Atomic Conc%**	**Mass conc%**	**Position BE (eV)**	**FWHM(eV)**	**Raw area (cps eV)**	**RSF**	**Atomic mass**	**Atomic conc%**	**Mass Conc%**	**Position BE (eV)**	**FWHM (eV)**	**Raw area (cps eV)**	**RSF**	**Atomic mass**	**Atomic conc%**	**Mass conc%**	**Position BE (eV)**	**FWHM (eV)**	**Raw area (cps eV)**	**RSF**	**Atomic mass**	**Atomic conc%**	**Mass conc%**
Underivatized (control fabric)	284.0	4.780	117181.4	0.278	12.011	74.4	67.79	530.0	4.416	111618.4	0.780	15.999	24.63	29.9	100.0	4.276	1260.4	0.328	28.086	0.67	1.43	294.0	4.271	2468.1	1.466	39.102	0.30	0.88
Derivatized (2% PEG+2% PHAMS treated fabric)	282.5	5.211	54662.9	0.278	12.011	54.06	45.01	529.5	4.906	119998.2	0.780	15.999	41.26	45.76	99.5	4.263	5439.4	0.328	28.086	4.51	8.79	293.5	4.998	884.4	1.466	39.102	0.17	0.45

16.3.4 Appearance Properties

YI is highest with treatment of Cetrimide and Chitosan as shown in Table 16.1, whereas in case of PEG-treated fabric, it is lower as compared to normal bleached cotton Khadi fabric. Even if in case of Chitosan, YI is reduced, but when combined with cetrimide, the grey color of catalyst (citric acid) may be responsible for increasing the YI of the fabric along with the formation of cellulose polyamide.

PEG being a good humectants, increase the rate and extent of moisture absorption, reduces the formation of unsaturated acids, improved the whiteness property of the fabric. The WI of PEG-treated fabric is at maximum which is followed by Chitosan and it is minimum with mixture of Chitosan and Cetrimide which may be attributed to addition of grey color catalyst (CA), which varies proportionately on the weight of the chemicals and causes formation of cellulose polyamide.

Brightness index of the PEG-treated fabric is maximum and it is minimum in case of mixture of chitosan and Cetrimide due to addition of grey color cross-linking agent (citric acid and simultaneously formation of cellulose polyamide.

16.4 Effect of Varying Concentration Level of Chitosan and PEG for Application of Mixture of Chitosan and PEG on Microbial and Other Properties of Cotton Khadi Fabric with CA and SHP as Mixed Catalyst and Their Optimization

The changes in rot resistance, crease resistance and related textile properties of cotton Khadi fabrics after treatment with varying concentrations of polyethylene glycol 200 in combination with chitosan in varying amount (both 2% to 4%) have been assessed and shown in Table 16.2.

Relevant data in Table 16.2 indicate that with varying proportion of chitosan and PEG blends (from 1:1, 1:1.5, 1:2 to 2:1), if the PEG content is increased from 1% to 2%, the other textile related properties mainly tenacity, CR, bending length and surface appearance in terms of WI and BI are better balanced with improvement in rot resistance properties, while in case of PEG above 2% (up to 4%) does not proportionately improve all these properties, rather impairs a few of them. This may be due to the fact that higher amount of PEG causing more hydrogen bonding interaction with chitosan restrains the movement of chitosan molecule and its immobility is increased causing the above impairing effect [26]. Addition of more PEG in proportionate to chitosan creates more elongated porous structure which ultimately result in a weak membrane causing some drop in tenacity values.

It has been found that the coated membrane on the fabric exhibit larger pore size and higher porous structure as the PEG content in Chitosan increases [27]. This may be attributed to the poor interaction of PEG with the Chitosan chains. As a matter of fact, the observed diminishing porous morphology in PEG added membrane may be the reflection of the limited interaction of these two components in the blended matrix. Based on the interaction of PEG with Chitosan along with the generated morphology as well as the porosity, it may be proposed that 2% PEG and 2% Chitosan is found to be most suitable for ensuring overall balance amongst the rot resistance properties and other textile-related properties of cotton Khadi fabrics in presence of 1/5th of CA and SHP mixed catalyst under specific conditions on treatment by pad-dry-cure method.

Moreover increase of chitosan from 1% to 2% is found to be advantageous, but increase of above 2% chitosan keeping PEG % same, impairs the overall balance in the property parameters of the treated cotton Khadi fabric. Chitosan has a strong stiff backbone with partly crystalline along with rigid amorphous phase with its heterocyclic units, hence, its further enhancement causes nonuniform agglomerated distribution of its film over cotton fabric surface imparting more nonuniformity and stiffness with no further improvement in rot resistance properties.

It is here mentioned that not only the stiff chitosan chain inhibits the crystallization of PEG, but also the more hydrogen bond interaction between chitosan and PEG restrains the movement of chitosan molecules and even partially reduces the original crystalline size of chitosan, which consequently reduces overall crystallization of the chitosan and PEG upon blending [27].

Addition of PEG to Chitosan reduces the bending length depending upon the amount of PEG content. The higher the PEG content in the Chitosan-PEG blend, the lower may be the bending length, which could be understood from the plasticizing effect of PEG component in the membrane. Being a rigid molecule, the coating of Chitosan may introduce a high level of rigidity in the cotton fabric. But, once PEG is added to Chitosan, the plasticization of the Chitosan chains by PEG molecules takes place which may be reflected as the development of a flexible structure. As the PEG content increases, more flexibility is introduced and it leads to reduction of the bending length values. The glycols are well known for imparting plasticization effect in the hydrogels and this is why, glycerine has been observed to introduce plasticization in Chitosan-based hydrogels [28].

Dry crease recovery angle (DCRA) value (W+F) is found to be slowly increased with further increase in chitosan to PEG ratio and finally reaches a level almost equal to normal (control) fabric. It is observed that while Chitosan increases both WI and BI of the bleached treated cotton Khadi fabric and enhancing the percentage of Cetrimide decreases these appearance properties in the fabric. On the other hand, with increase in chitosan percentage, all these mentioned aesthetic properties get enhanced.

The YI of the fabric increases with increase in percentage of Cetrimide making the fabric more yellowish and it reduces with increase in percentage of Chitosan. Cetrimide being amide in nature may form more cellulose polyamide turning the fabric yellowish. Table 16.4 shows the qualitative antimicrobial test results indicating bacteriostic activity on the cotton Khadi fabric.

It may be mentioned that AATCC 147 is a qualitative test to detect antibacterial activity of diffusible antimicrobial agents on treated textile materials. This is a widely used method for initial screening of bacteriostatic activity shown by different antimicrobial agents applied on textile materials. As mentioned in the Test standard, this method is not suitable for materials which tend to encapsulate and prevent the diffusion of the antibacterial agent.

Absence of presence of growth of bacteria under specimen with no zone of inhibition indicates a bacteriostatic activity whereas absence of growth of bacteria under specimen with presence of zone of inhibition shows a diffusible antimicrobial activity.

Table 16.5 shows the antimicrobial properties of four types of fabrics against two common microbes presents in the air and moisture wherein the PHAMS and PEG mixtures shows comparable protection of the fabric against the microbes when compared with EPTAC. After 24 hours of incubation the reduction in microbes is depicted in Figure 16.4. The data in Table 16.6 indicates that increase in PEG content is enhancing the bacteria reduction percentage whereas PHAMS content above 2% has no significant impact on the same. Increasing the content of PEG although, retains at par antimicrobial property, but it does not contribute substantially for tenacity retention% after soil burial in the said cotton fabric as shown in Table 16.2 earlier.

Table 16.4 Observation of presence of bacteria after 24 hours of Incubation as per AATCC 147-2011 standard.

	Staphylococcus aureus **ATCC 6538**			***Klebsiella pneumonia*** **ATCC 4352**		
Sample	**Growth under specimen**	**Zone of inhibition**	**Zone of inhibition (mm)**	**Growth under specimen**	**Zone of inhibition**	**Zone of inhibition (mm)**
Untreated Fabric	Present	Absent	Nil	Present	Absent	Nil
Treated with 2% Chitosan	Absent	Absent	Nil	Absent	Absent	Nil
Treated with 2% PEG	Absent	Present	2	Absent	Absent	Nil
Treated with 2% PEG+2% Chitosan	Absent	Absent	Nil	Absent	Absent	Nil
Treated with 2% PEG and 2% Cetrimide	Absent	Present	4.7	Absent	Present	2
Treated with 6% PEG +2% PHAMS	Absent	Absent	Nil	Absent	Absent	Nil

Table 16.5 Bacteria reduction percentage of treated Khadi fabric after 24 hours of test culture in the incubation conditions at 37 °C for 24 hours as per AATCC 100-2012 standard.

	Bacteria reduction % after 24 hours of test culture	
Khadi Fabric Treated with	*Klebsiella pneumonia* **ATCC4352**	*Staphylococcus aureus* **ATCC 6538**
2%PEG	90.28	89.8
2% PEG and 2% Chitosan (mixture)	92.32	90.5
2% EPTAC	99.58	99.7
6% PEG and 2% PHAMS (mixture)	97.5	99.2

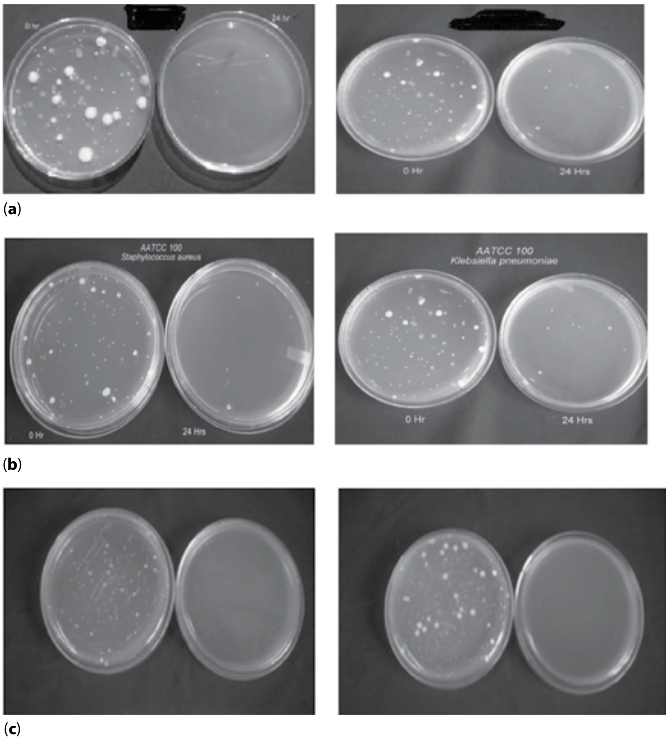

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Figure 16.4 Presence of two microbes *Staphylococcus aureus* and *Klebsiella pneumoniae* after 24 hours of incubation for (a) fabric treated with 2% Chitosan and 2% PEG (under CA and SHP catalyst), (b) fabric treated with 2% EPTAC, and (c) fabric treated with 2% PHAMS and 6% PEG.

Table 16.6 Bacteria reduction percentage of treated Khadi fabric after 24 hours of test culture in the incubation condition of 37 °C for 24 hours.

	Bacteria reduction percentage after 24 hours of test culture	
Khadi fabric treated with	***Klebsiella pneumoniae* ATCC 4352**	***Staphylococcus aureus* ATCC 6538**
2% EPTAC	99.58	99.7
2 % PEG+4 % PHAMS	98.1	97.1
2 % PEG+6 % PHAMS	98.2	85.2
2 % PEG+8 % PHAMS	87.2	95.5
4 % PEG+2 % PHAMS	95.3	92.4
6 % PEG+2 % PHAMS	97.5	99.2
8 % PEG+2 % PHAMS	99.1	99.2
4 % PEG+4 % PHAMS	99.1	97.3
1 % PEG+1 % PHAMS	75.3	80.0
2 % PEG+1 % PHAMS	83.3	80.4
2 % PHAMS+1 % PEG	70.7	75.3
2% PEG+2% PHAMS	83.7	80.2

16.5 Characterization of Control and Treated Cotton Fabrics by FTIR, TGA, and X-RD Analysis

The geometry and microstructure of the treated cellulose fibers may be observed by SEM and their particles disposition on the fiber surface. FTIR, XRD, and TGA may be used to characterize changes to chemical functionality. Particular emphasis should be given to the physical and chemical characterization of these treated cellulose fibers together with their thermal stability and crystallinity, in order to develop their suitability.

16.5.1 Analysis of FTIR Spectra for Untreated and Treated Cotton Khadi Fabric with PEG and its Mixture

Table 16.7 for FTIR spectra indicate all the common specific peaks/trough positions of FTIR spectra (a, b, and c in Figure 16.5) for untreated and

Table 16.7 FTIR Spectra of Cotton Showing Common Specific Peaks/Trough.

FTIR peak position (cm^{-1})	**Assignment of reasons for specific peak positions**
~3335–3337	ν(OH) (free) stretching
~2900–2917	ν(C–H) stretching
~2850	ν(CH_2) symmetrical stretching
~1735	ν(C=O) ester group vibration
~1635	adsorbed water/moisture
~1595	ν(C=C) aromatic in-plane stretching
~1505	ν(C=C) aromatic in-plane stretching
~1475	δ(CH_2) scissoring
~1455	δ(C–H); δ(C-OH) primary and secondary alcohol
~1420	δ(C–H) stretching
~1365	δ(C–H) stretching
~1335	δ(CH_2) wagging
~1315	δ(C–H) stretching
~1280	δ(CH_2) twisting
~1235	δ(C–OH) out-of-plane bending
~1200	δ(C–OH); δ (C–CH) stretching
~1155	ν(C–C) ring breathing, asymmetric
~1105	ν(C–O–C) glycosidic vibration
~1050	ν(C–OH) secondary alcohol stretching
~1025	ν(C–OH) primary alcohol stretching
~1005	ρ(–CH–) stretching
~985	ρ(–CH–) stretching
~895	ν(C–O–C) in plane, symmetric vibration

treated cotton fabric for specific FTIR-spectra band stretching/vibration of groups/twisting/swigging/wagging, etc. of cellulose molecule as a major constituent.

However, these common FTIR Spectra of four cotton Khadi fabrics reveals the stretching of OH groups usually occurs at 3336 to 3337 cm^{-1}. At 2901 to 2917 cm^{-1} stretching of C–H bond occurs making the presence of alkanes in cotton cellulose while the only difference found for cotton fabric treated with blend of Chitosan and PEG as shown in FTIR spectrum (d), in Figure 16.5 is the broadening of the peak at 1640 cm^{-1}, which is usually for absorbed moisture at 1635cm^{-1}. So the broadening of the FTIR peak at 1635 to 1640 cm^{-1} for FTIR spectrum may be explained by probable incorporation of amide group by reaction of Chitosan and cellulose by some interactions and that amide band is causing broadening of peak at 1640 cm^{-1} (1640 cm^{-1} is the vibrational stretching for amide group). So the FTIR spectrum (d) in Figure 16.5 at 1640 wave number has become more pronounced and the decrease in transmittance values indicates that an attractive intermolecular interaction of chitosan with PEG and cellulose have been ascribed to a strong possibility either through hydrogen bonding or ether bonding as shown in reaction Schemes 5 and 6. FTIR spectra of control fabric show peak at 3334 cm^{-1} for both (a) and (b) spectra is absorption of moisture. Peak at 855 cm^{-1} for fabric treated with mixture of PEG and PHAMS (b), shows Si–O–Si vibrations (for anchored PHAMS) which is absent at spectra (a) for control cotton. The broader peaks at 1000 to 1100 cm^{-1} in treated cotton (b) is attributed to –C–O–C– deformation and stretching confirming Reaction Schemes 7 and 8, which is absent in Spectra (a) for

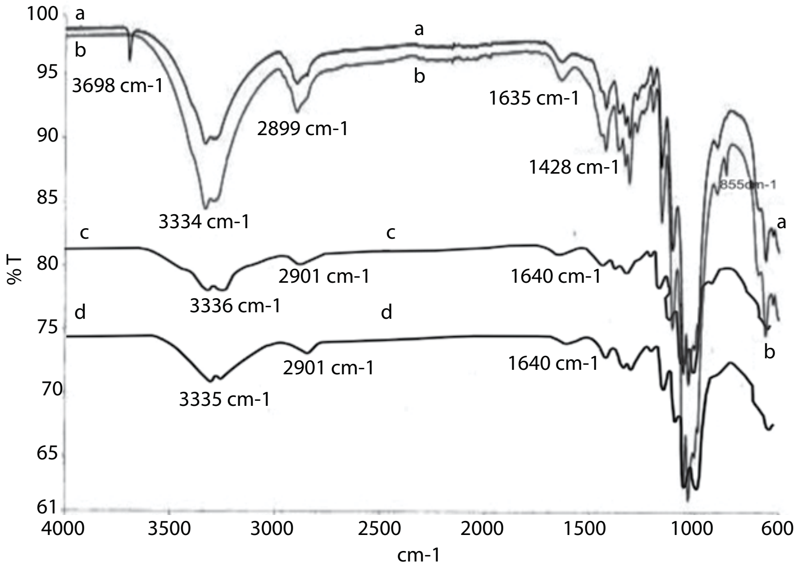

Figure 16.5 FTIR spectra of (a) untreated cotton, (b) cotton treated with mixture of 6% PEG and 2% PHAMS, (c) cotton treated with 2% PEG, and (d) cotton treated with mixture of 2% PEG and 2% Chitosan.

control fabric. A small and sharp peak of phenolic –OH of cellulose may be observed in Spectra (a) at 3698 cm^{-1} which vanished after treatment with PEG and PHAMS mixture on cotton (treated cotton) spectrum (b), possibly due to participation of fewer Secondary-hydroxyl (Phenolic –OH) in the reaction with PEG and PHAMS, beside Primary alcohol –(CH_2OH)– of cellulose (cotton).

16.5.2 Characterization of Thermal Stability of the Control and Treated Fabric

The thermo gravimetric analysis (TGA) of three types of cotton Khadi fabric shows that (A) untreated cotton Khadi fabric, (B) treated fabric with 2% PEG and 2% Chitosan and (C) treated with a blend of 6% PEG and 2% PHAMS show the thermal decomposition pattern of the materials similar TGA diagram as shown in Figure 16.6. At 500 °C the untreated fabric show leftover residue 13.5% and there is no change of thermal stability of the 2% Chitosan and 2% PEG-treated cotton fabric showing the same residue left at 500 °C, while the 6% PEG and 2% PHAMS treated fabric shows the residue leftover of 11.5%. However, this change is not that much significant. A list of residue left over at different temperature of heating stages at 40 °C to 500 °C increased at the rate of 10 °C per minute is given in Table 16.8.

TGA derivative curve/thermogram (as shown in Figure 16.7) show the only peak of thermal dissociation of cellulose molecules of cotton from 361

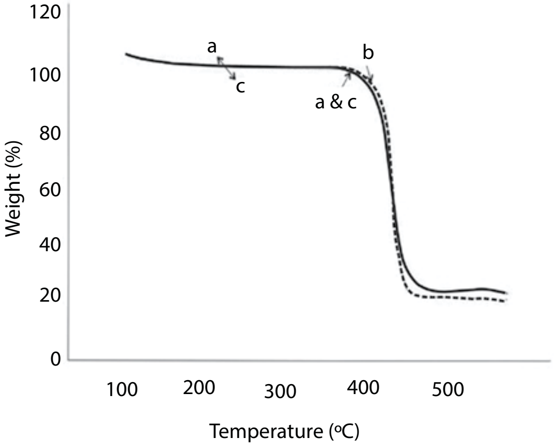

Figure 16.6 TGA diagram of (a), control fabric (b), fabric treated with mixture of 6% PEG and 2% PHAMS, and (c) fabric treated with 2% PEG and 2% Chitosan.

to 366 °C having almost no change in DSC pattern amongst the untreated and treated cotton Khadi fabrics.

Thus, it is proved that these treatments don't impair the thermal stability of the cotton Khadi fabric.

Table 16.8 Residue leftover at different stages of temperature for treated and untreated Khadi fabric.

Untreated fabric		**Treated with 2% PEG+2% chitosan**		**Treated with 6% PEG+2% PHAMS**	
Temperature (°C)	**Weight (%)**	**Temperature (°C)**	**Weight (%)**	**Temperature (°C)**	**Weight (%)**
40	98.17	40	98.19	40	98.08
100	95.06	100	94.67	100	94.49
200	94.95	200	94.56	200	94.3
300	91.66	300	91.66	300	91.96
360	52.59	360	52.58	360	48.06
400	16.17	400	16.48	400	13.75
500	13.58	500	13.56	500	11.55

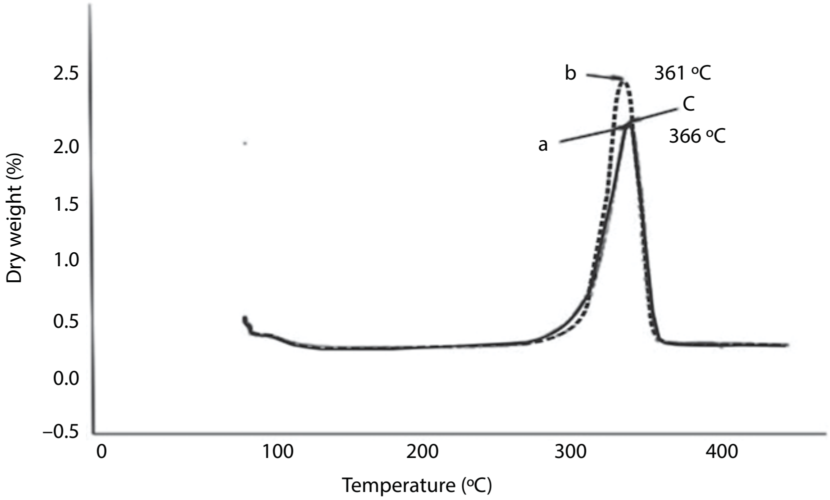

Figure 16.7 TGA derivative of (a) control fabric, (b) fabric treated with mixture of 2% PEG and 6% PHAMS, and (c) fabric treated with mixture 2% PEG and 2% Chitosan.

16.5.3 X-Ray Diffraction of Untreated and Treated Fabrics with CA and SHP as Catalyst

Data in Table 16.9 indicate that there is no change in crystallinity % between treated and control fiber, however the size of the crystallite blocks has reduced to some extent which may be assumed due to induced swelling effect disrupting crystal orientation integrity and breaking of the bigger crystals that is rearranged after the treatment is over, on drying, without alteration of total crystallinity.

The X-ray diffraction results indicate that fiber crystallinity and orientation has little effect on the treated cotton Khadi fabric strength. On the other hand, the PEG film may be spreading uniformly on the fabric surface thereby making a plastic coating covering up the nonuniform weaving of handspun yarn and ultimately results in better sharing of load among the yarns of the fabric which is unlikely in a uniform woven cotton fabric of regular count. As seen in the cross-section view in Figure 16.8, swelling of yarn occurs which may result in increasing the cover factor of the fabric resisting the yarn slippage. The mixture of chitosan and PEG with 50:50 ratio yields the comparable strength of the fabric due to addition of such a low mol wt PEG (DP:200) which causes less phase separation as compared to higher mol wt PEG. With higher number of terminal hydroxyl groups per unit mass may be expected to interact more intensely due to higher extent of hydrogen bonding with chitosan as seen in FTIR spectrum. Further, due to presence of stiff chitosan chains, the brittleness of binding film increases the stiffness of the fabric, which on the other hand resists the applied load as observed from maximum bending length value (Table 16.1). Table 16.9 indicates that there is marginal increase in crystallinity% due to presence

Table 16.9 Crystallinity and orientation values of treated and untreated cotton Khadi fabric.

Sample	Crystallinity Index (%)	Crystallite Size (°A)	Orientation at 2θ (°)
Control fabric	72	53.41	26.62
(2% PEG-treated fabric)	73	46.26	25.12
6% PEG+2% PHAMS	73.58	44.49	24.93
(2% PEG+2% Chitosan treated fabric)	72.64	46.28	27.65
2% EPTAC treated fabric	78.78	57.87	21.02

of crystallite part of small amount of PHAMS film developed and anchored by cellulose in (6% PEG and 2% PHAMS treated fabric).

16.6 Study of Residual Antimicrobial Effect after Repeated Washing Cycles

Table 16.10 shows antimicrobial effect of mixture of 2% Chitosan and 2% PEG and mixture of 6% PEG and 2% PHAMS treated Khadi fabric after repeated washing. After three cycles of washing it is seen to be retaining around 80% to 85% of the antimicrobial activity.

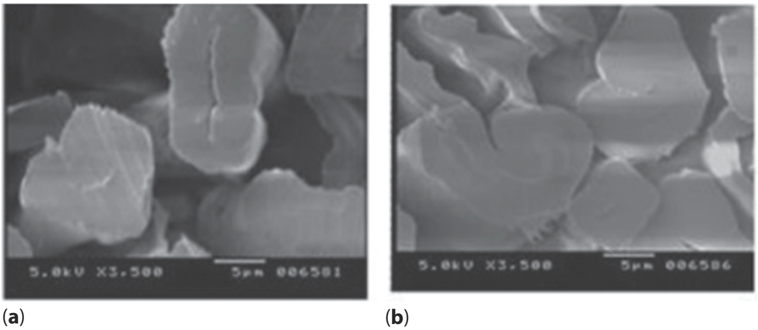

Figure 16.8 (a) SEM cross-section of control fiber and (b) SEM cross-section of fiber treated with 2% PEG and 2% chitosan.

Table 16.10 Effect of antimicrobial finishes after many washing.

Muslin fabric treated with	**Bacteria reduction % after 24 hours of test culture**		**Bacteria reduction % after 24 hours of test culture**	
	After 2 Washings		**After 3 Washings**	
	Klebsiella pneumoniae **ATCC4352**	*Klebsiella pneumoniae* **ATCC4352**	*Staphylococcus aureus* **ATCC 6538**	*Staphylococcus aureus* **ATCC 6538**
2% PEG	89	85	83	80
2% PEG and 2% Chitosan (mixture)	88	85	84	82
6% PEG and 2% PHAMS (mixture)	87	83	80	81

16.7 Analysis of Surface Properties by SEM

16.7.1 SEM of Treated and Untreated Cotton Fabrics

Cross-sectional view of the Chitosan and PEG-treated cotton fiber taken out from cotton Khadi fabric indicates the swelling of fiber by treatment with Chitosan/PEG or their mixture and hence, the gaps between fiber to fiber in the yarn is reduced than that found in SEM of fiber in untreated cotton Khadi fabric which is shown in Figure 16.8. As compared to (a) cross section of the fiber in untreated Khadi fabric, in (b) cross-section of the fiber of treated Khadi fabric, the frictional contact among the fibers in the yarn increased and hence it might then compensate the strength loss due to cross-linking with various agents.

16.8 Conclusion

Hence, following things may be inferred from this chapter of study – The PEG addition is an important criterion for designing a flexible membrane

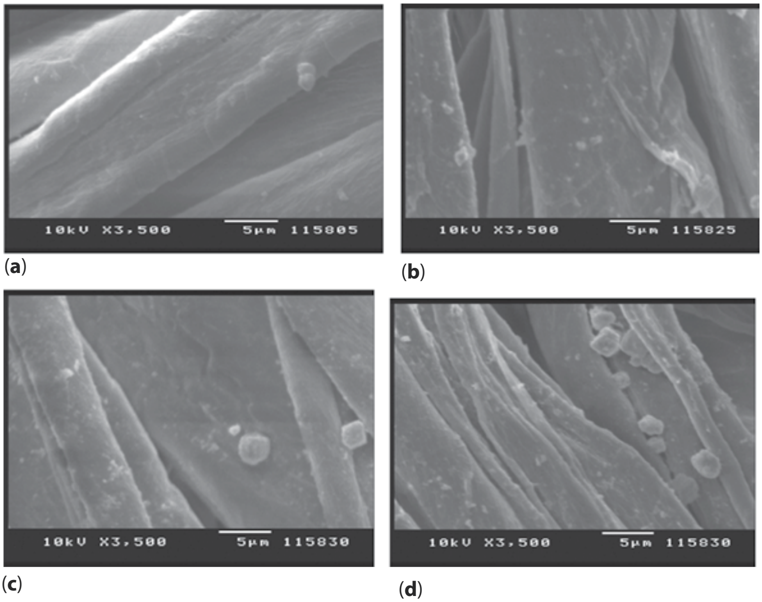

Figure 16.9 SEM of (a) untreated cotton, the surface of which is smooth enough as compared to cotton treated individually with (b) PEG (c) PEG and Chitosan, and (d) PEG and PHAMS. The fabric treated with PEG and PHAMS (d) shows anchoring of the PHAMS on the surface of cellulose (cotton).

on the cotton fabric surface of the delicate muslin fabrics. The fabric treated with chitosan and PEG (50:50) indicates thermal stability at par with untreated (control) fabric. As chitosan is a rigid molecule, it leads to the rigidity in the coated membrane on the fabric. The comfort and handling aspects are very important in cotton Khadi fabric to make the interface between the membrane and the fabric smooth. The air and water permeability which are key properties for cotton Khadi fabric are influenced in such a way that coated membrane possesses optimum values at chitosan and PEG-200 (50:50) content.

Amongst all the individual and combined applications of PHAMS and PEG, it is observed that the combined treatment of PEG and PHAMS (in 3:1 ratio) in presence of 1/5th of CA and SHP catalyst on cotton fabric shows an acceptable and appreciable good result in terms of antimicrobial/rot resistance performance with minimum loss of tenacity and offers an optimum balance in other textile-related properties, showing lowest degradation against microbial attack.

16.8.1 Ranking Index of Different Treatments on Loss of Tenacity and Antimicrobial Reduction Percentage Values

To compare and understand the overall effects obtained by different sets of chemical treatment and antimicrobial activities of cotton Khadi fabric studied in the present work, two major factors, i.e. Tenacity value retained and antimicrobial retention properties after eco-friendly treatment of all the treated fabrics, 50:50 weight-age are considered to be appropriate (as both the factors are equally important) and finally the ranking is calculated by simply weighted average method with the data for tenacity retention% and antimicrobial retention for the corresponding treatment as given below in Table 16.11.

From the weight-age average value, it is observed that to go for a single eco-friendly solution for improving antimicrobial properties of cotton Khadi fabric without much affect on tenacity under specific condition of treatment renders highest ranking index value, i.e. 95% and is, therefore, to be considered as a best option.

However, according to the end use, if good level of antimicrobial finish is desired only with a little bit compromise on tenacity retention, treatment with PEG and PHAMS with a ratio of 3:1 (more than 2% each) or in the ratio of 1:1 (more than 4% each) under specific condition of treatment may be considered as the best option to adopt.

Table 16.11 Comparative data for tenacity retention percentage and antimicrobial properties treated cotton Khadi fabric.

Samples	**Tenacity retention (%)**	**Average antimicrobial retention (%)**	**Weight-age average**
2% PEG	98.5	90.0	94.25
2% PEG and 2% Chitosan	98.8	91.2	95.0
6% PEG and 2%PHAMS	78.9	98.0	88.45
4% PEG and 4% PHAMS	76.5	98.0	87.25

Acknowledgement

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Reference

1. KVIC, *Annual Report*. Khadi and Village Industries Commission, India, 2014.
2. P. Ghosh, D. Das, A.K. Samanta, Modification of Jute with citric acid. *J. Polym. Mater.*, 12, 297, 1995.
3. A.K. Samanta, A. Bagchi, Effect of rot and crease resistance finishing of jute fabric using citric acid and poly ethylene glycol, *J. Polym. Mater.* 29(3), 349–359, 2012.
4. A.K. Samanta, A. Mukhopadyay, M.M. Bhagwat, T.R. Kar, Application of PEG, Cetrimide, Chitosan and their mixture on cotton muslin fabric to improve rot resistance/antimicrobial property and its salt free reactive dyeing, *J. Text. Inst.*, 107(11), 1386–1405, 2016.
5. D. Gupta and A. Haile, Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan, *Carbohydr. Polym.*, 69(1), 164–171, 2007.
6. B. Gupta and S. Saxena, Chitosan-Polyethylene glycol coated cotton membranes for wound dressings. *Ind. J. Fibre Text Res.*, 36, 272–280, 2011.
7. Y. Kitkulnumchai, A. Ajavakom, M. Sukwattanasinitt, Treatment of oxidized cellulose fabric with Chitosan and its surface activity towards anionic reactive dye, *Cellulose*, 15(4), 599–608, 2008.

8. E. Nasr, H.E., Sayyah, S.M, D.M. Essa, S.H. Samaha, A.M. Rabie, Utilisation of acrylates emulsion terpolymer with Chitosan as a finishing agent for Cotton Fabrics, *Carbohydr. Polym.* 76, 36–45, 2009.
9. T. Oktem, Surface treatment of cotton fabrics with Chitosan, *Color Technol.*, 119, 241–246, 2003.
10. J. Andrew, M.R.G. Ledder, L.E. Moore, C. Catrenich P. Gilbert, Effects of quaternary-ammonium-based formulations on bacterial community dynamics and antimicrobial susceptibility, *Appl. Environ. Microbiol.*, 70(6), 3449–3456, 2004.
11. Sarika Mishra, Ritu Pandey, Mukesh Kumar Singh, Development of sanitary napkin by flax carding waste as absorbent core with herbal and antimicrobial efficiency, *Intl. J. Sci. Environ. Technol.*, 5(2), 404–411, 2016.
12. Monica Periolatto, Franco Ferrero, Claudia Vineis, Alessio Varesano, Giuseppe Gozzelino, *Novel antimicrobial agents and processes for textile applications*, Dr. Ranjith Kumavath (ed.), InTech, 2017.
13. Fernando A.G. da Silva Jr *et al.*, Antibacterial behavior of polypyrrole: The influence of morphology and additives incorporation, *Mater. Sci. Eng. C Mater. Biol. Appl.*, 62, 317–322, 2016.
14. Anton Nikiforov, Xiaolong Deng, Qing Xiong, U. Cvelbar, N. DeGeyter, R. Morent, Christophe Leys, Non-thermal plasma technology for the development of antimicrobial surfaces: a review, *J. Phys. D: Appl. Phys.*, 49(20) Article ID 204002, 2016.
15. K.B. Ravindra and K. Murugesh Babu, Study of antimicrobial properties of fabrics treated with *Ocimum Sanctum* L. (*tulsi*) extract as a natural active agent. *J. Nat. Fibers*, 13(5), 619–627, 2016.
16. Diana Santos Morais, Rui Miranda Guedes, Maria Ascensão Lopes, Antimicrobial approaches for textiles: from research to market. *Materials*, 9(6), 498, 2016.
17. Jiraphorn Katewaraphorn and Arunee Kongdee Aldred, A study of microcapsules containing *Psidium guajava* leaf extract for antibacterial agent on cotton fabric, *Intl. J. Chem. Eng. Appl.*, 79(1), 1–5, 2016.
18. Lin Li, Kaikai Ma, Yin Liu, Ying Liu, Rong Li, Xuehong Ren, Tung-Shi Huang, Regenerablity and stability of antibacterial cellulose containing Triazine N-halamine, *J. Eng. Fabrics Fibers*, 11(1), 23–30, 2016.
19. S.M. Gawish, H.M. Mashaly, H.M. Helmy, A.M. Ramadan, R. Farouk, Effect of mordant on UV protection and antimicrobial activity of cotton, wool, silk and nylon fabrics dyed with some natural dyes, *J. Nano Med. Nanotechno.*, 8(1), 3–9, 2017.
20. C.H. Fisher, New cotton properties through chemical research, *Text. Res. J.*, 25(1), 1–11, 1995.
21. M. Montaze, R.M.A. Malek, A. Rahimi, Salt free reactive dyeing of cationized cotton, *Fibre Polym.*, 8(6), 608–612, 2007.

22. A.K. Samanata and A. Bagchi, A eco-friendly rot and crease resistance finishing of jute fabric using Citric Acid and Chitosan, *J. Inst. Eng.*, 94(1), 7–13, 2013.
23. Eda Jagst., Surface Functional Group Characterization Using Chemical Derivatization X-ray Photo Electron Spectroscopy (CD XPS), in: *BAM-Disertationsreihe*, Band, 69 (2011).
24. Thermo Fisher Scientific Inc., http://www.XPSsimplified.com/elements/nitogen.php2013, September, 2015.
25. Roger Smart *et al.*, *X-ray Photoelectron Spectroscopy Slides*, Department of Physics and Material Science, City University of Hong Kong, Surface Science Western, UWO, 30, September, 2015
26. Ling-Hao He, Rui Xue, De-Bin Yang, Ying Liua, Rui Song, Effects of blending Chitosan with PEG on surface morphology, crystallization and thermal properties, *Chin. J. Polym. Sci.*, 27(4), 501–510, 2009.
27. M. Zeng, Z. Fang, C. Xu, Effect of compatibility on structure of the microporous membrane prepared by the selective dissolution of Chitosan/Synthetic polymer blend membrane, *J. Membr. Sci.*, 230, 175–181, 2004.
28. S. Aly, A. Hashem, S.S. Hussain, Utilisation of Chitosan citrate crease resistance and antimicrobial finishing agent for cotton fabric, *Ind. J. Fibre Text. Res.* 34, 295, 2004.

17

Advanced Technologies for Coloration and Finishing Using Nanotechnology

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Abstract

In the textile technology, the use of unique dyes and finishes has a substantial influence on the appeal and functionality of textiles. Advanced technologies in late twentieth centuries have created huge progress in the textile technology. Focusing on the major advances in the field, coloration and finishing hold a major part. Biotechnology, nanotechnology, and chemical technologies have contributed to innumerable advancements and upgrades for the textile field. Among these, nanotechnology is the most recent advancement and has proved to be the near superior to all and hence this chapter deals with the role of nanotechnology in the advancement of coloration and fixing in textiles. Nanotechnology has the real commercial potential for the textile industry due to its high durability for fabrics compared with conventional methods because nanoparticles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics. Burlington Industries, a US-based fabric industry was the first to work on nanotechnology in textiles. Nanoparticles along with a surfactant, ingredients, and a carrier medium are usually coated on the surface of the textiles to modify the surface of textiles. Various methods used to coat a fabric are spraying, transfer printing, washing, rinsing, and padding. This chapter will elucidate the advancements in coloration and finishing by nanotechnology.

Keywords: Nanotechnology, printing, washing, rinsing, padding, durability

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17.1 Introduction

In the textile technology, the usage of unique dyes and finishes has a substantial say on the appeal and functionality of textiles. Coloration is a wet process where dyes, chemicals, and a large volume of water are used. The demand for advancements in chemical wet processing grows every year due to the need for cleaner, cost-effective, and value-added textile products [1]. Finishing in textile technology equally gains much importance as the purposes of clothing are varying and needs upgrade regularly. Various finsihings like water resistant, antimicrobial, UV-resistant, sunscreen, etc. have been incorporated in textiles in last few decades. In late twentieth centuries, there were enormous advancements in the textile technology, specifically coloration and finishing. Nanotechnology has been a key factor in the recent advancement and hence this chapter deals with the role of nanotechnology in the advancement of coloration and fixing in textiles. Nanotechnology has a real commercial potential for the textile industry due to high durability for fabrics than conventional methods, because nanoparticles have large surface area-to-volume ratio and high surface energy, thus rendering better affinity for fabrics [2]. Burlington Industries, a US-based fabric industry was the first to work on nanotechnology in textiles [3]. Nanoparticles along with a surfactant, ingredients and a carrier medium are usually coated on the surface of the textiles to modify the surface of textiles [4]. Various methods used to coat a fabric are spraying, transfer printing, washing, rinsing, and padding. This chapter will elucidate the advancements in coloration and finishing by nanotechnology.

17.2 Nanoparticles in Dyes

The heavy cost for using enormous water for dye and treating waste in industrial processes like conservative dyeing of textiles is a stern concern for textile industrialists and finishers. Nanoparticles are introduced into dyes to reduce the environmental hazards by reducing the hazardous salt and water content in the dye solution.Cotton is majorly colored with reactive dyes. Usually, the dye bath for coloring the cotton contain solid particles (cotton fiber), dyeing auxiliaries (organic compounds), hydrolyzed reactive dyes, substantial quantities of alkalis (sodium carbonate and soda ash), and very high concentration of sodium chloride or sodium sulfate. These dyes are harmful to ecology, as the effluents produced are relatively heavily colored, contain high concentrations of salt and exhibit high Biochemical Oxygen Demand (BOD)/Chemical Oxygen Demand (COD) values. Water required to dye 1 kg of cotton with reactive dye exceeds 100 L [5]. Soft handle and more brilliant shade with reduced pigment requirement have been achieved in exhaust dyeing of cationized cotton with nano-scale pigment dispersion [6]. Nanotechnology has answered these problems by replacing reactive dyes with eco-friendly nano colorants that require minimal water for dyeing.

Silica nanoparticles are commonly used fillers to overcome the above-mentioned problems. Silica nanoparticles absorb the dye and forms colored nanoparticles. These nanoparticles are used as dyes to color the cotton fabrics and can eliminate the use of salts in the dye solution [7].

Gold nanoparticles are used as stable colorfast colorants on wool and cotton fibers. These are mostly preferred in high-quality fabrics and textiles for high-end fashions.

Cobalt (III) nanoparticles are used as in dyes due to their high stability, long shelf life, use of aqueous solvent, large number of N–H donor groups, high positive charge (III) and potential applications. Bala *et al.* [8] synthesized Co (III) nanocomplexes, $[Co(NH_3)_6]Cl_3.2H_2O$, $[Co(en)_3]Cl3.3H_2O$ and $[Co(dien)_2]Cl_3.3.5H_2O$ by sonochemical synthesis method and tested their antimicrobial activity and textile dyeing behavior. They evaluated that the padding and curing method was ideal for dyeing Co(III) dyes on the cotton fabrics and also the dye was effective against the bacteria, *Bacillus subtilis*, and the fungi, *Alternaria alternata* [8].

Nanocomposites are materials that are part of the growing field of nanotechnology. By introducing nanoparticles into a macroscopic sample material (matrix), nanocomposites are created. Nanocomposite polypropylene was made by modifying nanoclays with quaternary ammonium salt which is acid dyeable (due to the ionic attraction between the negatively charged acid dye and the positively charged quaternary ammonium salts in the nanoclay) and disperses dyes (due to the van der Waals forces and hydrogen bonding).

Aiming at getting a new-added value for Polyethylene Terephthalate (PET) and better dyeability with disperse dye, Polyester PET nanocomposite fiber was made from polyester and silica (SiO_2) nanoparticles. PET/SiO_2 nanocomposite showed better weight loss on alkaline hydrolysis when compared with pure PET fibers. Introduction of superfine structures like cracks, craters, and cavities would facilitate application like deep coloration [1].

17.2.1 Plasma Technology

Plasma is an innovative eco-friendly technology for the development of durable multifunctional effects on a wide range of textile substrates. Since plasma does not require water and produce any residual effluents it plays an extraordinary role in eco-friendly coloration and functional finishing of textiles over the past few years. Plasma is produced by the interaction of electromagnetic field with gas under appropriate pressure. Briefly, plasma is a partially ionized gas containing ions, electrons, and neutral particles.

17.2.1.1 Coloration of Plasma-Treated Polyester Fibers

Methods like pad-dry-bake process (Thermosol process) disperse dyes at high temperature and pressure and usage of phenol-based carriers to bloat the fiber during coloration may pollute the environment. In order to overcome this problem, low-temperature plasma (LTP) was used instead of the chemical method for the treatment of PET fibers. An increase in color depth is obtained on treating PET fabrics with argon and air plasma, as the plasma induces the increase of surface roughness and surface area. Water swelling capability and the affinity of PET fibers for dyes containing polar groups is increased by introducing hydrophilic groups. They are induced by chemically both reactive and inert plasmas. Plasma-deposited and dyed polyester fabrics exhibit good rubbing and washing fastness, demonstrating the coating-functional permanency. Multi-functional thin film from ammonia/ethylene or acetylene mixture low-pressure plasma is used to deposit onto the polyester fiber.The coating permanently adheres to the substrate and provides excellent abrasion resistance.

17.2.1.2 Coloration of Plasma-Treated Wool Fibers

Wool is one of the important fibers in the textile industry despite its complicated surface structure. The technical difficulty associated with wool is its wettability which affects its ability to be dyed. Due to the presence of a high number of disulfide cysteine cross-linkages [–S–S–] in the A-layer of the exocuticle, and fatty acids on the fiber's surface wool fiber surface is hydrophobic in nature. This surface morphology of wool is difficult to determine the diffusion in fiber. So, LTP is used instead of the chemical method for the treatment of wool. LTP treatments improve the coloration behavior of wool fibers in different coloration systems due to plasma-induced cysteine oxidation leading to the reduced number of cross-linkages in the fiber surface which, in turn, facilitate the trans-cellular and intercellular dye diffusion.

17.2.1.3 Coloration of Plasma-Treated Cotton Fibers

In most cotton coloration methods, particularly exhaust coloration, reactive dyes are often used as they provide a complete color range and are easy to tint. But reactive dyes have only a moderate affinity for cotton fiber. To overcome this limitation several attempts have been made. One of the most feasible methods is to enhance dye–fiber interaction using cationized cotton which showed improved dyeability with reactive dyes when compared to the untreated fabric in the presence of amine compounds on plasma treated cotton fiber [1, 9].

17.3 Nano Finishing

The property upgrade of woven or knitted cloth into performance categorized yarn or fabric is the finishing in textile industry. The end use of the fabric determines the type of finish required on the textiles. Some finishes that are widely in practice like hydrophobic, anti-microbial, self-cleaning, flame retardant, UV-protectant, and wrinkle resistant along with the incorporation of nanotechnology in them are discussed below.

17.3.1 Hydrophobic Finishing

Researchers on textile and manufacturers have been aiming on water repellence for centuries. Hydrophobicity (*Hydro* – water; *phobicity* – fear) as the term indicates water fearing or water repellency by the fabric. A fabric surface can repel water by resisting adsorption, absorption, or penetration of water. Knowing the ultimate intended purpose of the textile is important before functionalizing a fabric for water repellency. Rendering a waterproof textile implies that the fabric will be repellent to water in both the liquid and vapor forms. The difference between waterproof and water repellent textiles becomes important when considering the end use of the textile. Textiles that are both water repellent and breathable are necessary for finishing such as performance clothing [10].

Water repellence from fabric surface can be achieved by multiple methods. Chemical method is most commonly used for hydrophobization. Water repellency is done by using following chemicals: Wax dispersions free of metal ions, Metallic salts and soaps, Wax dispersions containing Zirconium salts and Pyridinium compounds, Silicones, Organo chromium compounds, and Fluro-chemicals. Among these chemicals, Fluroalkylsilanes on coating have low surface free energy and the simple reaction of silane groups with the hydroxyl groups makes it, the most commonly used for water repellence [11, 12].

There are other two steps by which hydrophobic nature can be gained on any surface. They are, by creating rough surface and modification of the surface by the substance having low surface energy. Fluorocarbon contains perfluroalkyl residue in which all hydrogen atoms are replaced by fluorine compounds. High thermal stability and low reactivity of fluorocarbon reduce surface tension. Chain length determines the surface tension of fluorocarbon finishes and the minimum chain length can be represented as $n = 9$.

Water repellent property includes nano-whiskers (hydrocarbons) and nano-spheres. To create a peach fuzz effect, 1/1000th of the size of a typical cotton fiber is added to the fabric without lowering the strength of the cotton. Nano-whiskers are larger than water molecules, and the gaps between the whiskers on the fabric are smaller than the typical drop of water. Thus water retains on the top of whiskers and above the fabric surface but still liquid can pass through the fabric when pressure is applied.

Wettability is one of the most important properties of a solid surface and the contact angle has been commonly used to characterize the surface wettability. A surface with a water contact angle larger than 150°, but 180° and a low sliding angle (the critical angle where a water droplet with a certain weight begins to slide down the inclined plate) is usually called a super-hydrophobic surface. Porous structures, nanofibers, and carbon nanotubes have also been used to develop super-hydrophobic surfaces (see Figures 17.1 and 17.2) [3].

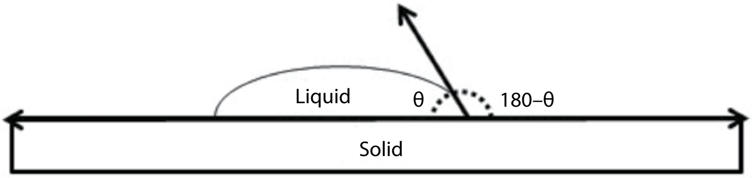

Figure 17.1 Contact angle measurement.

Figure 17.2 Water on the hydrophobic lotus leaves.

Nano-spheres, on the other hand, repel the water from the fabric surface by a mechanism similar to lotus leaf effect. Lotus plants are naturally super-hydrophobic in nature which is tough and textured. When water droplets fall on the lotus leaf, its surface tilts slightly and will roll off. This keeps the surface dry even after a heavy shower and the droplets remove the dirt when they roll down. In nanospheres, impregnation involves three-dimensional surface structures with gel-forming additives that repel water and dirt particles from attaching to the fabric surface. This property can be imparted by coating the cotton fabric with thin nanoparticulate plasma film. To deposit a nanoparticulate hydrophobic film onto the cotton fabric surface, audio frequency plasma of fluorocarbon chemical is applied and this improves the water repellent property. By affecting the softness and abrasion resistance of cotton super-hydrophobicity is obtained [3–7].

Water repellency and contact angle differentiation are important when measuring the repellency of a fabric. Water repellency describes how well a fabric resists the absorption, adsorption, and penetration of water on a fabric surface. The surface energy of the substrate quantitatively describes the contact angle of the liquid on the surface of the fabric [13]. The contact angle of a liquid on the surface of a material is an indirect measurement of the wettability and directly relates to the interactions of the solid, liquid, and gas phases. The contact angle of a droplet on a substrate is the angle formed between the solid–liquid interface and the liquid–vapour interface, When the contact angle exceeds 90°, wetting of the substrate does not occur, and the substrate is said to be hydrophobic [14].

Practically, it is a great challenge to sustain the super-hydrophobicity during laundering and abrasion. Mechanical stability of these surface-coated nanostructures is to be improved to retain the super-hydrophobicity. Formation of covalent bonds between nanostructures and the textile fibers has resulted in good enhancement of super-hydrophobicity [15].

Super-hydrophobic surface preparation as already mentioned in previous section, can be categorized broadly into (a) roughening of low surface energy material and (b) modification of rough surface with low surface energy materials.

For roughening of low surface energy materials, various physical aberration methods such as CO_2 pulsed laser aberration to introduce peroxides on the surface, Laser etching, Electro-spinning technique, Oxygen plasma treatment, Stretching of fluorinated Teflon (polytetrafluoroethylene) by creating a void and fibrous crystals, are employed. While there are coatings such as Low-Density Poly Ethylene (LDPE), alkyl ketene, polycarbonate, and polyamide are employed for the generation of rough surfaces [16].

17.3.2 Antimicrobial Finishing

Antimicrobial finishes add value to textiles and garments by preventing the growth of bacteria, fungi, yeast thus protecting textiles against unpleasant odors, mildew spots, premature loss of functional properties, and deterioration from insects and pests (see Figure 17.3).

Defining the term 'antimicrobial', they are various agents that act on specific forms of microorganism, such as bactericide (that inhibit bacterial growth), fungicide (that inhibit fungal growth), insect proofers, mothproofers, herbicides, algicides, rot proofers and anti-dustmite products and stop/disturb their growth. Antimicrobial Agents used in textiles are Quaternary Ammonium Compounds (QAC), Antimicrobial Cationic Dyes, Chitosan, and Polyethylene glycol [17].

Mechanisms of antimicrobial finishes include a variety of chemical methods which is divided majorly into two types based on the mode of attack on microbes.

i. First type operates by controlled release mechanism which is effective against microbes on fiber surface or surrounding environment. However, eventually the reservoir will be depleted and the finish will no longer be effective.
ii. Second type consists of molecules that are chemically bound to fiber surfaces which act only on the surface of the fiber, not on surrounding environment.

The actual mechanisms by which antimicrobial finishes control microbial growth are extremely varied, ranging from preventing cell reproduction, blocking of enzymes, reaction with the cell membrane (for example

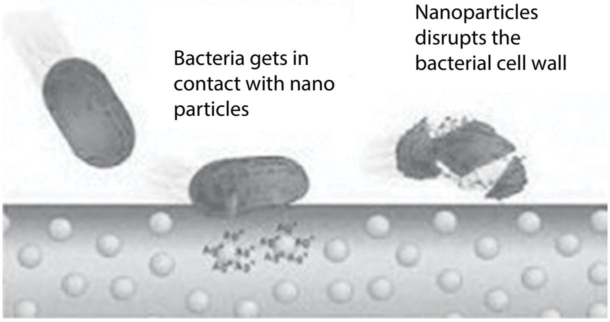

Figure 17.3 Antimicrobial action of nanoparticles.

with silver ions) to the destruction of the cell walls, and poisoning the cell from within [18].

For imparting antibacterial properties, nano-sized silver, titanium dioxide, zinc oxide, triclosan, and chitosan are commonly used. Nano-silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi thereby improving their bactericidal and fungicidal effectiveness. Nano-silver is very reactive with protein and has been reported to show antimicrobial properties at concentrations as low as 0.0003 to 0.0005%. When contacting bacteria and fungi, it adversely affects the cellular metabolism and inhibits cell growth. It also suppresses respiration, the basal metabolism of the electron transfer system, and the transport of the substrate into the microbial cell membrane [2, 19, 20]. There are numerous studies that say that silver nanoparticles have the tendency to accumulate on the cell wall of the Gram-negative bacteria prompting them death due to sealed cell membrane transportability. They are also capable of damaging the cell membrane [21].

In the research by Lee *et al.* [22], nanosized silver particles in colloidal solution have been found to possess excellent antibacterial effect on all specimens against Gram-positive and Gram-negative bacteria. Comparison was evaluated between polyester and woven samples which were padded through colloidal solution before dyeing with the padded and samples after dyeing for antibacterial effect. Results showed that bacterial reductions of all specimens were very excellent against *Staphylococcus aureus* and *Klebsiella pneumoniae.* The bacterial reduction was more effective when the specimens were treated with silver colloids after dyeing than when treated before dyeing. Rinsing after padding reduced the antibacterial efficacy of treated fabrics. But the numerical differences of bacterial reductions are not significant. Antibacterial efficacy on textile fabrics was easily achieved by using nanosized silver colloidal solution by padding process and had a good laundering durability [22].

The finishing procedure of nanosized silver usually involves encapsulation of the silver compounds. The nanoparticles of silver are encapsulated in the fiber reactive polymer. This encapsulation helps in the conjugation and retention of particles onto the surface of the textiles. The silver nanoparticles are dispersed in water-soluble styrene maleic anhydride polymer solution to coat on the fabric.

Zinc oxide nanoparticles are another class of nanoparticles that are testified to possess antimicrobial property. Natural fibers like cotton are more susceptible to microbial attack than synthetic fibers. Because of the lower toxicity and higher efficiency in preventing infection ZnO is preferred over the other inorganic forms of zinc [19]. Nano-ZnO coated fabric showed no growth on and surrounding the fabric when treated with *S. aureus* and

K. pneumoniae whereas bulk ZnO coated fabric and non-coated fabric showed growth on both fabrics as well as surrounding. Nano ZnO showed excellent antibacterial property despite the presence of soluble starch and acrylic binder. There are many disinfectants that are composed of metals or organic compounds for antibacterial treatment of fibers and polymers. But ZnO has been found to have several advantages, including marked antibacterial activity in the neutral region (pH = 7) without the presence of light and being non-toxic to humans [23]. ZnO is hygroscopic in nature that readily absorbs moisture in the environment. This property can dehydrate the environment for microbes to grow on the fabric.

In the research work of [24], it was studied that decrease in the size of titanium dioxide (TiO_2) nanoparticles particles fundamentally results in increased antimicrobial activity. Fabrics on treatment with TiO_2 nanoparticles showed bacterial resistance against *S. aureus* and *K. pneumonia*. Antibacterial activity was also tested after a number of washes which had shown a slight variation. This fully confirms the concept that the nanoparticles get bound to the fabric surface on their own because of their high surface energy. The larger nanoparticles possess less surface energy than the smaller nanoparticles and hence, the larger nanoparticles get desorbed faster than the smaller particles.

The antimicrobial properties of treated cotton fabrics were evaluated by quantitative assessment method as per AATCC test method 100-2004. The test was carried out with *S. aureus* and *K. pneumoniae*.

$$R = 100^*([B-A]/B)$$

where R – percentage reduction, A – the number of bacteria recovered from the inoculated, treated test specimen swatches in the jar incubated for over 24 hours, and B – the number of bacteria recovered from the inoculated, treated test specimen swatches in the jar immediately after inoculation (at ‘0’ contact time) [24].

Chaudhari *et al.* [25] tested antimicrobial property against *Staphylococcus aureus* and *Escherichia coli* bacterium on Cotton fabric treated with all concentrations of nano TiO_2. On increasing the concentration of nano TiO_2 there was a consistent improvement of antibacterial property of cotton fabric with *S. aureus* bacterium but there was no significant improvement found in antimicrobial property with *E. coli* bacterium [25].

17.3.3 Self Cleaning Finishing

A super-hydrophobic surface is the one that can bead off water droplets completely; such surfaces exhibit water droplet advancing angles of 150°

or higher. Thus self-cleaning surface leaves behind a clean surface as the dirt particles are being picked up by the rolling water droplets. To create the super-hydrophobic surface on textiles, several approaches have been researched by taking inspiration from nature, and this mimic the nano-structured Lotus leaf to exhibit self-cleaning properties [26]. The lotus leaf arrangement has already been discussed in Section 17.3.1.

Mechanism involved in self-cleaning process is super-hydrophobicity. Using nano techniques tree trunk like cotton fibers is covered in a fuzz of minute whiskers that creates a cushion of air around the fiber. Extra buoyancy is created between the whiskers by compressing the air in the cavities as the water hits the fabric, it beads on the points of the whiskers. Technically, the fabric has been rendered super-nonwettable or super-hydrophobic. When the force of absorption of the particle is higher than the static friction force between the particle and the surface, the droplet rolls over a contamination and the particle is removed from the surface. Because of the minimized contact area between the particle and the surface a very low force is required to remove a particle. As a result, by rolling off the surface, the droplet cleans the leaf. Hydrophobic water-repellent double structure of the surface is the cause of self-cleaning properties. By significant reduction of the contact area and the adhesion force between surface and droplet self-cleaning process results [27] (see Figure 17.4).

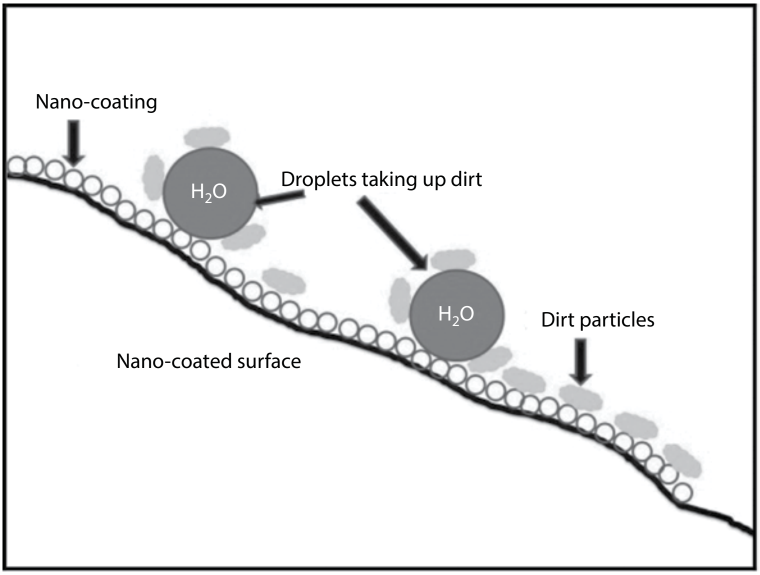

Figure 17.4 Nanocoated self-cleaning textile.

A process for the sol–gel coating on textile substrates at low temperature was developed which claimed that photocatalytic self-cleaning properties could be imparted to the coated fabric on coating cotton with TiO_2 nanoparticles that were about 20 nm in size. The coated textile structure demonstrated the significant self-cleaning activity when exposed under UV light spectrum. It is also confirmed that the self-cleaning activity increases with increase in percentage of TiO_2 nanoparticle and the high duration of exposing under UV light will also accelerate the self-cleaning action [28]. Md. Rahul Amin in his study reported that the combination of powerful oxidizing agents and UV lights has the ability to remove xenobiotics (synthetic chemicals) and organic pollutants from the textile products [29].

Contrastingly, in the research work done by Kamal *et al.* [30], it was found that the self-cleaning activity was improved only marginally by increased concentration of nanoparticles. Better self-cleaning activity was achieved by the use of lower amount of binder in nano finishes. This implies that on increasing binder and nanoparticles concentration, the nanoparticles are agglomerating. The size and morphology of the nanoparticles influenced the self-cleaning activity and have a significant effect on it. The smaller particles of TiO_2 with particle size less than 10 nm with monocrystalline morphology gave superior cleaning action under similar conditions compared to commercial nano TiO_2 of particle size 25 nm with polycrystalline morphology. The small-sized ZnO_2 nanoparticles with monocrystalline morphology could show self-cleaning activity similar to commercial TiO_2 [30, 25].

The self-cleaning activity was assessed for the nanocoated textile fabric by exposing the samples containing adsorbed coffee stain to visible irradiation. A 6% coffee solution was measured and introduced on the fabric and was allowed to spread. One-half of each stain on the fabric was exposed to sunlight for 12–48 hours, while the other half was prevented from sunlight. The exposed part of the stain was compared with that of covered part for self-cleaning action. Change in K/S value was measured and found the percentage of decrease in K/S value for the exposed samples in higher concentration of TiO_2 nanocoating. The rate of change in deterioration also depends upon the duration of the exposure as well. Higher the duration the percentage of decrease in K/S value increases [24, 28, 30].

$$\text{The } K/S \text{ value of exposed part} = \frac{(K/S)_{unexpected} - (K/S)_{expected}}{(K/S)_{unexpected}} \times 100$$

where K is the absorption, and S is scattering.

Nidhi *et al.* [31] reported that photocatalytic activity of the titania-treated fabrics expressed self-cleaning activity. The photodegradation of stain in terms of change in *K*/*S* values was determined with the help of a template using Gretag spectrophotometer. The SCA (Self Cleaning Activity) was determined in terms of % decrease in *K*/*S* value of the stain and was calculated using the following formula:

$$\%\ \text{Decrease in } K/S = \frac{(K/S)_{\text{unexposed}} - (K/S)_{\text{exposed}}}{(K/S)_{\text{unexposed}} - (K/S)_{\text{unstained}}} \times 100$$

where $[K/S]_{\text{unexposed}}$ = *K*/*S* of the stained specimen before exposure, $[K/S]_{\text{exposed}}$ = *K*/*S* of the stained specimen after exposure to ultraviolet (UV) light, $[K/S]_{\text{unstained}}$ = *K*/*S* of the original unstained fabric specimen [31].

The TiO_2 is a recognized catalytic compound. It shows its catalytic property by the absorption of a photon and jumped to the conduction band from the valence band. That is able to remove the organic pollutants and xenobiotic from the textile materials. Hence by treating the fabric or yarn by the particles, the fabric or yarn can be brought into a photocatalytic self-cleaning property. There is an absorbing capacity of UV rays in TiO_2 particles so the fabric of yarn also can be protected from UV rays for 20 washes [29].

17.3.4 Flame Retardant

Flame retardant products are highly required to use the low flammability fibers in the textile industry. Since synthetic fibers such as polyamide or polyester are highly inflammable, continuous investigations are carried out in the development of flame retardant products. The available systems for flame retardancy are composed of halogen-containing additives. Further new regulations are developed to use halogen-free compounds, particularly phosphorous-based systems as flame retardant products. Recently, the incorporation of nanoparticles in the finishing fabrics as flame retardant seems to be a valid and interesting approach. The main advantage is that a low amount of nanoparticle can be used for large surface area, albeit only certain specific nanoparticles can be used in the flame retardancy field. The resultant morphology (shape and size), chemical nature, concentration, as well as their distribution are some of the key points considered during nanoparticle use as flame retardant.

Pedro *et al.* [32] studied the use of zinc oxide (ZnO) nanoparticles as a flame retardant for their application to cellulosic fabrics (cotton polyester blend). To incorporate the ZnO nanoparticles onto the fabrics, a pad-dry-cure method was selected. The use of two different polycarboxylic acids (PAs) such as succinic acid (SA) or 1,2,3,4-butane tetarcarboxylic acid (BTCA) together with sodium hypophosphite (SHP) as the catalyst were employed for cross-linking fabrics. The formation of new ester cross-linking between cellulose chains and PAs was made possible at the curing temperature increasing from 160 to 180 °C. Influence of flame retardant was studied by char yield measurement. The results indicated that both SA and BTCA are effective agents in reducing the flammability of treated fabrics in the presence of SHP. Increasing the concentration of nanoparticle with an increase in BTCA and SHP decreases the fabric flammability.

Pedro *et al.* [32] worked on the Titanium dioxide (TiO_2) nanoparticle as flame retardant by mixing it with both cationic and anionic polyelectrolytes using the Layer by Layer (LbL) assembly. These nanocoatings have been performed onto both polyamide and polyesters fabrics, showing significant differences in surface properties (i.e., wettability and surface energy). Polyamide fabrics are covered homogeneously by a thin film of nanoparticle whereas polyester fabrics are covered partially with the presence of aggregates. The peak heat release rate (pHRR) value is reducing in polyamide fabrics, which is the key point that makes the difference in a coating. The incorporation of these TiO_2 nanoparticles into LbL films improved the fire retardant than other forms of nanoparticles. The team also reported that best results in flame retardant were shown by the smallest nanoparticles which increase the time to ignition and reduce the pHRR using cone calorimetry tests. Negative colloidal SiO_2 nanoparticles and positively charged alumina-coated SiO_2 are coated on polyester (PET) fabrics by LbL assembly reduced the pHRR value and showed very effective results of flammability. They also claim that multi-walled carbon nanotubes can also be used for improving the flame retardant properties when are applied onto polyester fabrics. Polyester fabric functionalized with carbon nanotubes halves the burning rate and duplicates the burning time in comparison with raw polyester fabrics [32].

Cheng *et al.* [33] studied and reported the flame retardant effect of the silk fabric treated with naturally occurring PA and nano-TiO_2 in the case of the use of BTCA as a cross-linker for wrinkle resistance. These multiple interactions among PA, TiO_2, BTCA, and silk fiber contributed to the good washing durability of the treated silk fabric The PA/TiO_2/BTCA treatment imparted excellent flame retardancy to silk fabric. The multiple interactions among PA, TiO_2, BTCA, and silk fiber contributed to the good washing durability of the treated silk fabric but compensating the softness and whiteness of the silk fabric [33].

The antimony pentoxide (Sb_2O_5) nanoparticles along with halogenated flame-retardants are also used for the flame retardant finishing. The antimony has a characteristic of flame retardancy. Hence, the presence of antimony particles along with halogenated flame retardant in the fabric increases a flame retardant property of the fabric [29].

The same has been substantiated by Subatra *et al.* who [34] developed colloidal antimony pentoxide which has been applied for flame retardant finish in textile. Colloidal antimony pentoxide has been offered as fine particle dispersion, for use as a flame retardant synergist with halogenated flame-retardants.

17.3.5 UV Protecting Finishing

Garments are in need to develop a method to protect the wearer from harmful sun rays. The rays in the wavelength region of 150 to 400 nm are known as ultraviolet radiations. The UV-blocking property of a fabric is enhanced when a dye, pigment, delustrant, or ultraviolet absorber finish is present that absorbs ultraviolet radiation and blocks its transmission through a fabric to the skin.

Asmaa [35], evaluated the UV protection finishes. UPF is the abbreviation of the ultraviolet protection factor. It indicates how long a person wearing the textile can stay in the sun before the start of skin reddening compared to an unprotected person. To create awareness among the end users of the negative impacts and effects of UV-radiation UPF has been adopted.

The UV protection factor is determined by using the following equation,

$$UPF = \frac{\int_{\lambda=280nm}^{400nm} E_\lambda S_\lambda \Delta_\lambda}{\int_{\lambda=280nm}^{400nm} E_\lambda S_\lambda T_\lambda \Delta_\lambda}$$

where, E_λ = the solar irradiance (W m^{-2} nm^{-1}), S_λ = the erythema action spectrum, describing the harmfulness of the different wavelengths, T_λ = the spectral transmittance through specimen at wavelength, λ, $\Delta\lambda$ = the wavelength interval of the measurements (nm) [35, 24].

Patel *et al.* [36] reported that to impart UV protection, several nanocompounds or nanoparticles can be applied on the textile material. When compared to organic UV-blocking agents, metal oxides like ZnO as UV-blocker are more stable. With increased surface area and intense absorption in the UV region, nano ZnO enhances the UV-blocking property. ZnO nanoparticles have advantages over nano-silver in cost-effectiveness, whiteness, and UV-blocking property. Titanium dioxide and zinc oxide of nanosize are the commonest nanocompounds used. By reflecting, scattering or absorbing harmful UV they provide a protective benefit [36]. This is due to the fact that nanoparticles have a larger surface area per unit mass and volume than the conventional materials, leading to the increase of the effectiveness of blocking UV radiation [34]. For small particles, light scattering predominates at approximately one-tenth of the wavelength of the scattered light. Rayleigh's scattering theory stated that the scattering was strongly dependent upon the wavelength, where the scattering was inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 and 400 nm, the optimum particle size will be between 20 and 40 nm [2].

On padding, nano particles not only accumulate on the surface of the fabric but also some portion of the nanoparticles penetrate into the interstices of the yarns and the fabric. Such nanoparticles that do not stay on the surface may not be very effective in shielding the UV rays. Meanwhile, only one side of the fabric gets exposed to the rays and hence, this surface needs to be covered with the nanoparticles for better UV protection. Spraying the nanoparticles on the fabric surface can be an alternate method of applying the nanoparticles [19].

A lot of efforts have been made on the application of UV blocking treatment to fabrics using nanotechnology. Using sol–gel method UV blocking treatments for cotton fabric has been developed. A thin layer of TiO_2 nanoparticle is formed on the surface of the treated cotton fabric, which provides excellent UV protection, the finish is durable up to 50 home launderings. Apart from TiO_2, ZnO nanorods of 10 to 50 nm in length are also applied to cotton fabric to provide UV protection. The rods exhibit excellent UV protection [37, 38].

Md. Rahul Amin in 2013 reported that clay nanoparticles or nanoflakes can be used for the UV protection. These types of substances contain hydrogen aluminosilicates, which has difference in the chemical composition and crystal structures. The clay nanoparticles have a property of locking UV light and also have electrical, chemical and heat resistance. Thus having a finish of clay nanoparticles the UV rays can be resisted by the fabric [29].

17.3.6 Wrinkle Resistant

Cellulose molecules in the cotton linearly organize themselves passing through the crystalline and amorphous sections of the fibers. Hydrogen bonds hold together cellulose molecules in their positions. Upon applying a force to the fibers, the cellulose chains displace from their original positions and hydrogen bonds re-form at new locations. By certain traditional wrinkle-free solution, wrinkle resistance is achieved which reduces fabric's tear and tensile strength, abrasion resistance, water absorbency, dyeability, and breathability. To overcome these, resin is used as a conventional method. To avoid the limitations of using resin, some researchers employed nano-titanium dioxide and nano-silica to improve the wrinkle resistance of cotton and silk respectively. Carboxylic acid is used as a catalyst with nano-titanium dioxide under UV irradiation to catalyze the cross-linking reaction between the cellulose molecules and the acid. On the other hand, nano-silica was applied with maleic anhydride as a catalyst; the results showed that the application of nano-silica with maleic anhydride could successfully improve the wrinkle resistance of silk [2, 19, 34]. Additionally, carboxylic-acid-treated fabrics with TiO_2 nanoparticles were softer compared to untreated fabric. Bombyxmori silk was also treated with TiO_2 nanoparticles in chitosan by cross-linking reactions of citric acid and maleic anhydride. However, the presence of TiO_2 nanoparticles reduced the tear and tensile strength of the cotton fabric. A highest dry crease recovery angle was obtained on employing 1,2,3,4-butane tetracarboxylic acid (BTCA) and wet crease recover angles with succinic acid as cross-linking agents. Dry and wet delay-wrinkle recovery angles of the treated silk were 267 and 250° compared to untreated fabric of 235° and 178°, respectively. Additionally, SiO_2 NPs, and maleic anhydrate as a catalyst have been applied to silk to improve wrinkle resistance [39].

17.4 Encapsulation Technology

Encapsulation is a process in which a particle is surrounded or coated by another particle. Encapsulation creates physical and chemical stabilization improve shelf life and protection of active agents from the surroundings. Two common encapsulations are microencapsulation and nanoencapsulation. These techniques provide long-lasting effects for the release of active agents. Nanoencapsulation technique is a process by which small particles are coated within wall materials which can be homogeneous or heterogeneous matrix to form capsules at a nanoscale range. The finishing of textiles using nanoencapsulation is claimed to be more durable. Micro-encapsulation is a process in which small capsules of many useful properties are made by using tiny particles or droplets called core material surrounded by a coating, shell or membrane. Diameter of microcapsules is between a few micrometers and a few millimeters [40].

Some of the encapsulation techniques and their applications studied by various researchers are documented below.

Microencapsulation is the cost-effective and long-lasting method in storing volatile substances over a long period of time. Microcapsules are available with a wide range of products. These products have different properties related to the nature of the encapsulated substances [41]. By microencapsulating the core material, significant and functional properties can be imparted to the fabrics and hence this technique is now widely used in Textile finishing. This core material can be any substance with a special function to perform for the fabric. Encapsulation has allowed moisturizers, therapeutic oils, and insecticides to be incorporated into fabrics [40]. The intention of microencapsulation besides the protection of core substances is also the separation of reactants, controlled release, reduction of toxicity, reduction of volatility, etc. [41]. Microencapsulation of anti-microbial agents is also gaining popularity in sportswear and medical textiles [40].

End-use applications like antimicrobial property, flame proof, and many more functional properties can be imparted to various substrates like polyester, nylon, polypropylene, etc., by many methods in which most of the methods may be durable or temporary. Microencapsulation technique is unique for its controlled release of the substrate and for the durability it can withstand for a longer duration. Microencapsulation provides a mean of packaging, separating and storing materials on a microscopic scale for triggered release under controlled conditions, such as mechanical rupture, electrical or chemical means or by leaching action in an appropriate liquid environment. Core substances may be perfumes, any healthcare active ingredients or even liquid crystal and solid one.

Microencapsulation offers many advantages over conventional processes, in terms of economy, energy saving, eco-friendliness and controlled release of substances [42].

Microencapsulation techniques include spray drying, air suspension coating and solvent evaporation. Spray drying is a low-cost commercial process mostly used for the encapsulation of fragrances, oils, and flavors. In this technique, core particles are dispersed in a polymer solution and sprayed into a hot chamber. The shell material solidifies onto the core particles as the solvent evaporates such that the microcapsules obtained are of poly-nuclear or matrix type. Water-soluble polymers are mainly used as shell materials because a solvent-borne system produces unpleasant odors and environmental problems.

Air-suspension coating gives a better control and flexibility. The particles are coated while suspended in an upward-moving air stream. They are supported by a perforated plate having different patterns of holes inside and outside a cylindrical insert. Just sufficient air is permitted to rise through the outer annular space to fluidize the settling particles. Most of the rising air (usually heated) flows inside the cylinder, causing the particles to rise rapidly. At the top, as the air stream diverges and slows, they settle back onto the outer bed and move downward to repeat the cycle. The particles pass through the inner cylinder many times in a few minutes methods. The air suspension process offers a wide variety of coating materials candidates for microencapsulation. The process has the capability of applying coatings in the form of solvent solutions, aqueous solution, emulsions, dispersions or hot melt in equipment ranging in capacities from 1 to 990 pounds. Core materials comprised of micron or submicron particles can be effectively encapsulated by air suspension techniques, but agglomeration of the particles to some larger size is normally achieved.

Solvent evaporation processes are carried out in a liquid manufacturing vehicle. The microcapsule coating is dissolved in a volatile solvent, which is immiscible with the liquid manufacturing vehicle phase. A core material to be microencapsulated is dissolved or dispersed in the coating polymer solution. With agitation, the core coating material mixture is dispersed in the liquid manufacturing vehicle phase to obtain the appropriate size microcapsule. The mixture is then heated to evaporate the solvent for the polymer. In the case in which the core material is dissolved in the coating polymer solution, a matrix-type microcapsule is formed. Once all the solvent for the polymer is evaporated, the liquid vehicle temperature is reduced to ambient temperature with continued agitation. At this stage the microcapsules can be used in suspension form, coated on to substrates or isolated as powders. *In situ* polymerization In a few microencapsulation processes, the direct polymerization of a single monomer is carried out on the particle surface. In one process, e.g. cellulose fibers are encapsulated in polyethylene while immersed in dry toluene. Usual deposition rates are about 0.5 μm/min. Coating thickness ranges 0.2–75 μm (0.0079–2.95 mils). The coating is uniform, even over sharp projections.

The release mechanisms of encapsulated materials depend on the purpose of microencapsulation. Commonly used is the mechanism of external pressure which breaks the microcapsule wall and releases the liquid from the core. Abrasion releases the core material of the microcapsule wall, e.g. in antistatic and fragrances for textiles (abrasion in washing machines and dryers), or for grinding and cutting additives. Heat is also a factor that releases core materials in many applications. Fire retardants that are microencapsulated are released by burning of capsule walls and have application in wallpapers, carpets, curtains, and fire protected clothes.

Use of microcapsules in textiles includes phase-change materials, fragrance finish, fire retardants, polychromic and thermo-chromic microcapsules, antimicrobial activity, and counterfeiting.

Phase-change materials perform the function of changing the aggregation from solid to liquid within certain range of temperature. Microcapsules of phase-change materials reduce the effect of extreme variations in temperatures. This facilitates the thermoregulation of clothing and the constant temperature is provided. These kinds of microcapsules are applied to different materials, vests, parkas, snowsuits, blankets, mattresses, duvets, etc. Fragrance finishes have been directly applied on to fibers and fabrics numerous times, but the aroma does not last for more than two wash cycles. Microencapsulation of fragrances is a technique which when used on the fabric gives a longer effect. This technique is commonly used in aromatherapy in which microcapsules may contain essential oil flavors like lavender, rosemary, pine, etc. This is basically done to treat insomnia, headache, and to prevent bad odor. Microcapsules with fire retardant core were developed to overcome the problem of reduced softness which is caused by the direct application of fire retardant materials. They are applied to fabrics used in military applications like tentage. The color changing systems changes color in response to temperature, which is termed as thermo-chromatic and the other changes color in response to UV light, this is known as photo-chromatic. In textiles, polychromic and thermo-chromic microcapsules can be found in product labeling, medical, and security applications. There are microencapsulated thermo-chromatic dyes that change color at specific temperature – in response to human contact. Bacteria often cause microbiological decay of fabrics which in turn causes loss of various useful properties of fabrics. This problem can be prevented by the use of anti-microbial finishes that can be applied with the help of microencapsulation. This finish is especially for textiles for medical and technical use. Counterfeiting is imitation of high added value textiles, branded, and designer goods can be dealt with by the use of microencapsulation. Microcapsules applied to label contain a color former or an activator. By the use of UV light or a solvent, microcapsules break open, the content is released, color is developed, and in this way detection is achieved [40–41].

There are several techniques used for the production of microcapsules. *In situ* polymerization is a chemical microencapsulation process in which the capsule shell formation occurs due to a polymerization process involving specific monomers/prepolymers added to a stable emulsion formed between a continuous solution and an immiscible core material. The relevance of this technology is that no reagents are added to the core material. The polymerization occurs exclusively in the continuous phase (not miscible with the core material). Emulsion crosslinking is Emulsion based preparation, also called emulsion stabilization, or "emulsion crosslinking", is a frequently used method for the preparation of protein- and polysaccharide-based microcapsules and microspheres. This technology may be used for microencapsulate solid agents, as well as, soluble or insoluble liquids. The emulsions can be of two types: single and double emulsions. Particularizing, when using a biopolymer (usually water soluble) to produce microspheres, the emulsions are of single type if the core material is water soluble; and double if the core material is hydrophobic.

Suspension polymerization is a technique where polymerization is carried out in an aqueous phase. In suspension polymerization the initiator is soluble in the monomer phase, which is dispersed into the dispersion medium by strong stirring and by the addition of stabilizers to initiate chain-growth polymerization and therefore droplets form. The polymer is obtained in the form of granules or beads, which may be dried and packed.

Molecular encapsulation using cyclodextrins a ring structured molecule with an internal cavity that makes them able to include guest molecules and therefore confer them new physicochemical properties. Molecular microencapsulation alters the properties of incorporated molecules in many ways, concerning their solubility, thermodynamics, and transport properties. Furthermore, this technology can be valuable to isolate some compounds from natural products, enabling its use in different applications that need to enhance the drug bioavailability and drug formulation stability. Cyclodextrins are compounds made with sugar molecules organized in a ring and have a molecular form like a cone. They develop a hydrophobic cavity which is able to incorporate small or medium molecules. The size and molecular properties of cyclodextrins, influence the stability and properties of the incorporated molecules.

Microencapsulation with cyclodextrins has been used for several years in industry, such as pharmaceutical, chemical and textile and also in environmental research. An example of this application is the incorporation of cyclodextrins in a textile fabric in order to remove the odor. Because of the hydrophobicity of odor molecules they are sequestered in the cyclodextrins cavities and are thereafter removed during laundering.

Coacervation is a physicochemical process for microencapsulation and the most frequently used. It is also called phase separation. This technology appears in the 1950s by National Cash Register Company, USA, and was used to produce a two-component ink system for carbonless copy paper. The concept is based on the capacity of cationic and anionic water-soluble polymers to interact in water thus forming a liquid polymer rich phase, called complex coacervate. Two types of coacervation exist, simple and complex, depending on the type of separation mechanism in the aqueous phase. In the first case, the polymer is formed by changing temperature, by electrolytes action, or by desolvation by addition of a water-miscible non-solvent. In the second case, the polymer is formed by combination of oppositely charged polyelectrolytes in aqueous media. Coacervation is affected by pH, ionic strength, temperature, molecular weight, and concentration.

Fluid bed coating is a mechanical microencapsulation method, which can only be applied when the core material is a solid or a liquid absorbed into porous solids. This technique is used extensively to encapsulate pharmaceuticals. With the increasing number of pharmaceutical sustained release products on the world market, there is also an increasing need for reliable processing equipment, warranting perfect reproducibility of the process parameters and therewith of the film morphology. This technology is well-known, and it owes to its optimal heat and mass exchange that enables a rapid and efficient evaporation of the liquid. The liquid transports the coating material to the surface of the substrate, if the latter is a powder, a granule, a pellet or a tablet. Whenever a solid particle to be encapsulated passes through the coating zone, small patches of coating material are applied, until the entire surface has been covered. Droplet formation, spreading, and evaporation occur almost simultaneously during the process.

The process of suspending, spraying, and cooling is repeated until the capsules walls reached the desired thickness. Usually, air atomized spray nozzles are used for all fluid bed film coating options, as the atomization air allows better control of droplet size compared with airless nozzles. Common target of each option is also to minimize droplet travel distance for uniform and optimal spreadability.

Extrusion technology is an industrial application of extrusion process appeared in 1930. In subsequent years this technology has been developed mainly focusing the plastics processing industry. Extrusion was also applied to other fields, for example, to produce controlled release formulations. The principle of encapsulation using extrusion is that the active agent dissolved in the extruded material will be entrapped after cooling.

The interfacial polymerization technique is described more detailed since it was the technique adopted in this study. Interfacial polymerization is based on a polycondensation reaction and is usually assumed as a simple technique to obtain the capsule wall. It consists in making an emulsion of two non-miscible phases, each one containing a dissolved monomer(s) able to react with the monomer(s) present in the other phase. After the initial formation of the wall, the polycondensation reaction is diffusion controlled. As a consequence, the polymer formation is the result of an interfacial reaction between the monomers, leading to the formation of capsules-like particles.

17.4.1 Application of Microcapsules in Textile Industry

The microcapsules can be applied by stamping works, exhaustion, impregnation, spraying, and coating or by incorporation in the fibber without modifying its sensation and color. In this work, microcapsules were impregnated into the fabrics on the finishing process using a foulard followed by drying and curing steps.

A crosslinking agent is required for the impregnation of microcapsules into the fabrics. This is the component that forms the continuous film, adherent to the substrate, and holds the microcapsules in the fabric. Crosslinking agents can be acrylic, polyurethane, silica, etc. Its function is to fix the microcapsules in the tissue and to keep them fixed during laundering. Several kinds of fabrics can be impregnated with microcapsules as silk, cotton or synthetic fibers (polyamide or polyester).

The processes for applying microcapsules to textile materials can be described as follows:

i. Microcapsules are initially introduced in the textile material (without crosslinking agent) by means of using a dispersant to disperse the microcapsules around and through the textile material followed by the addition of a crosslinking agent to promote adhesion of the microcapsules to the textile material or
ii. Microcapsules are applied during the finishing process of textiles fabrication using a foulard, in which the textile to be treated is impregnated using a finishing bath containing microcapsules, a softener, and a self-crosslinking agent.

Taking into account the type of application the microcapsules have to fulfill specific requirements, such as resistance to abrasion and dry cleaning wash cycles [41].

Khushboo *et al.* [40] in their research work revealed that polyurethane nanocapsules containing *Cassia alata* leaves extract showed antibacterial activity against *S. aureus* on finished cotton fabrics. Polyurethane nanocapsules containing *Cassia alata* leaves extract were synthesized by an emulsion diffusion process. The influences of stirring speed and dilution time were studied on the chemical and physical properties of nanocapsules. Fourier Transform Infrared Spectroscopy was used to study the chemical structure of nanocapsules and *Cassia alata* leaves extract. Size distribution and morphology of nanocapsules were examined using laser particle size analyzer and Scanning Electron Microscopy (SEM) respectively. The dilution time influenced encapsulation yield [40].

Gopalakrishnan in 2011 in his work explained the antibacterial effect of neem oil encapsulated on to the fabric. Micro-encapsulation is done by coacervation method. Gelatin microcapsules containing neem oil as core were prepared by this method. Neem oil was added to the gelatin and the reaction medium acidified to pH 2.0 by addition of 1 molar Hydrochloric acid. It is followed by emulsification and slow addition of NaOH 1 M up to pH 5.0 and the stirring was continued. Cross linking of the gelatin precipitated around oil droplets was performed by the addition of glutaraldehyde 25% aqueous solution. The pH was constantly adjusted to 5.0 the final product was collected after a decantation of the reaction medium, and then freeze-dried. The microcapsules were applied on to the fabric using binder by pad-dry-cure method. It is found that the microencapsulated finish application has more durability in terms of antimicrobial activity after washing than the direct application [43, 44].

Dr. Sumithra [45] showed that microencapsulation prepared from herbal extracts has high effect on finished fabric as Mosquito repellency. Microencapsulation of fabric is done by ionic gelatin process. Microcapsules containing extracts of herbal combinations were prepared employing sodium alginate. 3% sodium alginate was prepared and added 2% nanoparticles. This was sprayed into calcium chloride solution by means of a sprayer. The droplets were retained in calcium chloride for 15 minutes. The microcapsules were obtained by decantation and repeated washing with isopropyl alcohol followed by drying at 45 °C for 12 hours. The microcapsules were then used for finishing on the selected fabrics by pad dry cure method.

In order to increase the durability of the finished fabric, the effective herbal combination in equal proportions was microencapsulated by ionic gelatin method. The microcapsules were finished on the fabric by exhaustion method. The results showed that microencapsulation prepared from herbal extracts finished fabric was able to retain the efficiency of Mosquito repellency even after 25 industrial washes [45].

Anitha *et al.* [46], during 2011 in their study revealed that natural material, lemongrass oil is being capable of repelling mosquito on the fabric to a greater extent. The microcapsules of lemongrass oil extract were prepared with sodium alginate by Ionic Gelation Process. The microcapsules were then used for finishing on the selected fabrics by Pad dry cure method and used for checking the mosquito repellency property. The microencapsulated lemongrass oil extract was also studied for its repellency abilities and compared with the extract finished fabrics. The results showed 92% repellency activity for the polyester fabric finished with the lemongrass aqueous extract microcapsules. Whereas, the polyester fabric exhibited only 80% mosquito repellency activity finished with methanolic microcapsules of lemongrass leaves [46].

17.5 Conclusion

Nanotechnology and its allied field of research have boosted the textile dye industry economically as well as provided with new patterns and innovative textures. Also, the technology provides an environment-friendly outcome which is the major stress in any advancement. For past few decades, nanotechnology had become an inseparable part of the dye industry for its pros. In the chapter, nanotechnology on dye for cotton fabrics, wool fabrics, improvement of dyeing with encapsulation technology, and various finishing using nanotechnology as required by the applications were discussed. Textile industry being the evergreen commercial sector built on the needs of humankind, and the nanotechnology being the progressing field that re-invents itself every day, have come together to create a better economical global market. It is to be mentioned that the progress and inventions in this field are far beyond the scope of this chapter.

References

1. Nahed, S.E.A and El-Shishtawy, R.M., The use of new technologies in coloration of textile fibers. *J. Mater. Sci.*, 45, 1143–1153, 2009.
2. Wong, Y.W.H, Yuen, C.W.M, Leung, M.Y.S, Ku, S.K.A, Lam H.L.I., Selected applications of nanotechnology in textiles. *AUTEX Res. J.*, 6(1), 1–8, 2006.
3. Russell, E., Nanotechnologies and the shrinking world of textiles. *Text. Horiz.*, 9/10, 7–9, 2002.
4. D.R. Cramer, A.E. Ponomarenko, S. Laurent, J.C.T.R. Burckett, Method of applying nanoparticles, US Patent 6, 645,569, 2003.
5. Allègre, C., Moulin, P., Maisseu, M., Charbit, F, Treatment and reuse of reactive dyeing effluents. *J. Membr. Sci.*, 269, 15–34, 2006.
6. Fang, K., Wang, C., Zhang, X., Xu, Y., Dyeing of cationized cotton using nanoscale pigment dispersions. *Color Technology*, 121, 325–328, 2005.

7. Sampaio, S., Martins, C., Gomes, J.R., Colored nanoparticles for ecological dyeing of cellulosic fibres. *Adv. Mater. Res.*, 332–334, 1136–1139, 2011.
8. Bala, R., Behal, J., Kaur, V., Jain, S.K., Rani, R., Manhas, R.K., Prakash, V, Sonochemical synthesis, characterization, antimicrobial activity and textile dyeing behavior of nano-sized cobalt(III) complexes. *Ultrason. Sonochem.*, 35, 294–303, 2017.
9. Shahid-ul, I. and Faqeer, M., High-energy radiation induced sustainable coloration and functional finishing of textile materials. *Ind. Eng. Chem. Res.*, 54(15), 3727–3745, 2015.
10. Chinta, S.K., Landage, S.M., Swapnal, J., Water repellency of textiles through nanotechnology. *Int. J. Adv. Res. IT Eng.*, 2(1), 36–57, 2013.
11. Leadley, J., Sermon, P., Fluoroalkylsilane modification of sol-gel SiO_2-TiO_2 coatings. *J. Sol-Gel Sci. Technol.*, 32(1–3), 293, 2004.
12. Holme, I., Water repellency and waterproofing, in: *Textile Finishin, Society of Dyers and Colourists*, D. Heywood (Ed.), 137–213, West Yorkshire, UK, 2003.
13. Halbur, C.J., *Co-presence of durable flame retardant and repellent nano-finishes*, Thesis, 1–126, 2010.
14. Gilman, J.W., *New flame retardants consortium*, National Institute of Standards and Technology, 6357, 1999.
15. Xue, C.H., Li, Y.R., Ping, Z., Jian, Z.M, Jia, S.T., Zhang, J., Tian, L.Q., Washable and wear-resistant superhydrophobic surfaces with self-cleaning property by chemical etching of fibers and hydrophobization. *ACS Appl. Mater. Interfaces*, 6, 10153–10161, 2014.
16. Prathapan, R., Venkatesan, A.G., Nair, S.V., Nair S., A review on 'self-cleaning and multifunctional materials'. *J. of Materials Chemistry A: Materials for Energy and Sustainability*. 2. 14773–14797. 2014.
17. Naresh, M.S., Ashok, G.S., Vaishali, R., Antimicrobial finish: strengthening the next generation, *Sarex Antimicrobial: Santex Santashrink.qxd*, 10:14, 34, 2011.
18. Sheila, S. and Jakub, W., Antibacterial agents in textile industry, in: *Antimicrob. Agents*, Dr. Varaprasad Bobbarala (Ed.), InTech, 2012.
19. Patra, J.K. and Gouda, S., Application of nanotechnology in textile engineering: An overview. *J. Eng. Technol. Res.*, 5(5), 104–111, 2013.
20. Deepti, G. and Somes, B. Antimicrobial treatments for textiles. *Indian J. Fibre Text. Res.*, 32, 254–263, 2007.
21. Franci, G., Falanga, A., Galdiero, S., Palomba, L., Rai, M., Morelli, G., Galdiero, M., Silver nanoparticles as potential antibacterial agents. *Molecules*, 20(5), 8856–8874, 2015.
22. Lee, H.J., Yeo, S.Y., Jeong, S.H., Antibacterial effect of nanosized silver colloidal solution on textile fabrics. *J. Mater. Sci.*, 38, 2199–2204, 2003.
23. Nadanathangam, V., Sampath, K., Kathe, A.A., Varadarajan, P.V., Virendra, P., Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites. *Nanotechnology*, 17, 5087–5095, 2006.
24. Sundaresan, K., Sivakumar, A., Vigneswaran, C., Ramachandran, T., Influence of nano titanium dioxide finish, prepared by sol-gel technique, on

the ultraviolet protection, antimicrobial, and self-cleaning of cotton fabrics. *J. Ind. Text.*, http://jit.sagepub.com/content/early/2011/09/08/1528083711414962, 2011.

25. Chaudhari, S.B., Mandot, A.A., Patel, B.H., Effect of nano TiO_2 pretreatment on functional properties of cotton fabric. *Intl. J. Eng. Res. Dev.*, ISSN:2278-067X, 1(9), 24–29, 2012.
26. Busi, E., Maranghi. S., Corsi, L., Basosi, R., Environmental sustainability evaluation of innovative self-cleaning textiles. *J. Cleaner Prod.*, 133, 439–455, 2016.
27. Maruf, M., Self-cleaning cloths based on nano technology, http://textilelearner.blogspot.in/2013/08/self-cleaning-cloths-based-on-nano_19.html, 2013.
28. Senthil, B.K., Self-cleaning finish on cotton textile using sol-gel derived TiO_2 nano finish. *J. Polym. Text. Eng., [IOSR-JPTE]*, e-ISSN: 2348-019X, p-ISSN: 2348-0181, 2(1), 1–5, 2015.
29. Md. Ruhul, A., Application of nanotechnology in textile finishing, http://textilelearner.blogspot.in/2013/04/application-of-nanotechnology-in.html, 2013.
30. Kamal, K.G., Manjeet, J., Ashwini, K.A., Functional finishing of cotton using titanium dioxide and zinc oxide nanoparticles. *Res. J. Text. Apparel*, 11(3), 1–10, 2007.
31. Nidhi, G., Deepali, R., Manjeet, J., Ashwini, K.A., Dispersion stabilization of titania nanoparticles for textile: aggregation behavior and self-cleaning activity. *J. Dispers. Sci. Technol.*, 34(5), 611–622, 2013.
32. Pedro, J.R., Aitor, U., Javier, G., Francisco, J.A., Nanomaterials for functional textiles and fibers. *Nanoscale Res. Lett.*, 10(501), 2015.
33. Cheng, X.W., Guan, J.P., Yang, X.H., Tang, R.C., Improvement of flame retardancy of silk fabric by bio-based phytic acid, nano-TiO_2, and polycarboxylic acid. *Progr. Organ. Coat.*, 112, 18–26, 2017.
34. Subrata, C.D., Debasree, P., Mahamudul, Sk.M.H., Nasif, C., Sudipta, B., Application of nanotechnology in textiles: a review, International Conference on Mechanical Engineering and Renewable Energy 2013, [ICMERE2013], Chittagong, Bangladesh, ICMERE2013-PI-120, 2014.
35. Asmaa,F.A.S,Usingnanotechnologyinthefinishingofcellulosicfabrics,https://duepublico.uni-duisburg-essen.de/servlets/DerivateServlet/Derivate-26192/thesis_Asmaa_farouk.pdf, 2011.
36. Patel, B.H. and Chattopadhyay, D.P., Nano-particles & their uses in textile, *Indian Text. J. Nanotechnol. Nano-Mater. Text.*, http://www.essay.uk.com/free-essays/science/nanotechnology-nano-materials-textiles.php, 2007.
37. Kurapati, S., The role of nanotechnology in modern textiles. *J. Chem. Pharm. Res.*, 8(6), 173–180, 2016.
38. Jeevani, T., Nanotextiles: A broader perspective. *J. Nanomed. Nanotechnol.*, 2(7), 2011.
39. Yetisen, A.K., Hang, Q., Amir, M., Haider, B., Mehmet, R.D., Juan, P.H., Maksim, S., Ali, K., Seok, H.Y., Nanotechnology in textiles. *ACS Nano*, 10, 3042–3068, 2016.

40. Khushboo, S. and Ela, M.D., Microencapsulation for textile finishing, *IOSR J. Poly. Text. Eng. [IOSR-JPTE]*, 2(2), 1–4, 2015.
41. Ocepek, B. and Forte, T.P., Microencapsulation in textiles, http://impascience.eu/bioencapsulation/340_contribution_texts/2008-09-04_P48.pdf, 2008.
42. Chinta, S.K. and Wane, P.P., Imparting antimicrobial finish by microencapsulation technique. *Intl. J. Innov. Res. Sci. Eng. Technol.*, 2(6), 2326–2336, 2013
43. Rezwan, M., Farhatun, N., Application of nanotechnology in the field of textile, *IOSR J. Polym. Text. Eng. [IOSR-JPTE]*, 2348–0181, 4(1), 1–6, 2017.
44. Gopalakrishnan, D. and Aswini, R.K., Antimicrobial finishes, *Melliand Intl. J.*, 8, 148–151, 2002, http://www.scribd.com/doc/51654914/antimicrobialfinishes.
45. Sumithra, M. Effect of insect repellent property using microencapsulation technique. *World J. Pharm. Res.*, 5(4), 715–719, 2016.
46. Anitha, R., Ramachandran, T., Rajendran, R., Mahalakshmi, M. Microencapsulation of lemon grass oil for mosquito repellent finishes in polyester textiles. *Elixir Int. J., Elixir Bio. Phys,* 40, 5196–5200, 2011.

18

Sol–Gel Flame Retardant and/or Antimicrobial Finishings for Cellulosic Textiles

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Abstract

Cotton and cellulosic textiles easily burn when exposed to a flame or a heat source: this detrimental effect significantly limits the possible applications of these materials, especially where flame retardant fibers and fabrics are specifically required. As a consequence, one of the possible solutions may exploit surface engineering methods that aim at creating fully inorganic or hybrid organic-inorganic protective coatings on the fiber/fabric surface. This way, it is possible to reduce and limit the heat and mass transfer phenomena that take place during the fire stages: in fact, according to its structure and composition, the obtained coating is able to form a fully ceramic or a hybrid organic–inorganic protective layer on the underlying textile, hence providing this latter with the required flame retardant features. One of the most effective approaches utilizes the sol–gel technique, which is a very well consolidated approach for the fabrication of ceramics, but has started to be exploited also in the textile field because of its advantageous characteristics: among them, it is easily applicable to even irregular substrates as fibers and fabrics, it can be carried out using the already existing industrial finishing lines (such as impregnation/exhaustion units) and it is very efficient in providing the treated substrates with flame retardant features. Besides, it is possible to tailor the sol–gel derived coatings in order to provide the treated fibers/fabrics with more than a single functionality: in particular, the scientific literature reports on the use of sol–gel formulations that exhibit antimicrobial properties, too. Furthermore, the sol–gel method usually provides good washing fastness to the treated textiles, hence widening their possible applications.

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This chapter is aimed at summarizing the recent advances on the use of sol–gel treatments as efficient flame retardant and also antimicrobial systems; in particular, some recent examples are discussed, highlighting the further potential developments of this textile finishing technique and its current limitations.

Keywords: Antimicrobial finishing, flame retardant finishing, cotton, sol–gel processes, surface engineering, semi(metal)alkoxides

18.1 Introduction

If not inherently flame retarded or modified on purpose, most of the textile products are flammable: the annual U.K. fire statistics document that a considerable percentage of the fire incidents occur in the home and involve nightwear, bedding, and upholstered furniture [1].

In order to fulfill this requirement, from the 1950s, both the academic and industrial community has been involved in the design and development of efficient flame retardants (FRs), which are aimed at lowering the risk of fire: more specifically, they are able to decrease the ease of flammability of textiles by reducing the propensity of the material to ignition or slowing down the flame spread rate when required.

Generally speaking, because of the oxidative character of flaming combustion, this reaction, occurring in the gas phase, requires oxygen (or air) supply from the surrounding atmosphere. Flaming combustion is subsequent to the occurrence of the polymer degradation: this latter gives rise to the formation of combustible gaseous species, which mix together with atmospheric oxygen and promote a self-sustaining combustion process, exploiting the high exothermicity of the flame.

FRs are able to delay or even stop this self-sustaining combustion process of the textile material: according to their structure and chemical composition, they can act either in condensed or gas phase. In addition, the overall effects on either burning rate reduction or on the extinction of the flame are also dependent on chemical composition and on the thermal and fire characteristics of the textile material [2–5].

Besides, any of the FRs available on the market or specifically designed for scientific purposes contains certain elements in their molecule, such as halogens, metals, boron, phosphorus, sulfur, nitrogen, or a combination of them; the FR can be incorporated in the synthetic fibers during the spinning processes or can be covalently linked to the fibers, exploiting grafting or copolymerization reactions. Another possibility involves the application of FRs as surface treatments i.e. using a surface-engineered approach) that exploit either the impregnation of the textiles in solutions/

stable suspensions containing the FR additive (i.e. a standard finishing treatment), or the coating of the textile substrate with a continuous or discontinuous layer/film on both outer and back surfaces.

In doing so, if these treatments are very effective in providing the textile material with FR features, several outcomes should be attained:

- the heat developed should be lower than that necessary for sustaining the combustion process;
- the textile pyrolysis should be addressed towards the formation of a carbonaceous residue (i.e. char) in condensed phase, hence limiting the formation of flammable products that can fuel the combustion;
- the flame should be separated from the oxygen/air source;
- depending on the chemical composition of the FRs, chlorine or bromine atoms, which behave as flame inhibitors in gas phase, should be released as the textile material approaches the ignition temperature;
- the heat flow back to the textile substrate should be decreased: this limits the occurrence of additional pyrolysis reactions, suitable for the formation of gaseous flammable products;
- upon exposure to a heat flow or a flame, the creation of a barrier, usually consisting of an intumescent protective coating or a char, should be favored.

The toxicity issues arisen from the use of such halogenated FRs as polychlorinated biphenyls and pentabromodiphenyl or decabromodiphenyl ethers [6–8] have pushed both the academic and industrial world towards the seeking for less toxic products with low environmental impact. In this contest, phosphorus-based FRs have been identified as possible alternatives for replacing halogenated FRs [9, 10].

In parallel, the FR behavior of cotton and cellulosic-rich substrates has been remarkably enhanced by either designing efficient halogen-free FR products for coatings and back-coated textiles, or by using N-methylol phosphonopropionamide derivative (Pyrovatex®)/hydroxymethylphosphonium salts (Proban®).

Both these two commercially available FRs exhibit some pros and cons: more specifically, Proban® process requires a dedicated plant for stabilizing the treated fabrics; furthermore, there may be formaldehyde release during the fabric use [11]. On the other hand, Pyrovatex® process allows permanently fixing just about 50% of the FR product on the cellulosic substrate: all the rest is lost during the first washing cycle, the flame retarded fabric is subjected to.

From an overall point of view, the replacement of commercially available FR products with equivalent alternatives is not easy at all. In fact, several requirements have to be satisfied: among them, it is worthy to mention the need of comparable behavior as far as the textile service-life (in terms of durability, comfort and mechanical features) is considered. In addition, the alternative products should not exhibit higher toxicological and environmental issues with respect to the standard counterparts, notwithstanding that they should not affect either the fabric dyeability or outward appearance and aesthetics.

All these requirements stimulated the scientific and industrial community towards the seeking for valuable alternative FR treatments and products. In this context, sol–gel processes, which represent a very well established approach for the fabrication of ceramic materials, started to be exploited also in the textile field about 15 to 20 years ago, aiming at providing the treated fabrics with different functional features.

Undoubtedly, the sol–gel approach can be successfully applied to even as irregular substrates as textiles, using the already existing industrial finishing lines. Besides, the sol–gel treatments exhibit a good washing fastness, hence providing the treated substrates with durable features and widening their potential exploitation.

This way, it is possible to design multifunctional sol–gel treatments, mainly comprising flame retardancy and antimicrobial activity.

This chapter aims at summarizing the latest advances on the use of sol–gel treatments as efficient FR and/or antimicrobial systems; in particular, the recent scientific literature is discussed, emphasizing the further potential progresses of this textile finishing approach and its current limitations.

18.2 The Sol–Gel Process

The sol–gel technique is a synthetic approach suitable for designing new materials with a high degree of homogeneity at the molecular scale and with exceptional physico-chemical features. From an overall point of view, it exploits two-step hydrolysis/condensation reactions of selected reactive precursors (i.e. (semi)metal alkoxides). Among these latter, tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), aluminum isopropoxide and titanium tetraisopropoxide are frequently employed. As a result, fully inorganic or hybrid organic–inorganic coatings at or near room temperature can be obtained, according to the scheme shown in Figure 18.1.

The progress of the sol–gel reactions and the structure/morphology of the resulting oxidic 3D networks are affected by the selected experimental

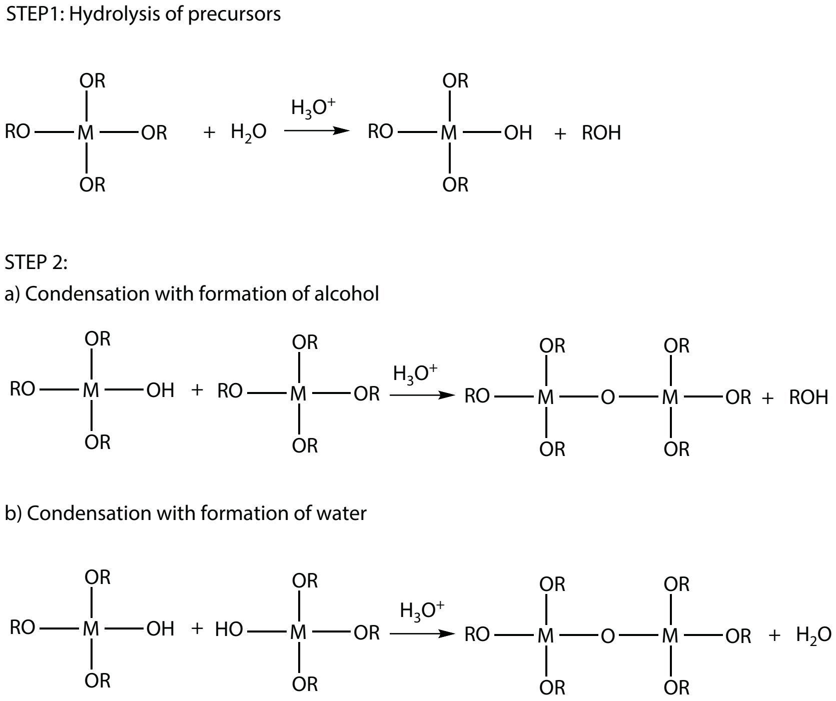

Figure 18.1 Sol–gel reactions carried out in acidic conditions (M=(semi)metal, such as Ti, Si).

parameters, namely: type of (semi)metal atom and alkyl/alkoxide groups, pH and temperature, water/precursor ratio, reaction time and presence of co-solvents [12].

Though the sol–gel methods appeared in the 1950s, their exploitation for the design of flame retarded and/or antimicrobial textiles are quite new and appealing for several reasons.

First of all, the ceramic phases (in the form of particles or coatings), *in situ* generated on the fabric substrate, can exert a thermal shielding effect during the exposure of the fabrics to a flame or a heat source.

As a consequence, a physical ceramic barrier to oxygen and heat transfer is created on the fabric surface, limiting the formation of volatile combustible species that fuel the further fabric degradation and favoring the development of a stable carbonaceous/inorganic residue [12, 13].

On the other hand, as the fabric substrate shows a limited thickness, only a partial shielding effect is provided by the sol–gel coatings on the fabric: as a consequence, it is possible to achieve acceptable FR properties only when the sol–gel derived ceramic phases are able to develop synergistic or at least

Table 18.1 Main characteristics of sol–gel finishing processes performed on fabrics.

Key approach	chemistry-based process usually accompanied by the formation of low MW by-products
Process sustainability	usually low, because of the utilization of impacting chemical precursors
Compatibility with existing textile finishing processes	good (it is possible to exploit standard industrial impregnation/exhaustion techniques)
Comfort of the treated textiles (in terms of stiffness and soft touch)	fair, depending on the use of fully inorganic or hybrid precursors
Durability (washing fastness)	usually good
Multifunctionality of the treatment	achievable, according to the sol–gel recipe

joint effects with other FR additives. Among these latter, phosphorus and/or nitrogen-containing species are efficient and exploitable systems.

In addition, it is possible to effectively utilize the sol–gel technique in dual-cure systems, for which a photo-induced polymerization process of organic reactive monomers is followed by a thermal treatment (in order to carry out the sol–gel reactions). This way, it is possible to design hybrid organic–inorganic FR coatings [14, 15].

The main pros and cons of the sol–gel finishing processes are listed in Table 18.1.

Next paragraphs will describe the structure-property relationships for sol–gel derived coatings, according to the following classification: inorganic coatings, phosphorus-doped coatings, hybrid organic–inorganic coatings.

18.2.1 Sol–Gel Fully Inorganic Coatings

Fully inorganic coatings are the most common types of sol–gel derived products, as well as the first, which have been successfully applied to fabrics in order to provide them with FR features. In a pioneering paper, Hribernik and co-workers utilized 350 nm thick silica coatings, aiming to lower the flammability of viscose fibers [16]. In particular, tetraethylorthosilicate (TEOS) was selected as silica precursor for the formulation of the sol solution. The treated fibers showed significant enhancements as far as their thermal stability and fire behavior are considered: more specifically, unlike neat viscose, the sol–gel treated fibers exhibited 20 °C increase of the first thermal degradation step and of the flame combustion of gaseous products; furthermore, the gloving combustion of the residue showed a appreciable 40 °C temperature increase.

Pursuing this research, Malucelli and co-workers investigated the fire resistance and the combustion behavior of cotton, polyester and cotton/polyester-rich blends treated with the same TEOS-derived coating [17]. This latter was able to delay the thermal degradation reactions occurring in nitrogen and air, as revealed by thermogravimetric analyses; in addition, cone calorimetry tests showed a decreased of the peak of the heat release rate (pkHRR) and an increase of the time to ignition (TTI) in the presence of the sol–gel derived coatings.

Then, the effect of the structure, composition of the sol–gel coatings and of the adopted experimental parameters was thoroughly investigated: to this aim, sol–gel reactions involving different types of alkoxy precursors were carried out on cotton fabrics, assessing the influence of time and temperature of the thermal treatment, and of the precursor:water molar ratio as well, on the morphology and overall fire performances of the obtained coatings [18]. More specifically, the most performing treatments were attained performing the sol–gel reactions at 80 °C for 15 h, using a 1:1 water:tetramethylortosilicate (TMOS) molar ratio. In fact, the resulting treated fabrics exhibited a significant reduction of pkHRR (−15%), hence demonstrating the coating effectiveness as thermal insulator, which is able to address the fabric degradation toward cellulose dehydration, with the development of a stable carbonaceous (aromatic) residue [13].

Then, the effect of the type of hydrolyzable groups in the alkoxy precursor on the fire retardant properties of cotton fabrics was studied, considering three different compounds, namely: TMOS (4 methoxy groups), TEOS (4 ethoxy groups) and tetrabuthylorthosilicate (TBOS, with 4 buthoxy groups) [19]. Vertical flame spread tests confirmed that the silica coating was capable to lower the burning rate (from 2.50 to 1.45 mm/s for untreated cotton and the TMOS-treated fabric, respectively), hence to increase the total burning time. Furthermore, a remarkable final residue at the end of the test was observed: in fact, as compared to the untreated fabric, for which the residue was 10 wt.%, the fabric substrates treated with TMOS and TEOS showed higher values (namely, 48 and 35 wt.%, respectively). Therefore, the flame spread decrease was strictly dependent on the alkoxy precursor chain length: in other words, the shorter was the chain length, the higher was the reduction. Similar trends were obtained from cone calorimetry tests.

In order to assess the relationship between the number of hydrolysable groups of the alkoxy precursor and the burning behavior under the cone, forced combustion tests were carried out on cotton fabrics treated with TEOS and other hydrolysable precursors, namely: 3-aminopropyl trimethoxysilane (APTES), triethoxy(ethyl)silane (TEES), 1,2-bis(triethoxysilyl) ethane (bTESE), diethoxy(methyl)phenylsilane (DEMPhS) and 1,4-bis(triethoxysilyl)benzene (bTESB) [20]. The presence of a different number of ethoxy groups (within 2 and 6) and the potential existence of phenyl rings were responsible for the overall fire behavior of the designed systems. More specifically, cone calorimetry tests revealed that:

- the presence of a limited number (i.e. 2 or 3) of hydrolysable groups in the alkoxy precursor shows an overall fire behavior very similar to that provided by TEOS, but with a remarkable and detrimental rise of smoke release; in addition, the formation of very thin and incoherent residues was observed at the end of the forced combustion tests;
- the replacement of amino groups (APTES) with alkyl chains (TEES) promotes the creation of a compact and thicker residue;
- the presence of a high number of hydrolyzable groups in the alkoxy precursor (as in bTESE and bTESB compounds) significantly affects cotton flammability: in particular, bTESB-treated cotton did not burn even when repeatedly ignited (i.e. with 10 flame applications of 5 s).

Pursuing this research, the FR features provided to cotton by the aforementioned silica coatings (from TEOS) were compared with alumina, zirconia or titania counterparts, derived from sol–gel reactions performed on aluminum isopropylate, tetraethylortho-zirconate, and tetraethylortho-titanate precursors, respectively. Thus, it was possible to assess the effect of the type of (semi)metal of the alkoxy precursor on the fire retardancy achieved by the treated fabrics [21]. Silica coatings were the best performing, showing 56% TTI increase and 20% pkHRR decrease in cone calorimetry tests; conversely, alumina- and titania-based coatings provided the fabrics with the highest abrasion resistance values.

These outcomes further addressed the research work towards the use of silica coatings embedding Al_2O_3 micro- or nanoparticles, which could not only improve the fire behavior of the treated cotton, but also its tribological features. The resulting sol–gel coatings, irrespective of the size of Al_2O_3 particles, turned out not only to increase the abrasion resistance of the underlying fabric, but also to lower the total burning time (−45%) and to favor the formation of a compact and coherent final reside (+46%) at the end of horizontal flame spread tests [22].

A similar behavior was observed for cotton fabrics treated with a with a silica-alumina xerogel [23].

18.2.2 Phosphorus-Doped Sol–Gel Coatings

The occurrence of synergistic or joint effects between sol–gel oxidic phases and other FRs can be successfully exploited for further enhancing the fire behavior of sol–gel treated fabrics.

Among all the possible systems, those preferred usually comprise phosphorus or phosphorus and nitrogen elements [24–32].

Three possible approaches can be adopted, namely:

- the use of alkoxysilane precursors bearing either silane or phosphate groups
- the design of tailored mixtures of an alkoxysilane precursor with a phosphoric acid source
- the incorporation of an alkoxysilane precursor that contains both silane and phosphate functionalities into phosphorus- and nitrogen-based structures.

The first approach implies the concurrent presence of P and Si elements in the alkoxy precursor: this way, the coating formed on the fabric surface is responsible for i) the formation of a mixed carbonaceous and inorganic residue (due to the activation of the phosphoric acid source) and for ii) the creation of a ceramic protective layer.

In this context, diethylphosphatoethyltriethoxysilane (DPTES) was exploited as an alkoxysilane precursor bearing phosphate groups for obtaining a hybrid phosphorus-silicon organic/inorganic coating on cotton: in particular, the sol–gel process was applied using a multistep technique, hence depositing 1 to 6 layers on the fabric substrate [28]. Cone calorimetry tests showed a significant decrease (up to 43%) of the combustion time of the treated fabrics with respect to the untreated ones: in fact, flame out values were remarkably lowered (66, 62 and 80 vs. 116 s for 1, 3 and 6 layers and the untreated fabric, respectively).The designed hybrid coatings also limited the development of volatile species, as shown by the low TSR values (20, 15 and 6 vs. 26 m^2/m^2 for 1, 3 and 6 layers and the untreated fabric, respectively).

Pursuing this research, the hybrid phosphorus-silicon organic/inorganic coatings were further optimized by encompassing a pre-hydrolysis step of the alkoxy precursor [29]: this way, it was possible to improve the resistance to washing of the flame retarded substrates, which were capable of facing up to 5 washing cycles according to the ISO 6330 standard.

DPTES was then utilized in combination with APTES or with APTES and a melamine-based resin – MR, N-source – in order to assess the possible occurrence of synergistic effects [30]. The designed coatings were responsible for the increase of the char formation, as indicated by the high residues found after thermogravimetric tests carried out in air (42 and 38 wt.% for APTES/DPTES- and APTES/DPTES/MR-treated samples, respectively).

Then, the melamine-based resin was replaced with N,N,N',N',N",N"-hexakis-methoxymethyl-[1,3,5] triazine-2,4,6-triamine (HMT), optimizing the relative ratios of the two components [32]: the high char-forming behavior of the resulting coatings was proven by the remarkable increase of the final residue (around 70 wt.%). Lewin's synergistic effectivity [33] was exploited for assessing possible synergistic or additive effects: these latter were found in N-doped hybrid phosphorus-doped silica coatings; conversely, hybrid phosphorus-doped silica coatings combined with 1-hydroxyethane 1,1-diphosphonic acid showed synergism in between the two components.

Besides, it was possible to assess synergism for the sol–gel derived coatings applied on cotton and combined with such phosphoric acid sources as ZrP nano-platelets, aluminum phosphinate, or a mixture of aluminum phosphinate, zinc and boron oxide and melamine poly(phosphate) [25]. In cone calorimetry tests, the treated fabrics showed a remarkable TTI increase (from 14 – untreated cotton – to 40 s); furthermore, LOI values turned out to increase from 19% (untreated fabric) to 30% (formulations containing the sol–gel precursor added of 5 wt.% of the selected phosphorus-based compounds).

Very recently, Kappes and co-workers designed a new formulation of sol–gel derived coating, based on the combination of (3-trimethoxysilylpropyl)diethylenetriamine and phenylphosphonic acid, for providing FR features to different fabrics (namely, polyester, cotton and a 65:35 cotton:polyester blend) [34]. The final dry add-on was kept below 10%, in order to avoid any detrimental effect on the comfort of the treated fabrics. The creation of a protective coating on the fabric surface provided self-extinguishing features to the treated substrates, as assessed by EN ISO 15025 small-scale flame tests with surface and edge ignition.

18.2.3 Smoke Suppressant Sol–Gel Coating Formulations

Sol–gel coatings have also been exploited in combination with smoke suppressants: this way, it is possible to confer not only the expected FR

Table 18.2 Influence of the presence of different smoke suppressants in sol–gel derived coatings applied to cotton, as assessed by cone calorimetry tests (adapted from [36]).

System	CO (ppm)		CO_2 (%)	TSR (m^2/m^2)
	1st Peak	2nd Peak	Peak	
Cotton	0.0011	0.0018	0.146	24
Cotton + silica coating	0.0005	0.0045	0.112	11
Cotton + silica coating + Zinc acetate dihydrate	0.0004	0.0040	0.110	18
Cotton + silica coating + Zinc oxide	0.0002	0.0032	0.095	9
Cotton + silica coating + Zinc borate	0.0004	0.0040	0.108	17

features to the underlying fabric, but also to limit the smoke production during a flame application, which is a desirable effect. It is noteworthy that silica nano- or micro-particles or sol–gel derived silica coatings represent some efficient smoke suppressants [35].

There are several smoke suppressants that can be added to selected alkoxy precursors in order to limit total smoke release, as well as CO and CO_2 yields; among them, it is worthy to mention zinc oxide, zinc acetate dehydrate and zinc borate [36]. Their effect, evaluated through cone calorimetry tests performed on the sol–gel treated cotton fabrics, is depicted in Table 18.2: in particular, these smoke suppressants were able to lower the smoke release, as demonstrated by the reduction of TSR values, as well as to limit the production of CO and CO_2, when added to the sol–gel coating formulation.

18.2.4 Hybrid Organic–Inorganic Sol–Gel Coatings

In order to provide FR features to cotton fabrics, it is possible to design dual-cure processes that allow obtaining hybrid organic–inorganic coatings on the fabric surface: this strategy combines the photocuring reaction of reactive monomers and/or oligomers with a subsequent thermal treatment that allows the occurrence of the sol–gel process [14, 37, 38]. As a consequence, a hybrid co-continuous network is formed, which acts as a thermal insulator and usually is able to withstand washing cycles without losing its FR features.

The first pioneering work reported on the use of a UV-curable acrylic formulation comprising different amounts of TMOS (ranging in between 30 and 80 wt.%), together with methacryloyloxypropyltrimethoxysilane (MEMO) as a coupling agent [15]. In fact, the resulting system is able to undergo the photo-curing process, exploiting the reactivity of the acrylic functionalities and the subsequent sol–gel process, thanks to the methoxy groups of the alkoxy precursor, which can also react with the hydroxyls located on the cellulosic substrate. The further presence of MEMO allows coupling the organic and inorganic phases, hence giving rise to the formation of a 3D protective network. Total burning time and final residue of the fabrics treated with the hybrid sol containing 60 wt.% of TMOS were found to increase in horizontal flame spread tests, with respect to untreated cotton. Furthermore, the coated fabrics, tested under the cone calorimeter (heat flux: 35 kW/m^2) exhibited an increase of both TTI and final residue, notwithstanding a growth of THR and pkHRR values.

Xing and co-workers designed an UV-curable system containing triglycidyl isocyanurate acrylate and tri(acryloyloxyethyl)phosphate, aiming at providing cotton fabrics with FR features [39]. In particular, microscale combustion calorimeter and limiting oxygen index tests were exploited for assessing the effectiveness of the resulting FR coatings: pkHRR, heat release capacity and total heat of combustion were lowered because of the presence of the hybrid coating. Conversely, this latter was responsible for a limited rise in LOI values.

Very recently, Przybylak and co-workers designed a two-step process for providing multifunctional features (i.e. flame retardancy and superhydrophobicity) to cotton fabrics [40]. For this purpose, ammonium dihydrogen phosphate and/or guanidine carbonate were first embedded into a sol–gel coating derived from aminopropyltriethoxysilane: this treatment allowed providing significant FR features to the cellulosic substrate. By further modifying the FR formulation through the addition of a polysiloxane or a fluorofunctional silane, the flame retarded fabrics gained hydrophobicity, too. Synergistic effects between phosphorus- and nitrogen-containing compounds as well as organosilicon structures were observed: as a consequence, LOI values as high as 71.6% and 90% reduction in Qmax (i.e the maximum specific heat release rate assessed in Pyrolysis-Combustion Flow Calorimetry tests) were measured for the treated fabrics.

Very recently, Liu and co-workers applied a hybrid organic–inorganic coating based on APTES and phenylphosphonic dichloride on cotton fabrics, exploiting a sol–gel process [41]. The fire behavior of the obtained coatings was investigated through vertical flame spread and microscale combustion calorimetry tests: the design coatings provided cotton fabrics with self-extinction, notwithstanding an increased thermal stability, as assessed by thermogravimetric analyses. These results were attributed to the deposited hybrid coatings that, upon heating, allow the creation of a ceramic protective and thermal insulating layer on the underlying fabric, hence favoring the formation of an aromatic thermally stable char, which efficiently restricts the oxygen and heat transfer phenomena occurring during the application of a flame/heat flux.

18.2.5 Antibacterial Effects Provided by Sol–Gel Coatings

As clearly reported in the scientific literature, it is possible to design tailored sol–gel coatings that exhibit antimicrobial properties, apart from the fire retardant features described in the previous paragraphs. In particular, these sol–gel antimicrobial coatings are able to inhibit possible biocontamination phenomena. Three different types of sol–gel antimicrobial coating formulations for fabrics (Figure 18.2) can be designed, namely:

- Photoactive coatings containing titania: they show permanent antimicrobial properties, which can be activated by exposing the treated fabrics to UV radiation. This way, photomineralization processes take place on treated fabrics [42];
- Polycationic coatings: similarly to the photoactive coatings, they show permanent antimicrobial properties; furthermore, they derive from the hydrolysis of long-chained tetraalkylammoniumsilane precursors [43];
- Sol–gel coatings embedding inorganic (namely, copper, silver or boric acid) or organic biocides: they show temporary antimicrobial properties and a controlled release of the antimicrobial agents [44]. Furthermore, this seems the most

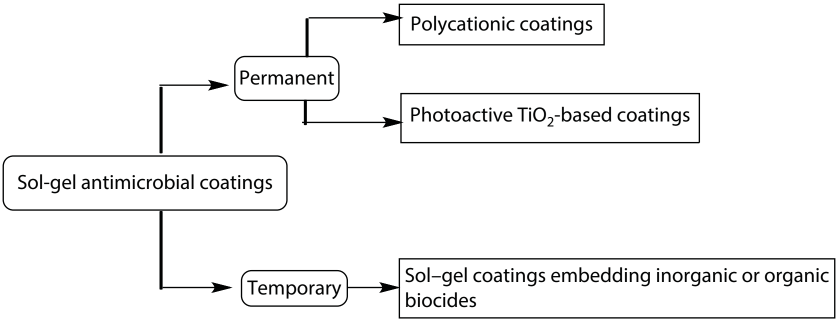

Figure 18.2 Classification of sol–gel antimicrobial coatings.

> performing approach for conferring antimicrobial properties to textiles, also considering the wide availability of different types of biocides.

Sol–gel silica coatings embedding silver, silver salts or biocidal quaternary ammonium salts (namely, octenidine, and cetyltrimethylammoniumbromide) were synthesized on purpose for providing antimicrobial properties to cotton/polyester blends. More specifically, the resulting sol–gel coatings were capable to prevent the growth of fungi and bacteria, especially when containing octenidine or silver [45].

Silica sols from water glass were first applied to cotton fabrics; then, the resulting modified substrates were treated with a solution of silver nitrate, aiming at assessing the antimicrobial activity against *Escherichia coli* [46]. The proposed treatments were found to provide a remarkable antimicrobial effect, which was maintained even after 50 washing cycles. In addition, as demonstrated by XPS analyses, the antimicrobial activity was ascribed to the presence of silver on the fabric surface in two different oxidation states (namely, Ag^{+} and Ag^{2+}).

Cotton fibers were treated with a commercially available fluoroalkyl-functional water-borne siloxane, in the presence of silver nanoparticles and of a reactive organic–inorganic binder by Tomsic *et al.* [47]: this way, it was possible to utilize a sol–gel reaction for obtaining water and oil repellent, as well as antimicrobial finishing systems. Two different approaches were exploited: the cellulosic substrates were either impregnated with a sol embedding all three components or first soaked with the sol containing silver nanoparticles and the binder and then with the fluoroalkylfunctional siloxane sol. Notwithstanding the permanent water and oil repellency provided to the fabrics by the sol–gel formulation (in fact, the treated fabrics were able to withstand up to 10 washing cycles without losing these surface properties), their antibacterial activity against *E. coli* and *Staphylococcus aureus* was strictly referred to the procedure adopted for applying the sol–gel coatings. More specifically, the deposition of silver nanoparticles followed by the application of the fluoroalkylfunctional siloxane was more effective in providing the fabrics with the envisaged features, with respect to the application of the sol mixture in a single step.

Then, cotton fabrics were treated with diureapropyltriethoxysi lane[bis(aminopropyl)-terminated polydimethylsiloxane (1000)] (PDMSU) sol–gel hybrid coating, in the presence of 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyltriethoxysilane (PFOTES) [48]. The resulting coatings not only provided both hydrophobic and oleophobic features to cotton, but also showed antibacterial activity against *E. coli*: this latter was about

100% for unwashed cotton fabrics and was still kept (60.6%) after 10 washing cycles.

Finally, a sol–gel method involving dodecanethiol-capped silver nanoparticle-doped silica was designed and applied to woven cotton fabrics, aiming at achieving good antibacterial activity against *E. coli.* [49]. The excellent performance of the proposed sol–gel finishing system suggested the possibility of using the treated cotton as one-use bandages.

18.3 Current Limitations

Despite the undeniable advantages showed by the sol–gel processes performed on cotton fabrics in terms of improved fire retardancy and antimicrobial activity, as clearly reported in Table 18.2, this finishing strategy has to face some current significant limitations. The most important issue, which is at present limiting the industrial scale-up and exploitation of the sol–gel approach, refers to the use of chemicals, mostly showing quite a high environmental impact. Therefore, this disadvantage deserves further investigation, trying to find less impacting chemical precursors, which are still capable to confer the final characteristics to the treated fabrics.

Another significant current limitation is related to the comfort (i.e. soft touch) of the fabrics after the sol–gel treatments: in fact, the deposition of fully inorganic fire retardant and/or antimicrobial coatings makes the underlying fabric stiffer, hence not suitable for clothing applications, but only for upholstery purposes. On the other hand, this detrimental effect exerted by the deposited sol–gel coating becomes relatively less important when sol–gel hybrid organic–inorganic coatings are taken into consideration, because of the flexibilization effect induced by the organic part. However, it is expected that this detrimental effect could be overcome by finely controlling the deposition of the sol–gel coating in order to minimize its thickness (i.e. the final dry add-on on the treated fabrics),without compromising the envisaged properties.

18.4 Conclusions and Future Outlook

This chapter has clearly demonstrated the importance, feasibility, and reliability of sol–gel processes as effective surface-engineered finishing treatments for cotton. In fact, it is easy to tailor the sol formulations in order to achieve significant improvements as far as the fire retardancy of the treated fabrics is considered. Besides, the sol–gel strategy has undoubtedly showed that it is also possible to provide the treated cellulosic substrate with antibacterial features, usually exhibiting good and acceptable washing fastness properties.

In conclusion, as confirmed by the scientific research work mostly carried out during the last ten years, it seems that the further development and optimization of this surface-engineered strategy could overcome its present limitations and lead to a possible industrial exploitation and valorization.

References

1. World Fire Statistics, *Information Bulletin of the World Fire Statistics Centre*, Vol. 29, Geneva, Switzerland, 2014.
2. Neisius, M., Stelzig, T., Liang, S., Gaan, S., Flame retardant finishes for textiles, in: *Functional Finishes for Textiles*, R. Paul (Ed.), pp. 429–461, Woodhead Publishing Series in Textiles, Amsterdam, 2015.
3. Bourbigot, S., Flame retardancy of textiles – new approaches, in: *Advances in Fire Retardant Materials*, A.R. Horrocks, D. Price (Eds.), pp. 9–40, Woodhead Publishing, Cambridge, 2008.
4. Weil, E.D. and Levchik, S.V., Flame retardants in commercial use or development for textiles, *J. Fire Sci.*, 26, 243, 2008.
5. Horrocks, A.R. and Price, D., *Fire Retardant Materials*. Woodhead Publishing Limited, Cambridge, 2000.
6. Weijs, L., Dirtu, A.C., Malarvannan, G., Covaci, A., Bioaccumulation and biotransformation of brominated flame retardants, *Compre. Anal. Chem.*, 67, 433, 2015.
7. Howard, P.H. and Muir, D.C.G., Identifying new persistent and bioaccumulative organics among chemicals in commerce, *Environ. Sci. Technol.*, 44, 2277, 2010.
8. Iqbal, M., Syed, J.H., Katsoyiannis, A., Malik, R.N., Farooqi, A., Butt, A., Li, J., Zhang, G., Cincinelli, A., Jones, K.C., Legacy and emerging flame retardants (FRs) in the freshwater ecosystem: A review, *Environ. Res.*, 152, 26, 2017.
9. Hull, T.R. and Law, R.J., Environmental Drivers for Replacement of Halogenated Flame Retardants, in: *Polymer Green Flame Retardants*, C.D. Papaspyrides, P. Kiliaris (Eds.), pp. 119–179, Elsevier, Amsterdam, 2014.
10. Horold, S., Phosphorus-based and Intumescent Flame Retardants, in: *Polymer Green Flame Retardants*, C.D. Papaspyrides, P. Kiliaris (Eds.), pp. 221–254, Elsevier, Amsterdam, 2014.
11. Muthu, S.S., *Handbook of Sustainable Apparel Production*, CRC Press, Boca Raton, 2015.
12. Alongi, J. and Malucelli, G., State of the art and perspectives on sol–gel derived hybrid architectures for flame retardancy of textiles, *J. Mater. Chem.*, 22, 21805, 2012.

13. Alongi, J. and Malucelli, G., Thermal degradation of cellulose and cellulosic substrates, in: *Reactions and Mechanisms in Thermal Analysis of Advanced Materials*, A. Tiwari, B. Raj, Wiley, Hoboken, USA, Beverly, pp. 301–332, 2015.
14. Malucelli, G., Hybrid organic/inorganic coatings through dual-cure processes: state of the art and perspectives, *Coatings*, 6, 1, 2016.
15. Alongi J., Ciobanu M., Malucelli G., Cotton fabrics treated with hybrid organic-inorganic coatings obtained through dual-cure processes, *Cellulose*, 18, 1335, 2011.
16. Hribernik, S., Smole, M.S., Kleinschek, K.S., Bele, M., Jamink, J., Gaberscek, M., Flame retardant activity of SiO_2-coated regenerated cellulose fibers, *Polym. Degrad. Stab.*, 92, 1957, 2007.
17. Alongi, J., Ciobanu, M., Carosio, F., Tata, J., Malucelli G., Thermal stability and flame retardancy of polyester, cotton and relative blend textile fabrics subjected to sol-gel treatments, *J. Appl. Polym. Sci.*, 119, 1961, 2011.
18. Alongi, J., Ciobanu, M., Malucelli, G., Sol-gel treatments for enhancing flame retardancy and thermal stability of cotton fabrics: optimization of the process and evaluation of durability, *Cellulose*, 18, 167, 2011.
19. Alongi, J., Ciobanu, M., Malucelli, G., Sol-gel treatments on cotton fabrics for improving thermal and flame stability: effect of the structure of the alkoxysilane precursor, *Carbohydr. Polym.*, 87, 627, 2012.
20. Alongi, J., Ciobanu, M., Malucelli, G., Sol-gel treatments on cotton fabrics for improving thermal and flame stability: effect of the structure of the alkoxysilane precursor, *Carbohydr. Polym.*, 87, 627, 2012.
21. Alongi, J., Ciobanu, M., Malucelli, G., Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol-gel processes, *Carbohydr. Polym.*, 87, 2093, 2012.
22. Alongi, J. and Malucelli, G., Thermal stability, flame retardancy and abrasion resistance of cotton and cotton-linen blends treated by sol-gel silica coatings containing alumina micro- or nano-particles, *Polym. Degrad. Stab.*, 98, 1428, 2013.
23. Brzezinski, S., Kowalczyk, D., Borak, B., Jasiorski, M., Tracz, A., Applying the sol-gel method to the deposition of nanocoats on textiles to improve their abrasion resistance, *J. Appl. Polym. Sci.*, 125, 3058, 2012.
24. Cireli, A., Onar, N., Ebeoglugil, M.F., Kayatekin, I., Kutlu, B., Culha, O., Celik, E., Development of flame retardancy properties of new halogen-free phosphorous doped SiO_2 thin films on fabrics, *J. Appl. Polym. Sci.*, 105, 3747, 2007.
25. Alongi, J., Ciobanu, M., Malucelli, G., Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol-gel processes, *Carbohydr. Polym.*, 85, 599, 2011.
26. Yaman, N., Preparation and flammability properties of hybrid materials containing phosphorous compounds via sol-gel process, *Fibers Polym.*, 10, 413, 2009.

27. Bonnet, J., Bounor-Legaré, V., Boisson, F., Melis, F., Camino, G., Cassagnau, P., Phosphorus based organic-inorganic hybrid materials prepared by reactive processing for EVA fire retardancy, *Polym. Degrad. Stab.*, 97, 513, 2012.
28. Alongi, J., Colleoni, C., Malucelli, G., Rosace, G., Hybrid phosphorus-doped silica architectures derived from a multistep sol-gel process for improving thermal stability and flame retardancy of cotton fabrics, *Polym. Degrad. Stab.*, 97, 1334, 2012.
29. Alongi, J., Colleoni, C., Rosace, G., Malucelli, G., The role of pre-hydrolysis on multistep sol-gel processes for enhancing the flame retardancy of cotton, *Cellulose*, 20, 525, 2013.
30. Brancatelli, G., Colleoni, C., Massafra, M.R., Rosace, G., Effect of hybrid phosphorus-doped silica thin films produced by sol-gel method on the thermal behavior of cotton fabrics, *Polym. Degrad. Stab.*, 96, 483, 2011.
31. Alongi, J., Colleoni, C., Rosace, G., Malucelli, G., Thermal and fire stability of cotton fabrics coated with hybrid phosphorus-doped silica films, *J. Therm. Anal. Calorim.*, 110, 1207, 2012.
32. Alongi, J., Colleoni, C., Rosace, G., Malucelli, G., Phosphorus- and nitrogen-doped silica coatings for enhancing the flame retardancy of cotton: synergisms or additive effects? *Polym. Degrad. Stab.*, 98, 579, 2013.
33. Lewin, M., Synergism and catalysis in flame retardancy of polymers, *Polym. Adv. Technol.*, 12, 215, 2011.
34. Kappes, R.S., Urbainczyk, T., Artz, U., Textor, T., Gutmann, J.S., Flame retardants based on amino silanes and phenylphosphonic acid, *Polym. Degrad. Stab.*, 129, 168, 2016.
35. Dasari, A., Yu, Z.Z., Cai, G.P., Mai, Y.W., Recent developments in the fire retardancy of polymeric materials, *Prog. Polym. Sci.*, 38, 1357, 2013.
36. Alongi, J. and Malucelli, G., Cotton fabrics treated with novel oxidic phases acting as effective smoke suppressants, *Carbohydr. Polym.*, 90, 251, 2012.
37. Giamberini, M. and Malucelli, G., Hybrid organic-inorganic UV-cured films containing liquid-crystalline units, *Thin Solid Films*, 548, 150, 2013.
38. Sangermano, M., Amerio, E., Malucelli, G., Hybrid organic-inorganic coatings obtained by cationic UV-Curing, in: *Basics and Applications of Photopolymerization Reactions*, Vol. 2, J.P. Fouassier, X. Allonas (Eds.), pp. 149–163, Research Signpost, Trivandrum, 2010.
39. Xing, W., Jie, G., Song, L., Hu, S., Lv, X., Wang, X., Flame retardancy and thermal degradation of cotton textiles based on UV-curable flame retardant coatings, *Thermochim. Acta*, 513, 75, 2011.
40. Przybylak, M., Maciejewski, H., Dutkiewicz, A., Wesołek, D., Władyka-Przybylak, M., Multifunctional, strongly hydrophobic and flame-retarded cotton fabrics modified with flame retardant agents and silicon compounds, *Polym. Degrad. Stab.*, 128, 55, 2016.
41. Liu, Y., Pan, Y.T., Wang, X., Acuña, P., Zhu, P., Wagenknecht, U., Heinrich, G., Zhang, X.Q., Wang, R., Wang, D.-Y., Effect of phosphorus-containing inorganic–organic hybrid coating on the flammability of cotton fabrics: Synthesis, characterization and flammability, *Chem. Eng. J.*, 294, 167, 2016.

42. Ollis, D.F., Photocatalytic purification and remediation of contaminated air and water, *C.R. Acad. Sci., Ser. IIc: Chim.*, 3, 405, 2000.
43. Isquith, A.J., Abbott, E.A., Walters, P.A., Surface bonded antimicrobial activity of an organosilicon quaternary ammonium chloride, *Appl. Microbiol.* 24, 859, 1972.
44. Bottcher, H., Specific optical and electrical properties of vacuum-deposited thin films of dyes, *J. Prakt. Chem.*, 334, 14, 1992.
45. Mahltig, B., Textor, T., Combination of silica sol and dyes on textiles, *J. Sol-Gel Sci. Technol.*, 39, 111, 2006.
46. Xing, Y.J., Yang, X.J., Dai, J.J., Antimicrobial finishing of cotton textile based on water glass by sol–gel method, *J. Sol-Gel Sci. Technol.*, 43, 187, 2007.
47. Tomsic, B., Simoncic, B., Orel, B., Cerne, L., Forte Tavcer, P., Zorko, M., Jerman, I., Vilcnik, A., Kovac, J., Sol–gel coating of cellulose fibres with antimicrobial and repellent properties, *J. Sol-Gel Sci. Technol.*, 47, 44, 2008.
48. Vilčnik, A., Jerman, I., Šurca Vuk A., Koželj, M., Orel, B., Tomšič, B., Simončič, B., Kovač, J., Structural properties and antibacterial effects of hydrophobic and oleophobic sol-gel coatings for cotton fabrics, *Langmuir*, 25, 5869, 2009.
49. Tarimala, S., Kothari, N., Abidi, N., Hequet, E., Fralick, J., Dai, L.L., New approach to antibacterial treatment of cotton fabric with silver nanoparticle–doped silica using sol–gel process, *J. Appl. Polym. Sci.*, 101, 2938, 2006.

PART IV

SUSTAINABILITY

19

Sustainable Coloration and Value Addition to Textiles

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Abstract

Chemical processing of textiles, starting from the preparatory processing to dyeing and finishing, is very important for value addition to them in terms of fashion and function. However, those processes are water, energy and chemical-intensive and more often, the source of serious ecological degradation. Due to the increased global awareness and tougher government legislation to combat environmental pollution in recent years, the demand for natural fibre based textiles dyed with eco-friendly sustainable chemicals/ natural dyes as well as finished subsequently with various bio-molecules (both plant and protein based) is gaining academic, research and industrial importance. As a result, dyeing of textiles is being carried out or attempted to carry out using various natural products, like plant and insect-based extracts owing to the presence of inherent coloring compounds in them. More recently, a super-critical dyeing process for the synthetic textiles (especially, the polyester textile) is also getting considerable attention in the sustainability domain of coloration. Since a long time, some of the cottons grown have exhibited attractive natural colors due to the variation of their inherent gene characteristics. Besides, some plant and protein-based bio-molecules reportedly have shown excellent UV protection, antimicrobial, mosquito-repellent, well-being and aroma functionality on application to the textiles. Such value-added finishing of textiles have been carried out by using a number of plant extracts, such as neem (antimicrobial), aloe vera (cosmeto-textile), turmeric (antimicrobial),

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Arjuna (well-being), sandalwood (cosmeto, well-being textile and skin nourishment), Tulasi (antimicrobial), jasmine, and eucalyptus oil (aroma). Cellulosic and ligno-cellulosic textiles being highly flammable in nature, the flame retardancy of such textiles has been improved by using different wastage plant bio-molecules like banana pseudostem sap, green coconut shell extract and such others and also, protein-based bio-molecule (DNA, casein, hydrophobin), nano-based metal oxides and by plasma application of textiles at a suitable atmosphere with polymeric gases like phosphine, etc. All these applications have resulted in production of fire retardant fabrics with minimal add-on of the chemicals, without compromising the quality of the finished textiles. The wash and wear finish of the textiles could be improved by low formaldehyde or zero formaldehyde based resin cross-linkers like di methylol dihydroxy ethylene urea (DMeDHEU), poly carboxylic acid-based resin like butane tetracarboxylic acid (BTCA based formulation), natural soya based resin, etc. Recently, enzyme based textile finishing is also gaining significant consideration in the textile industry, particularly in the areas of bio-polishing of cotton, denim washing and fading. Besides, enzyme-based desizing, scouring and bleaching of the cellulosic textiles are also popular in the industry. The enzyme-based processing has helped to reduce the amount of harsh toxic chemicals, which are conventionally used in the preparatory processing of textiles. More recently, various nano-based, eco-friendly insect and moth-proof textiles have also emerged in the market. So far as the sustainability of the textile processing is concerned, different eco-friendly irradiation techniques like plasma and UV exposure of textiles are helping in adopting energy, water and chemical saving dyeing and finishing processes, for example, self-cleaning, soil-release finish, etc. Very recently, bio-mimic textiles like self-cleaning lotus effect, shark skin-effect and nano gecko-feet textiles are also getting attention of the research community.

Keywords: Eco-friendly, plant bio-molecule, textile coloration, textile finishing, value-addition

19.1 Introduction

The chemical processing of textiles is an important area drawing constant attention, as it adds value to the textile and makes it more attractive, functional and acceptable to the consumers. Mainly, it includes the pretreatment process, followed by the dyeing or the coloration and the different finishing treatments imparted to the textile for their value addition. In fact, in these niche areas of processing, the industry is using various synthetic chemicals, primarily due to their easiness in applications, process ability, productivity, and durability [1]. However, a large quantity of the toxic chemicals like dyes, inorganic chemicals, alkali, acid, finishing agents, etc., released during the processing heightens the effluent problem by enhancing the BOD (biological oxygen demand), COD (chemical oxygen demand), TDS (total dissolved solid) levels of the discharged effluent. It also enhances the AOX (absorbable halogen) value due to the presence of non-biodegradable, chlorinated compounds in the waste water [2]. Moreover, some of the chemicals like proban and pyrovatex used in the processes for imparting fire retardancy to the textiles emit toxic formaldehyde from the process (over 50 ppm) as well as from the treated fabric [3]. However, due to enforcement of tougher government legislation and for the increased public awareness on environmental pollution in recent years, use of toxic synthetic chemicals for processing of textiles are being discouraged and as such, the industry and the researchers are looking for some non-toxic alternatives. In this direction, various researches and trials have been conducted and being performed throughout the world for the last one decade for making the textile wet processing more eco-friendly and sustainable. New technologies based on eco-friendly synthetic chemicals, nano-materials and particles, and enzymatic bio-based processing have occupied a large area in this domain, because of the less amount of chemical consumption and being the easier, cleaner, and more effective processing [4–8]. In the last decade, the different irradiation techniques (like UV, plasma, gamma rays) have also been employed for making the textile wet processing more water and energy saving process [9, 10]. Moreover, those techniques help to save significant quantum of energy in terms of temperature and duration of processing. More recently, different plant and protein-based bio-macromolecules have been used for making fire retardant, antimicrobial and mosquito-repellent textiles [11–15]. Besides, bio-mimic based value addition to textiles (e.g., shark-skin effect, lotus effect, gecko feet textile, etc.,) are also providing modern flavours in the sustainable concept in the textile value chain [16].

In this chapter, these new developments associated with coloration, finishing and the value addition to the textiles coalesce with the recent concepts of water-free, energy saving irradiation techniques and bio-mimic inspired processes are narrated to portray a unified state of the art of the sector and the probable course in its future development.

19.2 Sustainable Coloration of Textile Materials

19.2.1 Insect-Based Natural Color

The insect-based coloration technique has been used since long. Cochineal scales (*Dactylopius Coccus*), the insects/bugs living on the stem of the cactus plants are dried and then, grounded into a red color powder. This powder has a good tinctorial value that produces a dark red color, when dissolved into the water. Traditionally and popularly, this color has been used for coloration of food (e.g., cherries are colored by carmine) and cosmetics (e.g., lipstick, blushes, etc.). The main advantage of this color is its stability during cooking, freezing, and in acidic conditions [17]. The people of Canary Island are still producing this attractive dye. Beeswax, a compound secreted by the glands in the butt end of honeybee is commonly used in all sorts of lip balms for its attractive color. Mollusk shells also produce a natural purple color. Tyrian purple or crimson color has reportedly been extracted from the dried bodies of the marine snails. Most recently, Mohamed *et al.* has reported on the anthraquinone based natural color derived from the bodied of the insects [18]. They have reported the extraction of red color kermesic acid from the female insect in the genus Kermes (*Kermes Phylum*). Kermes insects are commonly found in the Mediterranean region and in the sap of the Kermes oak. Chemically, this dye is based on 1 methyl-2-carboxy-3,5,6,8-tetrahydroxy anthraquinone, can be used for the dyeing of the textiles. However, the major limitations on the usage of the insect-based natural dyes are their poor light and washing fastness, besides insufficient availability globally.

19.2.2 Naturally Colored Cotton

A good example of color with natural origin is the naturally grown colored cotton, believed to be originated from America as early as in 2500 BC. In India, color cottons were grown in specific locations like Rayalseema in Andhra Pradesh on commercial scale and were also exported up to 1950s. The natural color of the colored cotton fibre originates from natural pigments like caffeic acid and cinnamic acid and deposited in the alternating layers with cellulose, outside and around the cotton fibre. The green color of the cotton comes from wax layers, brown and tan are derived from tannin vacuoles in the lumen of the fiber cells. The natural colored cotton is said to be softer in feel to the skin and has a pleasant smell [19]. This statement is subjective and needs verification. Some of the colored cotton varieties have found to exhibit antimicrobial property, probably due to the presence of tannin, caffeic acid, etc., and UV protectiveness due to the presence of natural pigments with large molecular weights that absorb harmful UVB light of the sun. Some of the color cotton varieties are intrinsically salt and drought tolerant. The naturally colored cotton is still a rarity, because it requires specialized harvest techniques and facilities, making it more expensive to harvest than white cotton. Early in 1980s, the detailed basic studies on the development of colored linted genotypes were conducted in the USA. However, by the 1990s, most of the indigenous colored cotton landraces or cultivars grown in Africa, Asia and the Central and the South America were replaced by all-white, commercial varieties. Due to the renewed interest on environmental concern, the agricultural scientists in India took some trials for developing new colored cottons around 1995 and spanning a couple of years under the AICCIP (All India Coordinated Cotton Improvement Project). Some of the cotton samples with brown to dark brown color were subjected to both the ring and the rotor spinning trials for yarn manufacturing, and further to fabric forming trials (i.e., weaving and knitting). To this end, detail research has been reported by Chattopadhyay *et al.* Spinning and fabric forming trials on naturally colored cottons – some observations, *Asian Textile Journal*, 2001, 50–56). In generals, fibres were found shorter in length, weaker and with poor maturity. However, the fibres were easy to open and clean, caused lower loading on carding cylinder and exhibited better running behavior during the drawing operations, which was mainly ascribed to the higher wax content in the fibres. The colored cotton fabrics produced were found good in color fastness properties, when subjected to washing, perspiration, light and rubbing tests. Yet, the production of the naturally colored cotton in the world is still a rarity, because it requires specialized agricultural harvest techniques and facilities, which is more technical and expensive compared to the white cotton [20, 21], besides the need of a separate processing area during the yarn spinning. Another problem is the excessive end breakages during ring spinning due to the short length of the fibre, and it has been advocated to spin such cotton with a lower spindle speed and employing a higher twist multiple. Commonly, colored fibres have been blended with white cotton fibres with a proper blend ratio so as to minimize such breakages during the yarn spinning.

19.2.3 Natural Dye from Plants

Since the ancient times, various colors have been extracted from plants to be explored for natural dyeing of the cellulosic fibres. Synthetic dyes have come in the market for the last five decades, and started cutting the usage of natural dyes, because of their advantages of cheapness and excellent fastness properties. However, for the last one decade, the concern of eco-friendliness and sustainability is driving the consumers, producers and researchers to reinvent the wheel of coloring textiles with natural dyes, albeit with newer methodologies and technologies. The natural red color on cellulosic textiles has been made possible, even resorting to any prior mordanting or dye fixation process. In this regard, it is mentionable that Carthamin from safflower (*Carthamus tinctorious*) petals and bark extracts can produce a strong red color with good fastness properties. Root extract of ratanjot (*Onosma echioides*) has also reportedly produced similar color due to the presence of Carthamin. The coloring matter from the roots of Indian madder (*Rubia cordifolia*) and European madder (*Rubia tinctorium*) have also provided red color to the cotton fabric. However, for these dyes, use of mordants (metal salt) was essential. The active coloring molecule of Indian madder is mainly anthraquinone based, whereas for European madder, it is alizarin based. Further, in both these madders, the color of the dyed fabric could be changed by changing the mordant. For example, the Indian madder produces red and pink colors with alum, violet color with iron, and purple color with a mixture of alum and iron. The color change phenomenon of the natural dyes by using various mordant may be related to the electron stability, when the mordant conjugates with the chromophore of the natural dye molecules. All these dyed fabrics showed an adequate light and wash fastness. Chay root (*Oldenlandia umbellate*) can be used to produce deep red color on the cotton fabric due to its alizarin based colorants. Lac dye, which is obtained from the resin secreted by the *Laccifer lacca* was mainly used in earlier days for dyeing of Protein wool and silk fabrics. This natural dye has recently been applied to chitosan pretreated cotton fabric to produce a violet color [1, 22]. As far as the yellow color natural dye is concerned, turmeric obtained from the rhizomes of the plant *Curcuma longa* is the popular one for textile coloration. Here, the dye molecule is diaroylmethane that can be used directly and without mordanting onto the cellulosic fabrics. The fruit pulp of annatto, which contains two major carotenoids (colorants) namely bixin and norbixin, also produce orange-yellow color on the textiles. However, the fastness properties of such dyes are questionable. Coral jasmine flowers also contain carotenoid pigment nictanthin that can be utilised for producing yellow, orange and brownish-yellow shades. The orange flower of Tesu (*Butea monosperma*), onion (*Allium cepa*) skins and marigold (*Tagetus patula*) have also been explored to produce a yellow color on to the cellulosic cotton textile. But, in all those cases, the mordanting was an essential pre-requisite. While dyeing of premordanted cotton fabric with marigold flower and pomegranate (*Punica granatum*) peel, the dyed fabric showed adequate antimicrobial properties, besides the yellow color [23, 24]. Researchers reported that tannic acid and the tartaremetic mordanted cotton fabric can be dyed with Berberin from *Berberis aristata* roots, bark and stem extracts. Here, the coloring matter was alkaloid berberine that acted as a basic dye. Besides its application on to the cellulosic textiles, the particular dye could also be used in silk and wool dyeing [25]. Very recently, Basak *et al.* [5], in 2015 has reported the usage of yellow color extracted from banana pseudostem sap (BPS) for dyeing of the cotton fabric. As per their process, the cotton fabric was mordanted with tannic acid and alum, followed by treatment with the BPS at an elevated temperature for 30 min. They could also get an attractive Khaki color in an alkaline medium. Moreover, the prescribed mordanting process resulted in good wash durability, light and rubbing fastness as well as weathering durability in the dyed fabric. The same researchers have also reported good thermal stability, i.e., the fire retardant property of the above-dyed fabric [26]. Further, they have demonstrated that a cotton fabric when dyed with the spinach leave extracts in an alkaline medium, it was possible to produce an attractive green color with a good washing fastness and a fairly good wet-rubbing fastness, even without any mordanting. Though the light fastness needed to be further improved, the treated fabric, besides the attractive color showed an adequate thermal stability additionally [27]. Indigo is another most common and the known example of a natural dye that provides a blue color, which is derived from the plant belonging to genus *Indigofera*. Indigo has the all-round good fastness properties, and is mostly used for the coloration and production of cotton denims. It provides a blue color with a reddish tinge due to the presence of the trace amount of red coloring matter, indirubin. Woad (*Isatis tinctoria*), a variety of indigo which is mainly found in the European country, to produce a blue color onto the cellulose cotton and jute fabrics with good fastness properties [28]. Plant extracts that contain a high amount of tannin generally produce brown to black shades. Catechu (*Acaica catechu*) produces dark brown color in cotton fabrics. Apart from tannic acid, catechu also contains catechin and quercetin. These molecules are also responsible for color production, besides being used as an astringent and antioxidant. Logwood, Harda and custard apple also belong to these categories possess antiseptic abilities [29]. Samanta *et al.* [22] reported that tannin-rich brown to black color dyes are suitable for coloration of both the cellulosic and the protein fibers. One major advantage of these groups of dyes is that there need no mordanting process, as the dye itself self-act as a mordant [30]. Natural dyes are also being used for dyeing of the ligno-cellulosic fibre, protein-based wool and silk fibres. Lignin present in the jute fabric helps to uptake the natural dye at a neutral to alkaline pH. Natural dye extracts of jackfruit leaf, annatto, myrobalan, manjistha and ratanjot have been utilized for dyeing of jute, whereas kenduka, haritaki, and lodhra extracts have been used as bio-mordants. On the contrary, amine ($-NH_2$) and carboxylic acid ($-COOH$) group present in the wool polymer help to pick up the natural dye in the pH range of 4.5–5 (i.e., the isoelectric point of the wool polymer). Almost all the natural dyes can be used for dyeing of wool polymer because of its amphoteric nature.

19.2.4 Sustainable Synthetic Color

Synthetic dyes have emerged into the market for the last fifty to sixty years. As far as the synthetic dyeing process is concerned, they are reliable in terms of shade and its depth. Unlike the natural dyes, synthetic dyes do not contain any impurities or generate waste materials requiring any additional action for their disposal. While dyeing with the synthetic dyes, no toxic mordanting chemical is used and they also produce bright shades on the textiles even with a much lesser add-on. Besides, they have the advantages of lower-cost, larger availability, more batch to batch uniformity and excellent all-round fastness properties, making them more attractive compared to the natural dyes. Salt-free synthetic reactive dyeing is an innovative approach to make the dyeing process sustainable. It may be noted that it is the salt that causes the effluent problem and increases BOD, COD, pH and AOX values of the effluent. Though the cationisation of the cotton fabric and the application of various organic polymeric chemicals like dendritic polymer, etc., have been done to avoid the usage of salt, however, the associated treatment cost has restricted such processes to be used commercially. Some newer kind of reactive dyes have also been developed that can be applied onto the textiles at neutral pH. Besides, no extra-addition of salt is required for the dyeing process. Levafix (free from regulatory controlled amines), bifunctional and the Lanasol based reactive dyes are the common examples of this brand. Lanasol based dyes contain alpha bromoacrylamide groups, which can be attached to the amine groups of the wool fibre to provide excellent fastness properties [2]. Reactive high exhaustion (HE) and cold brand (ME) dyes are also very much in demand, because of less-wastage of the dye molecules in the exhausted dye bath and less-energy (temperature, time, etc.) requirement for the dyeing process, respectively. Modern industries are running continuous processes in place of the batch dyeing to minimize the dye wastage and increase the production. The synthetic-based dye (i.e., the cationic dye group) has the advantage of high tinctorial value. As a result, a very less amount (0.1–0.2%) of dye is required to get the adequate dyeing effect on the natural textiles. The synthetic dyes based on vat and sulphur group are not normally used by the industry for their toxicity levels and the high amount of alkali required for the dyeing process. As far as the acid dyeing is concerned, super milling acid dyes have also come into the market, as it can be applied from the weak acid medium, in contrast to the levelling acid dyes requiring a pH range of 3–3.5. It could be possible due to the more affinity of the super milling dyes towards the wool fibre.

19.3 Easy Care Finishing of Textile Products

Easy care finishes are generally applied to a cellulosic and its blended fabrics. Because of the moisture absorption and the molecular chain movement in the amorphous region of the cellulosic polymer in the stressed condition, the hydrogen bonds get disturbed and reformed in the new positions, forming the wrinkle or crease effect. Such effects reduce the aesthetic look of the textiles. Many chemicals are now available in the market since the last ten decades, which can foster crosslinking between two adjacent –OH groups of the cellulosic polymer and minimize the creasing tendency by providing the iron effect. However, the treatment has the effect of reducing the physical properties (e.g., handle, tensile strength, tear strength, bending length, etc.,) of the treated fabric. As far as the easy care finishing of the natural textiles is concerned, formaldehyde release during the treatment as well as the finished products is one of the major problems. The released formaldehyde is a known human carcinogen, which causes allergic reactions, eczema, teary eyes, cough, and headache, besides irritating mucous membranes. Chemicals like urea formaldehyde resin, phenol formaldehyde resin, melamine formaldehyde and trimethyl melamine finished easy-care cotton fabrics have been reported to release more than 100 ppm of formaldehyde. These chemicals cross-link with the cellulose polymer by nitrogen protonation mechanism and release formaldehyde. For mitigating the formaldehyde release problem, glyoxal and DMDHEU (Di methylol di hydroxyl ethylene urea) resin have been used. As per the information available in the public domain, DMDHEU releases less than 75 ppm of formaldehyde [31]. As per Oko-Tex Standard, 100 DMDHEU finished fabric can be capped/ labelled as a low formaldehyde based finished product. A low formaldehyde release is due to the crosslinking action of the DMDHEU with the cotton fabric by oxygen protonation mechanism instead of the nitrogen protonation, as the steric hindrance of the ethylene bridge in its structure restricts the nitrogen protonation. The DMDHEU finished fabric has also showed a good durable press property (DP rating – 4), laundering durability, low-reactivity, and chlorine retention. However, for the last one decade the textile world is more interested in formaldehyde free, eco-friendly finishing. In this direction, it may be noted that N, N-Dimethyl-4, 5-dihydroxyethylene urea (DMeDHEU) has notably emerged in the market, because of its formaldehyde free release property. Moreover, it has a low reactivity and low chlorine retention property. However, DMeDHEU is four times costlier than the DMDHEU and it has also, the low laundering durability. To tackle such issues, therefore, both the products (DMDHEU and DMeDHEU) are normally applied in a proper stoichiometric ratio to get the desired easy-care effect on the cotton fabric. Polycarboxylic acid based BTCA (1,2,3,4-Butanetetracarboxylic acid) with sodium hypophosphite catalyst is another formaldehyde-free formulation for making the easy-care cotton fabric [32]. This material has shown a good crosslinking property without hampering the tensile strength and the other physical properties of the treated fabric. However, it is also very costly to be used commercially in the industry. Very recently, researchers have developed phosphono and phosphinocarboxylic acids (APCM), a modified polycarboxylic acid, which has also showed good easy-care properties and an adequate durability against washing. Further, this chemical finish is nontoxic and do not create any skin irritation.

19.4 Antimicrobial Finishing of Textiles

The antimicrobial finishing is essential nowadays for garments and clothing as well as for the home textiles to control the infestation by microbes, arrest their metabolism and reduce the odor formation. It may be noted that the inherent properties of textile fibers, the structure of the substrate made from them, the applied chemical processes and the humid and warm environments in which the textile substrate is to negotiate continuously are all conducive enough for the growth of micro-organisms. Cross-infection by pathogens, foul odor, staining, and loss in performance properties are the expected fall-out from the infestation and the attack by microbes. Textile materials used in screens, tents, tarpaulins, ropes and different home furnishing products like carpets and mattresses are also frequently imparted with hygienic antimicrobial finishes. Apparel textiles like shirting, trousers and saris used by the humans, and which directly come in contact with the skin, also need hygienic finishes. Presently, a large number of synthetic antimicrobial agents are available in the market to impart textiles with antimicrobial, antibacterial and antifungal properties. Out of them, formalin solutions, tributyl tin oxide, dihydroxy dichlorodiphenyl methane and triclosan are being used widely as the antibacterial chemicals for a long time. Quaternary ammonium compounds, since they contain positive ammonium ion have been used as the most effective and popular antimicrobial agent. However, all those chemicals are water soluble and cannot provide the requisite durability to the finished end products.

Antimicrobial chemicals like silylpropylammonium chloride and polyhexamethylene biguanide though can bind tightly to the fibre surfaces, however, they are not used normally due to the large quantity requirement and concern on their eco-friendliness. For the last two decades, various metal nanoparticles have been synthesised and applied to the natural (i.e., cellulosic and ligno-celulosic) as well as synthetic textiles (like polyester and nylon) to impart non-durable to durable antimicrobial functionality. Some of the common nanoparticles used for textiles are silver (Ag), ZnO, TiO_2, and CuO. Though they are very effective even at a low add-on, however, their interactions with the human, plant and animal body for any adversities have still not been investigated scientifically. The advantages of using plant-based antimicrobial agents are their eco-friendliness, bio-degradability and economy, as they are produced from renewable and diversified sources of plants and herbs. Plants that contain phenols and oxygen based derivatives, and anti-oxidants are considered as the secondary metabolites, which also act as the antimicrobial and insecticidal agents. It has also been reported that tannin, which is naturally occurring as polyphenols are also responsible for the antibacterial properties of the natural dye. Herbal and plant products, like chitosan, aloe-vera, neem, tea oil, eucalyptus oil, and tulsi leaf extracts have showed excellent antimicrobial activity on various textile substrates. Chitoson is an effective natural antimicrobial agent derived from chitin. It contains reactive amine group that can easily react with the negatively charged bacterial cell wall to destroy it. Chitosan citrate has also been utilised for the durable press and antimicrobial finishing of the cotton textile. Neem-chitosan nano-composite has been used to make cotton textiles antimicrobial [33]. Chitosan has also been used in layer by layer process with one negatively charged polymeric materials for improving the antimicrobial efficacy and durability. Thilagavathi *et al.* [34] found that neem, pomegranate and prickly chaff flower have the active antimicrobial ingredient to control the growth of microbes [34]. Neem leaves contain limonoids based azadirachtin, sallannin, and nimbin, which are responsible for the production of good antimicrobial and insecticidal textile products. A recent patent on microencapsulation of neem oil and its application on cellulose and blended textiles have showed a good antimicrobial efficacy. Joshi *et al.*, in 2007 reported the antimicrobial property of polyester/cotton blended textiles treated with the neem seed extract. The neem seed extracted molecules were applied on cotton with glyoxal, aluminium sulphate and tartaric acid by two-dip, two-nip method in a padding machine, and the treated fabric was found to exhibit excellent antimicrobial activity against both gram positive and gram-negative bacteria. The treatment was found to be durable to five washes [35].

Pomegranate rind extract (PRE) contains different nitrogenous compound and the positively charged amino guanidine. This chemical's interact and destroy the negatively charged bacterial cell wall. Moreover, due to their nitrogenous content, the extracts also showed fire resistant property [36]. Henna and juglone obtained from the walnut contain napthaquinone that acts as an antibacterial and antifungal agent. Curcumin has been used as a natural dye as well as an antibacterial agent for woollen textiles. Recently, aloe-vera gel has been applied to the cotton textile to improve the antibacterial activity against *Staphylococcus aureus* bacteria [37]. Tulasi is very popular as a medicinal plant in India from the ancient time, and has a good potential to cure or resist many infection/diseases. Tulasi leaf (*Ocimum sanctum*) extract contains caryophyllene, phytol, and germacrene antimicrobial compounds and its efficacy was studied on cotton textiles after the methanol extraction. Tulasi and the PREs also have been applied by microencapsulation technique for achieving more durability of the antimicrobial cotton fabric. Tulasi herb dyed bed sheet (fabric) has shown good antimicrobial properties and have been used to cure patients suffering from chest cold, cough, itchiness and mucus problems. Sathianarayanan *et al.* [38] applied tulasi leave and pomegranate extracts on cotton textiles by using three different methods, viz., direct application, cross-linking and microencapsulation. They found that the methanolic extract of the pomegranate molecules showed 99.9% reduction in the bacterial growth on cotton fabrics, when applied by a direct pad-dry method. However and as expected, the microencapsulation and cross-linking methods of application showed better results in terms of wash durability (with 15 wash cycles) with very little decrease in gram-negative bacterial growth to 94% and 87%, respectively for tulasi and pomegranate extracted molecules [38]. Turmeric, cumin, clove oil, Karanga, cashew shell oil and onion skin treated cotton textiles has also reported to exhibit good antibacterial properties with the possibility that these kinds of fabrics can also be used as medical textiles, well-being and casual apparels. Recently, Ahamed *et al.* has developed a new method of preparing antimicrobial textiles, i.e., by herbal coating in nano form using neem extract nanoparticles. Nano herbal extract treated textiles were found to show excellent antimicrobial activity against both gram-positive and gram-negative bacteria. It was interesting to note that the applied finish was durable to 20 washing cycles, whereas only the neem extract treated fabric was durable to 10 washing cycles [39].

Very recently, Teli *et al.* have used the green coconut shell extract for making multifunctional cotton and wool fabrics. It is a 100% wastage product and rich in tannin, saponin and flavonoid content. The treated cotton fabric reportedly showed excellent antimicrobial efficacy against gram-positive and gram-negative bacteria. The treated fabric was also found to restrict the passage of UV rays with improved sun protective factor (SPF) and make its burning slower. The fabric showed a clear self-extinguishing effect when applied from the alkaline medium. It is reported that the improved SPF is due to the presence of the large molecular weight organic materials present in the extract [40, 41]. The PRE is also a wastage product, and has been used for making multi-value added cotton fabrics owing to its UV protective, antimicrobial and fire resistant behavior. Nitrogen containing materials like amino guanidine, aromatic based organic large molecular weight compound and positively charged guanidine, piperidine, tannin etc., help to impart multifunctional effects to the treated fabric.

19.5 Flame Retardant Finishing of Textile

Flame retardant textiles are in great demand not only for home textile and home furnishing usages, but also for apparels, particularly those made for the children, because of the concern of safety from fire. Borax, boric acid, sulphur based thio-urea, Phosphorous-nitrogen based chemicals, halogen-based synthetic chemicals, commonly available in the market were used as the flame retardant agents. However, due to the environmental concern, as they release dioxins and furanes, use of such chemicals was discouraged and for the last one decade, the textile industries are mainly using proban (tetrakis hydroxyl methyl phosphonium chloride), pyrovatex (N-methylol dimethyl phosphonium chloride) in combination with nitrogen-based melamine for delivering durable fire retardant and toxic smoke suppressant cotton fabrics. However, the treatment process is not eco-friendly and a larger quantity of costly synthetic chemical is still consumed by the industry [43]. Moreover, the acidic treatment condition and more add-on of chemicals on the fabric hamper both the hand value and the physical properties like the tensile strength, of the treated fabric. Hence, there is an increasing demand for a cheap, eco-friendly fire retardant chemical that, when applied to the fabric will maintain its hand value and the physical property. In this direction, the researchers have introduced various nano-based metal oxide formulations, UV, and plasma applications by using different polymerising gases for fire retardant treatments. So far as the nano-based fire retardant finishing is concerned, different metal oxides like nano zinc oxide and nano titanium dioxide are most commonly used by the researchers. These processes have shown promises to control the chemical add-on the fabric, yet maintain its physical property. However, these technologies are costly and not easy to apply uniformly on the fabric surface, apart from the fact that the durability of the treatment after finishing is also not satisfactory. Alternately, a few research groups are involved for the last five years to develop fire retardant textiles by using plant and the protein-based bio-molecules [44–47]. The researchers have used wastage protein based chicken feather [48], whey protein [49], casein, hydrophobin [12], DNA [8], etc., plant-based banana pseudostem sap, spinach extract [27, 50], starch [51], etc., for making the fire retardant cotton textiles. Very recently, the researchers have also used natural nucleic acid-based protein from agro-industrial waste for making fire retardant textiles. Basak *et al.* [4], has established the use of wastage PRE for making the fire retardant lingo-cellulosic jute textile, which has reportedly demonstrated an excellent self-extinguishing property, because of the nitrogen content in PRE. Nitrogen is mainly present in it as a protein that contains amino guanidine, mono ammonium salt, piperidine, carbamic acid, etc. Amino guanidine present in the PRE is reported to be a very effective intumescent material, which enhanced the char formation behavior of the treated textile in the reported study [36]. Wastage coconut shell extract is another example of being an efficient fire resistant bio-material for the cellulosic textiles, because of its tannin content [13, 40, 41]. Moreover, it also contains phenolic based aromatic organic compound that helps in the aromatisation of the cellulosic structure, turning the material a thermally stable one. Plant-based banana pseudostem sap and coconut shell extract also have been used by the researchers for making a thermally stable cellulosic paper [44]. Banana pseudostem sap contains phosphate, phosphite, chloride, tannin, etc., responsible for the phosphorylation of the cellulosic structure and reducing the formation of the flammable gases by catalysing the pyrolysis phenomena at a lower temperature. A slow pyrolysis helped to restrict the rate of weight degradation and enhance the dehydration of the cellulose polymer. Bio-enrich banana pseudostem sap contains more amount of nitrogen due to the fermentation process and thus, showed better fire retardancy compared to the normal banana pseudostem sap. The coconut shell extract has also been used in combination with boric acid for self-extinguishment of the cellulosic paper. Conceptually, boric acid is helping to absorb the after-glow and the coconut shell extract is mitigating the fire generation from the treated fabric. As far as the mechanism of the fire retardancy is concerned, coconut shell extract reduces the rate of the weight degradation, catalyses the dehydration of the treated cellulosic polymer and enhances the amount of carbonaceous char-mass formation. On the contrary, the control cotton fabric showed a rapid weight fall and depolymerisation at 350 °C, with the remaining char mass at the higher temperature being negligible.

The field of research to impart fire retardancy to the textiles by using different plant and the protein-based bio-molecules, which is being pursued for the last five years is still at a nascent stage, but a promising line of work so far as the fire science is concerned.

19.6 UV Protective Textile

UV rays of wavelength below 300 nm, normally referred to as the UVC is harmful to the human beings. These rays are highly intensive and can cause damage to our skin. Therefore, for saving the human skin from harmful UV rays of the sun, a protective finish over the apparel textile is very much desired. The effectiveness of the UV protection of the treated fabric is generally measured in terms of the sun protective factor (SPF). Textiles have their different protective capability depending on their structural composition. For example, wool fibre itself has the SPF of 45 that is quite good, as a fabric having SPF of 50+ considered as UV protective fabric. Cotton, jute, silk suffers very poor SPF (below 10). Similarly, lighter fabric has poorer SPF. It has been reported that cotton fabric having GSM (i.e., the fabric weight in grams per square metre) more than 150 has the SPF over 15. However, a 90–100 GSM fabric has showed a SPF below 10. A high cover factor of the fabric can also enhance the SPF of the fabric as well. Any dark coloring materials like royal blue, black, etc., also assist to enhance the fabric UV protection. Many chemicals like phenyl salicylates, benzophenones, benzotriazole, oxalic acid and dianilide derivative, etc., are available in the market for enhancing the UV protective property of the fabric [52]. However, these chemicals are not eco-friendly. For the last one decade, various biomolecules based eco-friendly agents have been used for making the UV protective textiles. Plant extracts like babool, manjistha, ratanjot, annatto, etc., have been used by the researchers for getting the desired UV protective property [26]. More recently, different wastage plant biomolecule like banana pseudostem sap, coconut shell extract and PRE also have been used for enhancing the UPF of the light-weight cellulosic cotton fabric [5, 13, 36]. Some of the extracts mentioned here also have been used on the lingo-cellulosic jute fabric to derive the same objective. Recently, different nano-based formulations for UV protective finishing of the textiles have been introduced in the market. Among them, nano-based titanium dioxide, zinc oxide, and selenium dioxide finish formulations have been used more popularly by the researchers. A few recent studies have reported that some of the natural dyes have the active molecules that can absorb UV light and block its passage through the fabric. Earlier, European researchers have reported that dyes extracted from the madder wodes, knotgrass, fengruk, and marigold possess very good UV protective property. They have dyed the linen, hemp and silk fabrics with these natural plant extracts. The linen fabric was dyed with India madder that showed a UPF rating of more than 50, which is considered as 'excellent' as far as the UV protection is concerned [53]. Sarkar *et al.* [54] reported that dyeing of cotton with madder and Indigo could also improve the UV protective performance [54]. It was observed that by increasing the amount of natural dye applied to the textile substrate from 2% to 6%, the UPF value was increased to 50.

19.7 Mosquito, Insect and Moth Repellent Finishing of Textile

Health, hygiene, and safe lifestyle textiles are important for human beings to enable them to work with the maximum efficiency. Mosquitoes are attracted towards people, as they emit carbon di-oxide, lactic acid, odor, and heat. Mosquito repellent chemicals help human beings to prevent themselves from serious diseases like dengue and malaria. Mainly synthetic chemicals are available in the market to make textiles mosquito repellent, and N, N Diethyl 3 Benzamide (DEET) is the most popular chemical for the same. Besides DEET, pyrethrene, and permythrene based chemicals can also be used for the said purpose, however, they are toxic in nature [55]. Therefore, in the last decade, several researches have been carried out to develop eco-friendly chemical formulation for preparation of mosquito repellent textiles. Different plant-based extracts of tulasi, neem, notchi, lemon grass, citronella, keelanalli, cinnamon oil, eucalyptus oil, turmeric, pine oil, garlic, and peppermint oil can be used as environmentally friendly mosquito repellent chemicals. Very recently clove oil also has been used for making the mosquito repellent textile. Clove oil has the aromatic property and euganol based composition, which can easily repel the mosquitoes as well as other small insects, ants, etc. Indeed, mosquitoes are dyed if they are come in contact with the clove oil finished textiles. Very recently, two other bio-molecules named Nirgundi leave and the custard apple extracts also have been used for making mosquito repellent textiles. Normally, it is the cellulosic textiles those get attacked by the microbes rather than the moth. Therefore, a moth-proof finishing is not essential for the cellulosic fabric. However, wool textiles, more often get attacked by moths because of their protein-based structure. Thus, a moth-proof finishing is normal for the wool fabric and chlorinated compound chemicals like pentachlorobenzene, hexamethylene biguanide, and quaternary ammonium compounds are normally used. However, because of the concern for ecology, recently various metal nanoparticles, such as silver (Ag), ZnO, TiO_2, and CuO have also been explored for similar applications. Very recently, various plant extracts also have been explored for making the moth repellent wool textile.

19.8 Irradiation-Induced Value Addition to Textiles

Various irradiation techniques (e.g., UV, plasma, gamma rays) also have been developed for value addition to the textiles. Among those techniques, the UV and the plasma exposure is most popular. The plasma ray is packed of highly intensive ions, protons etc., whereas UV rays consist of highly energized photons, which breaks the oxygen into the nascent oxygen and ozone by continuous association and the dissociation processes. Such irradiation technique is used by the researchers to modify the surface layer of the textile substrate. Indeed, after the irradiation, physico-chemical changes occur on the fabric surface, causing capillary channels to be developed and new functional groups to be generated on to the nanolayer surface. Such changes have been observed more prominently on the proteinous wool fabric because of its amphoteric character. The scales present in the outer surface of the wool fibre have been etched out and some new polar functional groups have been generated, depending on the atmosphere used during the treatment. New functional groups like amine groups (in nitrogen atmosphere) and carboxylic groups (in air and oxygen atmosphere) were found to facilitate the wetting and the dyeing behavior of the fibre [9, 53]. More explicitly, extra amine groups and carboxylic groups help to catch the anionic (direct dye, acid dye) and the cationic dye (Basic dye) respectively, at a lower temperature and treatment period. For example, a 172 nm UV treated wool fabric in nitrogen atmosphere was found to have 99% uptake of acid dye in 10 min of dyeing period at room temperature, whereas the control wool fabric recorded an uptake of 65% dye in the same treatment condition [9]. It was because of the generation of the extra amine groups in the wool fibre surface that helped to attract anionic acid dye molecules. Besides, the scale ablading phenomena was likely to assist in catching up more dye molecules in lesser time and treatment temperature. When the wool fabric was exposed in the air atmosphere, showed an uptake of 55% Basic dye (Methylene blue) in comparison to 70% uptake measured in the control wool fabric [9]. It may be because of the creation of the extra carboxylic and the carbonyl groups, which repel the anionic dye moleucles. Moreover, the ablation of scales reduces the directional friction effect of the wool fibre and enhance the shrink-proof capability of the wool. On the contrary, the irradiation treatment enhanced the saturation dye uptake of the cellulosic cotton fibre within a limited time period. However, the fastness of the dyed material and the dye uniformity were not satisfactory in the case of both the cotton and the wool fibres, as the higher dyeing rate is normally associated with the non-uniformity of dyeing. It is the major challenge needs to overcome before the irradiation techniques for value addition to textiles get accepted by the industry in a big way.

UV treated polyester fibres also can be dyed with basic dyes at a normal dyeing condition. Here, the UV treatment creates extra anionic groups (carboxylic groups) on the surface of the polyester fibre and help to attract the cationic basic dye [56]. The UV treatment also has been used to induce cross-linking polymerization on to the textile substrates, for example, for making double hydrophilic/hydrophobic wool and silk fabric. In this regard, it may be mentioned that Basak *et al.* [5] has reported that wool fabric can be made hydrophilic/ hydrophobic by using a fluorocarbon treatment, and the 172 nm UV exposure only on one side of the fluorocarbon treated fabric. Indeed, the UV treatment could break the strong C-F linkage of the nanolayer fluorocarbon-based coating and ablade/etched the scaly wool fibre surface and enhanced the water penetration capability only in that particular side of the fabric, which had undergone the UV treatment [10]. This kind of fabric is suitable for use in the sports sector and for providing different comfort levels. The Plasma treatment can be used for making both hydrophilic (by using air atmosphere) as well as hydrophobic (by using fluorocarbon based gases) cotton textiles depending on the gas system used, in which the textile was exposed. Very recently, different phosphorous based polymerizing gases also have been used for making the fire retardant cellulosic textile. These technologies have the promising future, as no water-based formulation is used for the treatment, besides the chemicals used for the treatment and their wastage are also minimal.

19.9 Enzyme-Based Textile Pretreatment

Pretreatment processes like desizing, scouring and bleaching are important peripheries of the textile wet processing. Different toxic chemicals like soap, soda ash, hydrogen peroxide and sodium silicate have been used for such pretreatment processes. These chemicals are responsible for the toxic effluent discharge with more BOD and COD levels and also, generate AOX (Absorbable Organic Halides) problems. Due to such and other ecological concerns, different enzyme based formulations are now being used for the pretreatment processes of the cellulosic textiles. Moreover, enzymes are also non-toxic and bio-degradable. Amylase, pectinase and gluco-oxidase like enzymes have been used for cellulose desizing, scouring and bleaching, respectively. Enzymes like pectinase mainly remove the fat, oil, wax and glucose from the textile substrate, and oxidate, catalase and degrade the natural coloring matters in it. Each enzyme requires a particular temperature and the pH condition for initiation and sustention of its activity. Lipase enzyme can also be used for removal of fat and oil from the fabric surface. These enzymes can also be used in combination in a single bath process as a pretreatment exercise before the final coloration and finishing of the textiles. The pretreatment of the wool fabric requires proteinase enzyme for bleaching process owing to its protein-based composition. On the contrary, ligno-cellulosic jute fabric requires combination of amylase, lipase, pectinase, hemicelulase, and lignase for the pretreatment process. However, a challenge to overcome is the bleaching efficacy in terms of the whiteness index of the treated fabric, which is somehow lower than that achieved in the synthetic inorganic chemical treated cotton fabric [57]. Besides, the cost of the enzyme is much higher than the inorganic chemicals. The enzyme, popularly the cellulase, is also used for the bio-polishing finishing of the cellulosic cotton fabric. This treatment is carried out for the removal of the undesirable hairs, pills, fuzz etc., from the surface of the cellulosic textiles, so as to make them more attractive and aesthetically appealing to the consumers. The treatment affects the amorphous part of the cellulose polymer, changes the hairiness/ fuzziness characteristics of the textile, reduces its weight and polishes the surface [58]. Enzymes (especially, the catalase and the glucose oxidase) are also used for the washing and fading of the denim garments instead of the chlorinated and sand-blast based washing or fading process, which are not only non eco-friendly, but also provide a harsh feel to the fabric [7]. The enzyme-based process helps in to get the desire fashionable-faded effect of the indigo or vat dyed denim garment by degradation of the vat or indigo color from certain portions of the fabric surface, thus ensuring an eco-friendly way of getting the fading effects.

19.10 Bio-Mimic Based Value Addition to Textile

Of late, Researchers are deriving inspiration from nature to develop new ideas concerning value-addition to the textiles. Some of the examples are shark-skin effect, hand and loop fastener, dry adhesion gecko-feet, lotus effect, etc., of the textiles. The skin of the shark fish contains finely distributed scales of size 0.2–0.5 mm, which are distributed or regularly spaced in between 30 and 100 μm viewed from the surface morphology of the shark skin. These fine, small riblets present on the shark body influence the fluid flow in the transverse direction and reduces the frictional effect of water and the surface drag [16]. This micro-features of the riblet based shark-skin technology is mimicked popularly in the pipe for free flowing of water, in aeroplane for reducing the air drag and also, in swimwear suit in 2004. Sharklet, a plastic sheet has been developed by the researchers by mimicking the micro features of the shark scale arrangement for reducing the growth of the microorganism, bacterial colonies. These kinds of materials have promising applications in the hospitals, home furnishing and restaurants, etc. The morphological view of the seeds of the plant, Arctium Lappa contains hundreds of the hooks that can be fastened with the loops. This technology is popular in clothing, where it replaces the buttons, zippers, etc. It has also been mimicked in the shoe fastening. The geckos have the clinging property of dry adhesion, because of the presence of the microscale hairs on its surface. It enables the feet of the animal to come in contact with the large surface area. Vanderwall force and the capillary forces, in combination act in the contact area and adhere the feet with the material surface. However, animals and insects like lizard, spiders, chameleon have special curl path walking technique to overcome those adhesion forces, and move easily. Synthetic gecko foot fibres have been developed by the nano-moulding of nano silicone, polyamide, polyvinyl siloxane and carbon nanotube. The lotus effect has been observed naturally on the outer surface of the lotus leaf. Here, the water particles do not spread, but only roll-off from the surface. The morphology of the lotus leaves showed a three dimensional wax like structure of the papillose epidermal cells with a microscale rough surface. This rough hydrophobic surface of the lotus leaf repels the water molecule from its surface and aids in the roll-off of the water droplet from the leaf surface. The roll-off technology helps to remove the dirt particles from the surface. By mimicking this natural technology, the self-cleaning, super-hydrophobic textile finishes has come into the market. Nano silica, nano-clay, nano titanium di-oxide, fluorocarbon-based polymer, poly-tetra fluroethylene, etc., have been used by the researchers for making water repellent, self-cleaned textile surface [59–63]. Actually, these chemicals reduce the surface energy of the treated textile surface and improve its repel characteristics that can be quantitatively assessed by measuring the contact angle. Camouflage textiles have also been developed by mimicking the natural color change phenomenon of chameleon in different weather and the surrounding condition. The nanotechnology based finishes have also brought a new pathway in the research for the development of the military garments.

19.11 Conclusion and Future Outlook

As the world is moving more and more towards eco-friendliness and inclined to observe the strict compliances for upholding the natural rules, the textile wet processing is also aligning itself to follow the same path, and trying to restrict the usage of toxic and non-biodegradable chemicals. In this direction, various new nano-based solution, plant bio-molecule based formulation, irradiation induced water and chemical-free processes, and bio-mimic concepts are emerging for value addition to the textiles and getting utmost attention in the R&D as well as in the industry. The major advantages of the nano-based formulations are their high effectivity, yet low chemical consumption. Plant extracts and enzymes, mainly derived from the wastage resource are entirely eco-friendly. Plasma and UV based irradiation reduce the usage of water, energy, and toxic chemicals, etc., by nano-scale surface modification. Very recently, multifunctional value addition of the protein and the cellulosic textile substrates have also been realized by the researchers either by using single, low-cost chemical or by using wastage plant resource. However, only a few of them have been commercially attempted in the industry, like the nano-silver based formulation is being used for making the antimicrobial textiles. The major challenges behind the usage of all these products are their insufficient durability, uniformity and also, the reproducibility, when applied on to a textile substrate. For the last five years, extensive researches are going on throughout the world to overcome those aforementioned challenges and to make the process more viable for the commercial applications.

References

1. Joshi, D., Experimental study of antimicrobial activity of cotton fabric treated with aloe gel extract from aloe vera plant for controlling the *Staphylococcus aureus* (bacterium), *Afr. J. Microbiol. Res.*, 3, 228–232, 2009.
2. Joshi M., Wazed Ali, S., Purwar, R., Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products, *Ind. J Fibre Text. Res.*, 34, 295–304, 2009.
3. Basak, S. Ali, S.W., Sustainable fire retardancy of textiles using bio-macromolecules, *Polym. Degrad. Stabil.*, 133, 47–64, 2016.
4. Sheshma, M., Khatri, H., Suthar, M., Basak, S., Ali, S.W., Bulk Vs. nano ZnO: Influence of fire retardant behaviour on sisal yarn, *Carbohydr. Polym.*, 175, 257–264, 2017.
5. Basak, S., Samanta, K.K., Saxena, S., Chattopadhyay, S.K., Narkar, R,. Mahangade, R. Flame retardant cellulosic substrate using banana pseudostem sap, *Pol. J. Chem. Technol.*, 17, 123–133, 2015.

6. Basak, S., Samanta, K.K., Chattopadhyay, S.K., Narkar, R., Self-extinguishable lingo-cellulosic fabric by using banana pseudostem sap, *Curr. Sci.*, 108(3), 372–383, 2015.
7. Decanik, T., Pusic, T, Soljacic, I., Influence of special finishes on denim properties, *Ind. J. Fibre. Text. Res.*, 40(2), 170–174, 2015.
8. Alongi, J., Carletto, R.A., Bosco, F., Carosio, F., Blasio, A.D., Cuttica, F., Giordano, M., Malucelli, G., Intrinsic intumescent like properties of the DNA treated cotton fabrics, *Carbohydr. Polym.*, 96(1), 296–304, 2013.
9. Gupta, D., Basak, S., Surface functionalization of wool using 172 nm UV Excimer lamp, *J. Appl. Polym. Sci.*, 117(6), 3448–3453, 2010.
10. Basak, S., Samanta, K.K., Chatopadhyay, S.K., Narkar, R., Development of double hydrophilic/hydrophobic wool fabric by 172 nm VUV irradiation, *J. Sci. Ind. Res.*, 75(7), 439–443, 2016.
11. Basak, S., Samanta, K.K., Chattopadhyay, S.K., Das, S., Bhowmik, M., Narkar, R., Fire retardant and mosquito repellent jute fabric treated with thio-urea, *J. Text. Assoc.*, 74(5), 273–282, 2014.
12. Alongi, J., Carletto, R.A., Bosco, F., Carosio, F., Blasio, A.D., Cuttica, F., Antonucci, V., Giordano, M., and Malucelli, G., Caseins and hydrophobins as novel green flame retardant for cotton fabrics, *Polym. Degrad. Stabil.*, 99, 111–117, 2014.
13. Basak, S., Patil, P.G., Shaikh, A.J., Samanta, K.K., Green coconut shell extract and boric acid: new formulation for making thermally stable cellulosic paper, *J. Chem. Technol. Biotechnol.*, 91(11), 2871–2881, 2016.
14. Devatkal, S.K., Jaiswal, P., Jha, S.N., Bhardawaj, R., Viswas, K.N., Antibacterial activity of the aqueous extract of the pomegranate peel against *Pseudomonous stutzeri* isolated from poultry meat, *J. Food Sci. Technol.*, 50, 555–560, 2013.
15. Basak, S., Samanta, K.K., Saxena, S., Chattopadhyay, S.K., Narkar, R, Mahangade, R., Flame retardant cellulosic textile using banana pseudostem sap, *Int. J. Cloth. Sci. Tech.*, 27(2), 247–261, 2015.
16. Das, S., Bhowmick, M., Chattopadhyay, S.K., and Basak, S., Application of biomimicry in textiles, *Curr. Sci.*, 109, 893–901, 2015.
17. Salah, S.M., Antibacterial activity and UV protective property of some Egyptian cotton fabrics treated with aquous extract of banana peel, *Int. J. Clothing Sci.*, 1(1), 1–6, 2012.
18. Rajendran, R.C., Balakumar, T., Kalaivani, M., R. Sivakumar, Dyeability and antimicrobial properties of the cotton fabrics finished with Punica Granatum extracts, *J. Text. Apparel Technol. Manag.*, 7(2), 1–12, 2011.
19. Katarzyna, P. and S. Prezewozna, Natural dyeing plants as a source of compounds protecting against UV irradiation, *Herba Policia*, 55(3), 311–318, 2009.
20. Li, S.H., Boyter, Jr., Qian, L., UV curing for encapsulated aroma finishing of cotton fabrics, *J. Text. Inst.*, 96, 407–411, 2010.
21. Neog, S.R. and Deka, C.D., Salt substitute from banana plant, *J. Chem. Pharma. Res.*, 5(6), 155–159, 2013.

22. Samanta, A.K., Konar, A., and Chakrabarti, S., Dyeing of jute fabric with tissue extract: Part 1-Effect of different mordants and dyeing process variables, *Ind. J. Fibre Text. Res.*, 36(1), 63–73, 2011.
23. Samanta, A.K. and Konar, A., Dyeing of textiles with natural dyes, in: *Natural Dyes*, E.P.A. Kumbasar (Ed.), pp. 29–56, InTech Publisher, Croatia, EU, 2011.
24. Samanta, A. K. and Agrawal, P., Application of natural dyes on textiles, *Ind. J. Fibre Text. Res.*, 34, 384–399, 2009.
25. Gupta, D., *Protective Properties of Textiles Dyed with Natural Dyes*, The Textile Institute, Woodhead Publication Ltd., New York, 2006.
26. Chattopadhyay, S.N., Pan, N.C., Roy, A.K., Saxena, S., Khan, A., Development of natural dyed jute fabric with improved color yield and UV protection characteristics, *J. Text. Inst.*, 104(8), 808–818, 2013.
27. Basak, S., Saxena, S., Chattopadhyay, S.K., Narkar, R., Mahangade, R., Banana pseudostem sap: a waste resource for making thermally stable cellulosic substrate, *J. Ind. Text.*, 46(4), 1003–1023, 2016.
28. Samanta, A.K., Bagchi, A., Biswas, S.K., Fire retardant finishing of jute fabric and its thermal behavior by using phosphorous and nitrogen based compound, *J. Polym. Mater.*, 28, 149–169, 2011.
29. Ramya, K. and Maheshwari, V., Antiseptic treatment for human foot wounds using piper betel extract finished bamboo/cotton fabrics, *Indian J. Fibre Text. Res.*, 40(2), 213–216, 2015.
30. Samanta, A.K., Bhattacharya, R., Chowdhury, R., Fire retardant chemical finishing of jute fabric using sulfamate and urea mixture, *AASCIT J. Mater.*, 1(4), 98–110, 2015.
31. Shukla, A., Basak, S., Ali, S.W., Chattopadhyay, R., Development of fire retardant sisal yarn, *Cellulose*, 24(1), 423–434, 2016.
32. Gohl, E.P.G., Vilensky, L.D., *Textile Science: An Explanation of Fibre Properties*, 2nd ed., CBS Publishers, India, 2005.
33. Rajendran, R., Radhai, R., Balakumar, C., Synthesis and characterization of neem chitosan nanocomposite for development of antimicrobial cotton textiles, *J. Engineer. Fibre. Fabrics*, 7(1), 136–141, 2012.
34. Thilagavathi, G. and Kannaian, T., Combined antimicrobial and aroma finishing treatment for cotton using microencapsulated geranium leaves extract, *Indian J. Nat. Prod. Resour.*, 1(3), 348–352, 2010.
35. Joshi, M., Wazed Ali, S., Purwar, R., Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products, *Ind. J. Fibre Text. Res.*, 34, 295–304, 2009.
36. Basak, S. and Ali, S.W., Leveraging flame retardant efficacy of pomegranate rindextract, a novel biomolecule, on ligno-cellulosic materials, *Polym. Degrad. Stabil.*, 144, 2017.
37. Banupriya, J. and Maheswari, V., Comparative studies on antibacterial finishes by herbal and conventional methods on woven fabrics, *J. Text. Sci. Eng.*, 3(1), 1–2, 2013.

38. Sathianarayanan, M.P., Bhatt, N.V., Kokate, S.S., Walung, V.L., Antibacterial finishing of cotton fabrics from herbal products, *Ind. J. Fibre. Text. Res.*, 35, 50–58, 2010.
39. Ahmed, H.A., Rajendran, R., Balakumar, C., Nanoherbal coating of cotton fabric to enhance antimicrobial durability, *Elix. Appl. Chem.*, 45, 7840–7843, 2012.
40. Teli, M.D., Pandit, P., Basak, S., Coconut shell extract imparting multifunctional finishing of lingo-cellulosic material, *J. Ind. Text.*, 2017.
41. Teli, M.D. and Pandit, P., Novel method of ecofriendly single bath dyeing and functional finishing of wool protein with coconut shell extract biomolecules, *ACS Sustain. Chem.Eng.*, 5(9), 8323–8333, 2017.
42. Horrocks, A.R., Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions, *Polym. Degrad. Stab.*, 96, 377–392, 2011.
43. Horrocks, A.R., Textiles, 2nd ed, Woodhead Publishing Limited, Cambridge, England, UK, 2009.
44. Basak, S., Samanta, K.K., Chattopadhyay, S.K., Narkar, R., Thermally stable cellulosic paper made using banana pseudostem sap, a wasted by-product, *Cellulose*, 22, 2767–2776, 2015.
45. Basak, S., Samanta, K.K., Chattopadhyay, S.K., Pandit, P., Maity, S., Green fire retardant finishing and combined dyeing of proteinous wool fabric, *Color. Technol.* 132(2), 135–143, 2016.
46. Bosco, F., Casale, A., Gribaudo, G., Malucelli, G., Nucleic acids from agro-industrial wastes: A green recovery method for fire retardant application, *Ind. Crops Prod.*, 108, 208–218, 2017.
47. Coquelle, M., Duquensene, S., Casetta, M., Sun, J., Gu, X., Zhang S., Bourbigot S.. Flame retardancy of PA6 using a guanidine sulfamate/melamine phosphate mixture. *Polym.* 7, 316–332, 2015.
48. Carosio, F., Fontaine, G., Alongi, J., & Bourbigot, S., Starch based layer by layer assembly: efficient and sustainable approach to cotton fire protection, *Appl. Mater. Interfaces*, 7(22), 12158–12167, 2015.
49. Bosco, F., Carletto, R.A., Alongi, J., Marmo L., Blasio, A.D., Malucelli, G., Thermal stability and flame resistance of cotton fabric treated with whey protein, *Carbohydr. Polym.*, 94(1), 372–377, 2013.
50. Basak,S., Samanta, K.K., Chattopadhyay, S.K., Saxena, S., Parmar, M.S., Wastage spinach leaf: Source for making self-extinguishable cellulosic substrate, *Ind. J Fibre Text. Res.*, 42(2), 215–222, 2017.
51. Alongi, J., Blasio, A.D., Cutica, F., Carosio, F., Malucelli, G., Bulk or surface treatments of ethylene vinyl acetate copolymers with DNA: Investigation on the flame retardant properties, *Eur. Polym. J.*, 51, 112–119, 2014.
52. Ramaya K. and Maheswari, V., Analysis of antimicrobial efficacy of bamboo/cotton knitted fabrics finished with the *Syzygium aromaticum* buds, *J. Text. Sci. Eng.*, 3(3), 1–5, 2013.

53. Sun S.S. and Tang, R.C., Adsorption and UV protection properties of the extent form honeysuckle into wool, *Indus. Eng. Chem. Res. J.*, 50(8), 4217–4224, 2011.
54. Sarkar, A.K., An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants, *BMC Dermatol.*, 4, 15, 1–15, 2004.
55. Marsh, J.T., *Mothproofing in Textile Science, an Introductory Manual*, pp. 371–374, Chapman and Hall limited, London, 1948.
56. Gupta, D., Periyasamy, S., Abhishek, B., Basic dye able polyester: A new approach by using VUV Excimer lamp, *Color. Technol.*, 123(4), 248–251, 2007.
57. Marsh, J.T., *Mildew-and rot-proofing in Textile Science, an introductory manual*, pp. 377–383, Chapman and Hall limited, London, 1948.
58. Kartick K. Samanta, Gayatri T.N., S. Saxena, S. Basak, S.K. Chattopadhyay, A. Arputharaj, and V. Prasad, "Hydrophobic Functionalization of Cellulosic Substrates using Atmospheric Pressure Plasma", *Cellulose Chem. Technol.*, 50 (7–8), 745–754, 2016.
59. M. D. Teli, Kartick K. Samanta, Pintu Pandit, S. Basak and S. K. Chattopadhyay, "Low-temperature dyeing of silk fabric using atmospheric pressure helium/nitrogen plasma", *Fibres and Polymers*, Vol. 16. No. 11, 2375–2383, 2015.
60. Samanta, K. K., Joshi, A. G., Jassal, M., & Agrawal, A. K., "Study the hydrophobic finishing of cellulosic substrates using He/1,3 butadiene plasma at atmospheric pressure" *Surface and Coating Technology*, 213, 65–76, 2012.
61. Samanta, K. K., Jassal, M., & Agrawal, A. K., "Antistatic Effect of Atmospheric Pressure Glow Discharge Cold Plasma Treatment on Textile Substrates", *Fibers and Polymers*, 11 (3), 431–437, 2010.
62. Samanta, K. K., Jassal, M., & Agrawal, A. K., "Atmospheric pressure plasma polymerization of 1,3- butadiene for hydrophobic finishing of textile substrates" *Journal of Physics: Conference Series*, 208, 012098, 2010.
63. Kartick K. Samanta, S. Basak, and S. K. Chattopadhyay, "Environment Friendly Textile Processing using Plasma and UV Treatment", Springer Publication, *Roadmap to Sustainable Textiles and Clothing: Eco-friendly Raw Materials, Technologies and Processing Methods*, S.S. Muthu (ed). pp. 161–201, 2014.

20

Interconnection Between Biotechnology and Textile: A New Horizon of Sustainable Technology

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Abstract

Modern day science and technology is showing a keen interest in interdisciplinary studies. There are already a significant number of examples of this, and many are to be exploited. Textile industries, being one of the oldest, most resource consuming systems, definitely require eco-friendly, efficient, and economical alternatives to sustain in this era. Application of biotechnology in textile processing is a very positive approach to attain sustainability. At the same time, modern day textile can offer much help to different biotechnology processes. In this article, two applied fields of technology *viz.* Biotechnology and Textile technology are discussed, and how they are interconnected has been described.

Keywords: Sustainability, biotechnology, textile, antimicrobial activity, protective textiles

20.1 Introduction

Bioprocess and textile are two well established practical subjects of immense importance. Textile is the field well known to us since the dawn of the civilization. Ancient civilizations like Egyptian, Mayan, and Indus Civilization were famous for their particular specialties in a different part of textiles like weaving, dyeing,etc. Till then, Textile is one of the core

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Mohd Yusuf (ed.) Handbook of Renewable Materials for Coloration and Finishing, (549–574)

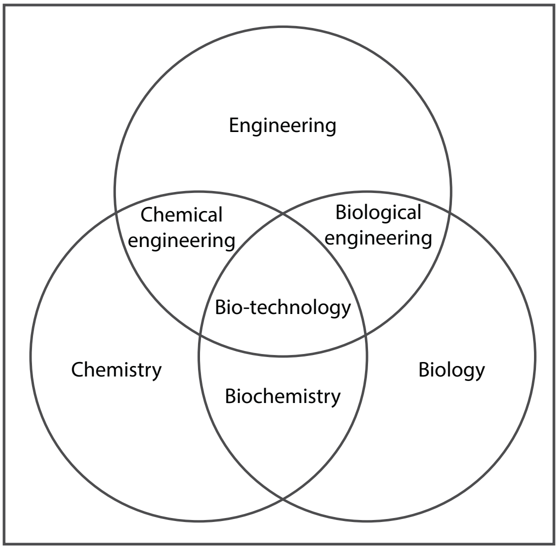

Figure 20.1 Biotechnology at a glance.

needs of every person, both for apparel and other purposes. On the other hand, bioprocess is also a vast field of knowledge. European Federation of Biotechnology defines Biotechnology as "The integrated use of biochemistry, microbiology, and engineering sciences to achieve technological (industrial) application of the capabilities of microorganisms, cultured tissue cells and parts thereof [1]. People use biotechnology nearly from as early as they are using textiles without knowing what it is and how it works. The invention of Microscope by Antonie van Leeuwenhoek showed the presence of a microorganism in the atmosphere in 1653, and Louis Pasteur demonstrated that the microorganisms are responsible for fermentation in 1862 and gave microbiology and biotechnology, an establishment in the field of modern science. Application of biotechnology (Figure 20.1) in textile is also an age-old process where retting of bast fibers, as well as desizing of fabric before dyeing, is well established. In this chapter, the mutual relation between textile and biotechnology is discussed.

20.2 Influence of Bioprocess on Textile

The textile industry is one of the pioneering industries to use enzymes. Crude amylase was introduced as early as at the turn of Twentieth Century to desize starch from the woven fabric, thereby overcoming the fabric-damaging effects of conventional acid-based steeping process.

The mild enzymatic treatments have led to improved process quality, efficiency and effectiveness and reduced environmental impact [2].

20.2.1 Fibers and Polymers

20.2.1.1 Modified Cotton

20.2.1.1.1 Transgenic Cotton

Cotton is undisputedly known as the king of textile fibers and its production gets highly affected by various pests. One of the main such insect is cotton boll weevil. Very strong and harmful pesticides are used in order to destroy these insects before these destroy the maturing cotton bolls. These chemicals are detrimental to both human health and environment. An alternative economic, environmental, and low pesticide consuming process was attempted by several researchers by using *Bacillus thuringensis* (Bt) for controlling these insects. Genes of Bt transgenic cotton plants were such altered so that these expressed some proteins which destroy digestive system of the larvae of lepidopteran pests when they consume the cotton. These proteins are not harmful to mammals or birds and have limited effect on non-target invertebrates, which is the main advantage of those proteins over conventional pesticides [3]. However, plantation of Bt cotton evoked some serious controversies in terms of the transfer of genes from crops to wild relatives and related species, the resistance evolution to herbicide tolerant crops, virus-resistant crops, and insect-resistant crops over the period of time, and the impacts on non-target organisms and thus on the ecosystems [4–7]. Therefore, Bt cotton plantation needs a thoroughly monitored risk assessment, and utilization of these modified seeds has been restrained by many countries [8–10].

20.2.1.1.2 Colored Cotton

Naturally colored cotton is a century old phenomena and had been cultivated and used even before 2,500 B.C. in Peru. Modern-day genetic engineering also trying to form pigments to get lodged inside the lumen of the fiber and thus color is generated [11]. The color formation or pigmentation is genetically controlled and influenced by humidity, soil type, and other ambient parameters. Except for the particular gene that controls the pigmentation, the colored cotton plant resembles conventional cotton. Green and brown are the generally available color in this type of cotton which is the main limitation of colored cotton [12]. Research is also carried out to cultivate blue, red, and black cotton by transferring an external colored gene into natural white cotton by using genetic engineering technology [13].

20.2.1.2 Biopolymers

Biopolymers, as the name suggest, are polymeric biomolecules. These polymeric compounds are generated in living organisms. Like all polymers, these are also made up of units called monomers which are covalently bonded and form a large structure as compared to the repeating units. The physiochemical properties of the biopolymers are dependent upon their repeating units and their arrangement of bonding. The different biopolymers present in the environment can broadly classified chemically into three categories; polysaccharides, polypeptides, and polyneucleotides. On another approach, biopolymers can be categorized according to their source as mentioned below:

- Polymers directly obtained from natural resources such as polysaccharides and polypeptides
- Polymers that are obtained by chemical modification and synthesis from biomass based monomers like polylactic acid
- Polymers generated by naturally occurring or genetically modified microorganisms such as bacterial cellulose, bacterial polyesters, etc [14].

The abundant renewable sources, biodegradability, biocompatibility are some of the important advantages of biopolymers. Utilization of biopolymer in textile was quite limited to application of starch in preparing printing paste and in making size material. However, recent knowledge of biotechnology enhanced the application of new biopolymers, which could suffice the demand of the customers while keeping the environmental norms within limit. Use of biopolymer for imparting antimicrobial property is a result of stringent environment norms and advancement in biotechnology. Most of the widely used antimicrobial chemicals like organo metallic salts, derivatives of formaldehyde, amines, etc. are now under strict vigilance and use of alternative process and products are getting more interest [15]. Some of these biopolymers which came out to be quite useful in textile finishing process are listed below.

20.2.1.2.1 Chitin and Chitosan

Chitin is a polysaccharide with nearly same structure of cellulose except it contains nitrogen in the glucose ring. Chitin is a homopolymer of

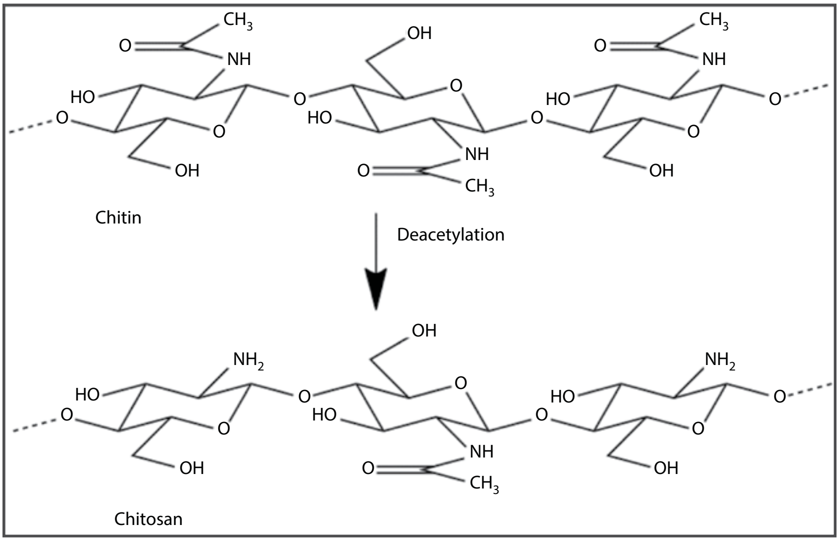

Figure 20.2 Structure of Chitin and Chitosan.

β(1–4) – linked N-acetyl –D–glucosamine (Figure 20.2). It constitutes exoskeletons of arthropods and insects and the radula of mollusks along with the cell walls of the fungi. When chitin is partially deacetylated under alkaline condition, its solubility increases and this deacetylated chitin is known as chitosan (Figure 20.2). Chitosan is biodegradable and non-toxic that made it second most abundant renewable biopolymer after cellulose. Chitosan is a very useful product for textile. The major application of chitosan in textile is in antimicrobial finishing. Along with that, chitosan has various other applications such as dyeing of cotton with acid dyes or reactive dyes with less to no salt, crease recovery finish, antifelting finishing of wool, as dyeing improving agent for polypropylene, combined thickener and binder for pigment printing, etc. According to Pang (2003), the fiber made out of blend solution of cellulose xanthate and chitin xanthate has excellent filtering properties as compared to cellulosic viscose as well as higher bacteriostatic properties [16–18].

20.2.1.2.2 Sodium Alginate

Sodium alginate is the Na salt of natural anionic polysaccharide based biopolymer and is obtained from brown seaweeds (Figure 20.3). It has industrial uses in textile printing, paper, food, pharmaceuticals, etc. as it is water soluble, gel forming and has an excellent wound healing property. Around 20–40% alginic acid is available in different variants of brown seaweeds

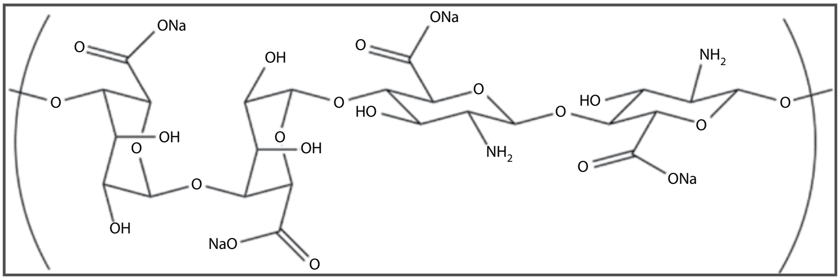

Figure 20.3 Sodium Alginate.

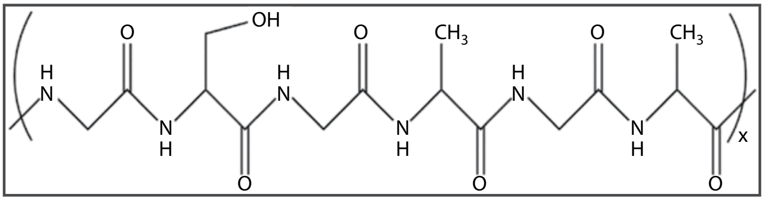

Figure 20.4 Structure of Sericin.

viz. ascophyllum, durvillaea, ecklonia, laminaria, etc. The extraction process consists of treatment with sodium hydroxide solution which converts alginic acid into water soluble sodium alginate which is further filtered and then precipitated using calcium chloride. Alginic acid is a linear copolymer with homopolymeric blocks of (1–4)-linked β-D-mannuronate and α-L-guluronate covalently linked together in different sequences or blocks. Sodium alginate is widely used because of its great ability to form a highly viscous solution at moderate concentration. This property has been successfully utilized in printing of cellulosics with reactive dyes, as starch based thickeners are not suitable for this purpose. Alginate fibers are useful for wound dressing purposes and thus has made its place in medical textiles [19, 20].

20.2.1.2.3 Sericin

Sericin (Figure 20.4) and fibroin are the two component of raw silk filament. Fibroin is the fibrous part whereas sericin acts as an envelope for the fibroins during its formation. Sericin is a natural macromolecular protein with a molecular size of about 65 to 400 kDa. Sericin is biocompatible, antibacterial, biodegradable, UV resistant, oxidation resistant and it has good moisture absorption ability and therefore it got applicability in pharmaceuticals, cosmetics, and textiles. Membrane based on pure sericin as

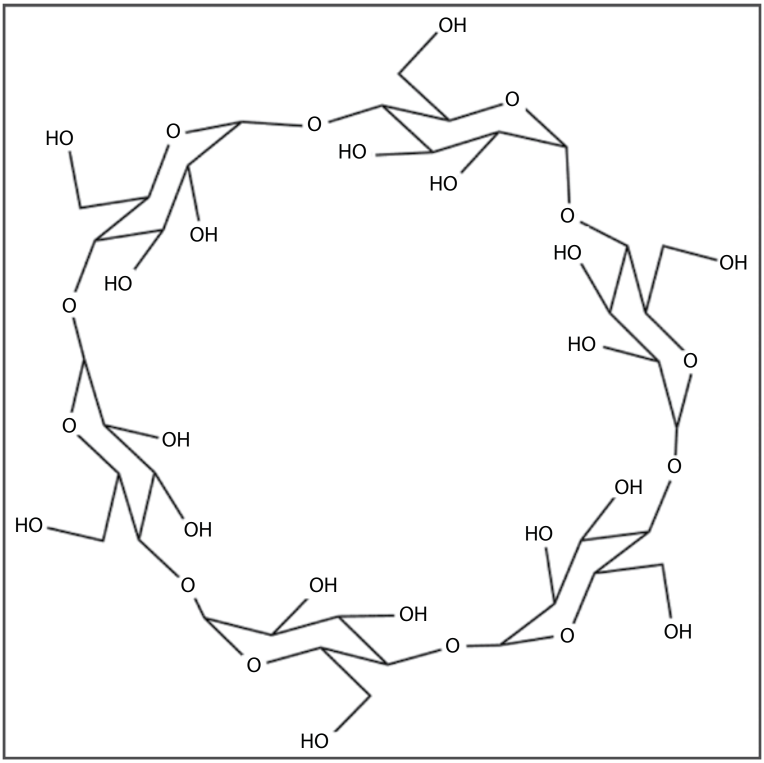

Figure 20.5 Structure of Cyclodextrin.

well as sericin along with other substances via crosslinking, blending or copolymerizing can be readily made. These membranes are generally used in membrane based separators as well as in wound dressing [15, 21].

20.2.1.2.4 Cyclodextrin

Cyclodextrin (Figure 20.5) is a cyclic oligosaccharides produced by degradation of starch by cyclodextrin glycosyltransferase enzyme. Cyclodextrins are composed of 6–8 α-1,4-linked glucopyronase sub-units. They have the ability to form inclusion complexes selectively with other substances and therefore have potential in functional finishing of textiles, such as aroma finish, antibacterial finish, and other controlled release finishing processes [15].

20.2.1.3 Thermoplastic Polymers Derived from Natural Sources

Most of the widely used synthetic textile polymers are thermoplastic in nature. These are derived from petroleum condensates and are not biodegradable. Polyester, nylon, acrylonitrile, etc. are some of the common example of this. However, some of the thermoplastic polymers, generally biodegradable polyesters, are now possible to create from renewable sources.

20.2.1.3.1 Poly Lactic Acid

As the name suggests, this one is derived from lactic acid (2-hydroxy propionic acid). Lactic acid is produced by bacterial fermentation of carbohydrates obtained from corn, potato, and cassava. Poly lactic acid (PLA) (Figure 20.6) can therefore be produced entirely from biomass, and the final products can easily be recycled, composted, or incinerated. PLA can be spun by melt spinning, dry or wet spinning, dry jet wet spinning and electrospinning. It is a biodegradable polyester and has extensive use in medical textiles, especially sutures, implants, scaffolds, etc because of its bioresorbability and biocompatibility in the human body [22, 23]. It also is the first truly synthetic fiber which is entirely biodegradable.The physical properties depend on preparation process, molecular weight and also the ratio of l-lactic acid and d-lactic acid ratio which determines the crystallinity of the fiber [24].

20.2.1.3.2 Bacterial Polyesters

There are certain bacteria which can produce biodegradable polyesters as their intercellular food and energy source. They are termed as bacterial polyester (Figure 20.7). The most common polymer among this class is poly(3-hydroxybutyrate) (PHB), which was discovered in 1920 as

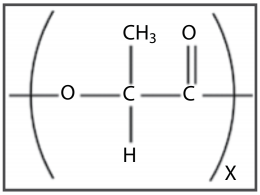

Figure 20.6 Structure of Poly lactic acid.

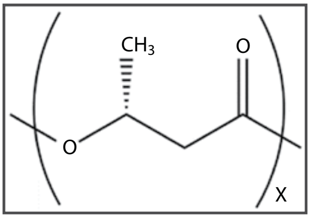

Figure 20.7 Bacterial Polyester.

produced by the bacteria "*Bacillus megaterium*". Since then, it was found that several other bacterial strains can produce the same polymer. PHB is a semicrystalline isotactic polymer. It undergoes surface erosion by hydrolytic cleavage of the ester bonds and has a melting temperature in the range of 160–180 °C and glass transition temperature (T_g) in between -5 to 20 °C [25, 26]. It is found that PHB can be easily processed because it is readily soluble in a variety of solvents and can be transformed into different shapes and structures, such as films, sheets, spheres, and fibers. It can be used to make films and sheets, and it has also been investigated as a material for developing bone pins and plates [27]. The hydrolytic degradation of PHB results in the formation of D-(-)-3-hydroxy-butyric acid which is a normal constituent of blood (concentrations between 0.3 and 1.3 mM) [28].

20.2.1.3.3 Genetically Engineered Biopolymer

Genetic engineering studies have developed a way to incorporate spiders' silk-spinning genes into goats, allowing the researchers to combine spider silk protein with goats' milk for a variety of applications (Table 20.1). This ultra strong fiber with high elasticity could have several medical uses, such as, for making artificial ligaments and tendons, for eye sutures, and for jaw repair. The silk could also have applications in bulletproof vests and improved car airbags [29, 30].

20.2.2 Pretreatment

Textile pretreatment mainly consists of cleaning of the outer surface of the fiber or filament, and removing unnecessary pigments and thereby

Table 20.1 Application of the biopolymers.

Name of biopolymers	**Applications**
Chitin	Artificial skin, blood vessels, surgical sutures, antitumor homeostatic agent, immunity promoter and anticholesterol agent.
Chitosan	The chemical industry, medicines, food, cosmetic, printing, papermaking, agriculture, etc.
Alginate	Fluid handling, gel blocking, pain control, and healing properties
PLA	Nonwoven disposables, paper coating, fiber fill, furnishing, industrial application, etc.

increasing its uniform absorbency and whiteness. Textile pretreatment mainly broadly divided insingeing, desizing, scouring, bleaching, etc. Normally these processes are carried out using various chemicals including strong alkali, acid at a relatively higher temperature. Subsequently, these chemicals are removed from the textile materials after the respective processes by thorough washing, which further requires huge amount of water. There are suitable enzymes for each process to reduce the use of harsh chemicals and high temperature and thereby to reduce the effluent load.

20.2.2.1 *Desizing*

Starch is widely used as a sizing agent, being readily available, relatively cheap and based on natural, sustainable raw materials. Figure 20.8 represents the desizing of starch into glucose. 75% of the sizing agents used worldwide is starch and its derivatives. Conventionally, the fabric is treated with mineral acid to degrade the starch. If this process is not very carefully controlled, cellulose present in the cotton material also get degraded. α-amylase is the enzyme to degrade starch without causing any damage to the fabric structure as compared to the acid treatment [31, 32].

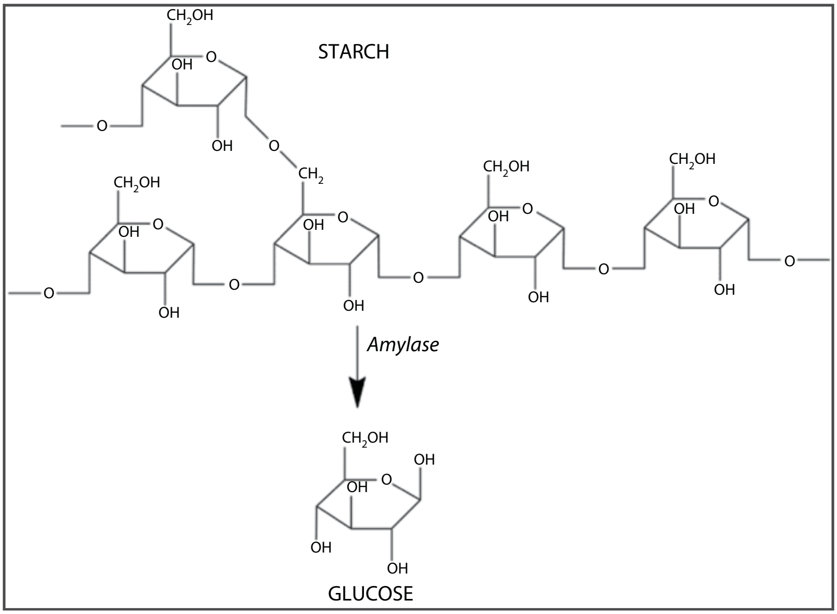

Figure 20.8 Desizing of Starch into Glucose.

20.2.2.2 *Scouring*

The scouring of the cotton fabrics is a process, which aims to improve the absorbency and the whiteness of textile materials, removing from the fibers the non-cellulosic natural matter, i.e., fats, waxes, pectins, and proteins. Pectin in fiber acts as a cementing material to the fiber and natural waxes and other impurities. Traditionally, this preparation process was performed in alkaline medium at boiling temperature. Alkaline scouring consumes large quantities of alkali and requires an extensive rinsing process that loads the washing effluent with environmentally harmful chemicals. Cellulose is susceptible to oxidation damage under these treatment conditions, which might result in decreased tensile strength of the fabrics. Alkaline scouring may also cause fabric shrinkage and changes in physicomechanical properties of fabrics, e.g., their handle [33, 34]. Pectinase is a useful enzyme which hydrolyses pectins present in cotton as a non-cellulosic impurity. The addition of cellulase and lipase enzyme to the treatment enhances the treatment efficiency.

20.2.2.3 *Bleaching*

Glucose oxidases (GOD) are flavoproteins with a flavin-adenine-dinucleotide (FAD) active site. The enzyme is highly specific for β-D-glucose and catalyzes the following reaction for hydrogen peroxide generation at pH-4.5–7 and temperatures of around 40 °C [35]:

$$\beta\text{-D-glucose} + \text{GOD-FAD} \rightarrow \text{GOD-FAD} + H_2O_2 + \beta\text{-D-glucono-}\delta\text{-lactone}$$

This way in neutral condition hydrogen peroxide can be generated in bleaching bath with minimum effluent load and lower temperature with optimized efficiency. Biobleaching of flax fiber by degrading lignin with laccase is also reported [36].

20.2.2.4 *Peroxide Killing*

During cotton materials bleaching using hydrogen peroxide, fabric whiteness is increased as natural pigments inside lumen and “motes” (dark seed coat fragments) are decolorized or degraded. However, if the material is not thoroughly washed with water, residual peroxide inside the fabric becomes a problem since it may degrade the material by over oxidation in warm alkaline treatments such as dyeing or washing. It may also cause less shade depth in dyeing process by oxidizing the colors and thus the removal of residual peroxide is crucial. Earlier some inorganic reducing agents were applied post bleaching to remove these remaining hydrogen peroxide molecules. This was never advisable as finding the optimum dosage of these chemicals were almost impossible in a textile processing shop floor. This, in turn, caused presence of either residual oxidative agent or added reducing agents in the material, which either way hampered the dyeing process. Therefore, immediately after bleaching using hydrogen peroxide, catalase, which is an oxidoreductase enzyme, can be used to decompose residual hydrogen peroxide efficiently. This, in turn also saves water and time by reducing the number of rinses needed after bleaching, before dyeing [37, 38].

20.2.3 Dyes and Dyeing

20.2.3.1 Natural Dyes and Dyeing

There is always an interest in the dyeing of textile fibers with natural dyes, because of their high compatibility with the environment and because of their lower toxicity, low allergic reactions and in some cases, their medicinal properties. Less exhaustion of the dyes and medium to poor color fastness of the dyed fabrics are the limitations of this type of dyeing. Normally, metallic salts as mordants are used to improve fastness properties and to develop different shades with the same dye. It has been reported that when cotton and wool were treated with a combination of cellulase, α-amylase, and trypsin, its dyeability using chlorophyll and carmine were notably increased. Enzymatic pretreatment had a positive influence on both dye uptake and fastness properties [39]. Better dyeing properties are also observed in the case of ultrasonic textile dyeing with natural dyes such as *Acacia catechu* and *Tectonagrandis* and faster dye uptake after enzymes such as amylase, lipase, and diasterase pretreatment on cotton fabric and results of dyeing are better than metal mordanted fabric [40]. In the same way, experiments were performed by applying tannic acid as pretreatment substance which forms a complex structure with enzymes. Cotton and silk fabric were treated with dyes obtained from *Terminalia arjuna, Punicagranatum,* and *Rheum emodi* by this process and showed higher adsorption of dyes [41]. Recent trends in research are trying to formulate natural color like chlorophylls and the carotenoids, flavonoids, and betalains in the laboratory and confirm their structure with the natural ones [42].

Extraction of natural dyes from plants with enzymatic reactions is also proven to be effective. The pigment extracted from the root of *Lithospermumerythrorhizon* are used as natural red dyes. In this process, a method of enzymatic pigment production is based on the introduction of hydrolytic enzymes before the usual extraction to avoid repeated pigment extraction. The matrix destruction in the epidermal layer of the root by the xylanase from *Bacillussp* was found to improve the pigment extractability [43]. One step chemoenzymatic reaction has been formulated for extraction of blue pigment from Gardenia extracts. It has shown fairly good color fastness properties, even in the absence of mordants [44].

20.2.3.2 Bacteria Derived Pigments

It is a worldwide interest in searching for new pigments from natural resources. Natural pigments are available from a variety of plants, animals, microorganisms (Table 20.2). Among all those natural pigments, only a few are available for industrial purpose due to the higher productivity. Therefore, it is preferable to use microorganisms for producing pigments as they give a high yield of production, are feasible of bioprocess development and lot more to be explored [45]. Red, yellow, and blue are primary pigments. Few of these microorganisms and the color name has been listed below [46–52].

Production of a violet pigment by *Janthinobacterium lividum XT1* has been reported by Lu *et al.* [53]. The color of the pigments may have sensitivity towards surrounding pH [45].

20.2.4 After or Post-Treatment

To produce some fade effects in denim fabrics, the abrasive action is commonly applied using lightweight pumice stones on the garment surface which remove some of the dye. However, it is a process where extra care is to be taken, or else hems and waistbands might be heavily damaged. That is why, denim finishers today use acidic, hybrid or neutral cellulase to accelerate the loosening of indigo dyes from the denim fabric surface.

Table 20.2 Natural pigments obtained from microorganisms.

Natural pigments	Producing microorganisms
monascus	*Monascus sp.*
carotenoid	*Phaffiarhodozyma*, *Micrococcus roseus,Brevibacteriumlinens* and *Bradyrhizobium sp.*
xanthomonadin	*Xanthomonascampestrispv.*

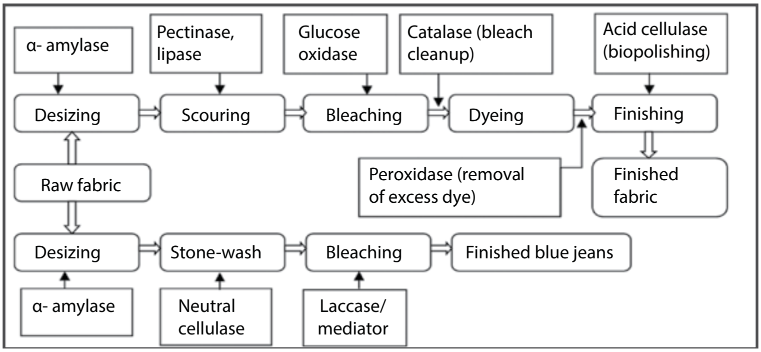

Figure 20.9 Application of different enzymes in textile processing.

Since a small amount of enzyme can replace several kilograms of stones, the use of fewer stones or no stones results in less damage to garments, less wear on machines and less pumice dust in the working environment. The possibility of back staining is reduced by using different back-staining removing enzyme blend which mainly contains various proteases, lipase, and endolase. Other denim finishes are also accomplished by using laccase or peroxidase instead of using hypochlorites or peroxides[54]. Figure 20.9 shows the application of different enzymes in textile processing. Mild acidic or neutral cellulases are also very widely used in a process known as biopolishing, wherein the protruding surface fibers of cotton materials are removed by enzymatic hydrolyzation than conventional burning process. It also reduces the pilling tendency of the fabric and thereby forms a smooth and soft hand property [55].

20.2.5 Decolorization of Textile Dyes Waste

Textile materials cannot absorb 100% of dyes from the dye bath mainly because of the structure of both dye and fiber as well as the surface potential of the fibers. Remaining dyes of the dye bath are wastes and were earlier drained to the environment. It was found out that dyes hinder light penetration in water and oxygen transfer in organism living in it. Without proper treatment, most of the dyes are stable and remain in the environment for a prolonged period. Moreover, there are some dyes which produce carcinogenic and mutagenic chemicals while degrading [56]. With the stringent environment norms across the globe, this effluent water is prohibited from draining directly without proper treatment. These treatments mainly contain chemical flocculation and settling of chemicals and separating in sludge form. These chemicals used for waste water treatment are also generally not eco-friendly. Therefore, alternative processes are searched, and it is found out that different *Pseudomonas sp.* such as *Pseudomonas aeruginosa, Pseudomonas oleovorans,* and *Pseudomonas putida* have shown considerable decolourisation, 80% in case of *Pseudomonas oleovorans* in liquid medium [57]. In another experiment, *Aspergillus foetidus* is found to be very much effective to decolorize the media containing azo reactive dyes up to the extent of 95% within 48 hours of growth of the fungus. It even showed 85% decrease in a mixture of dyes within 72 hours. This experiment also came up with the fact that the process of decolourisation is proportional to the growth of these microbes and requires a biodegradable substrate such as glucose. Alternate and cheaper carbon source can also be effectively used [58]. In the case of Indigoid vat dyes, some ligninolytic basidiomycete fungi have shown sufficient decolourisation after four days of growth. After four days the removal of dye by *Phellinus gilvus* culture was in 100%, by *Pleurotussajor-caju* 94%, by *Pycnoporussanguineus* 91% and by *Phanerochaetechrysosporium* 75% whereas no color decrease was observed in a sterile control [59].

20.2.6 Biosurfactants

Petroleum based synthetic surfactants are widely used in different industries due to their efficacy. However, with the increasing awareness towards biodegradability, and production of renewable-resource substrates, biosurfactants may eventually replace chemically synthesized counterparts [60]. Bio based surface active agents are amphiphilic chemicals. There are certain microorganisms which can produce these surfactants which can reduce the surface tension of various interfaces,can be successfully utilized in reducing marine and soil pollutions and thus there are a lot of industrial uses of biosurfactants [61]. Enzo Montoneri *et al.* reported on isolation of biosurfactant from urban waste compost and its application on textile dyeing [62]. Biosurfactants have also been used for removal of heavy metals from an aqueous solution of industrial wastewater [63].

20.2.7 Antimicrobial Activities and the Tests

Textile materials, like all organic compounds, have a finite life in the environment. They are attacked by microorganisms that use these organic materials as a source of nutrition. To prevent the degradation, antimicrobial agents are applied to textiles. The first antimicrobial agent used in spin finishes was probably silver nitrate. Later on, many non-toxic and cheaper antimicrobial chemicals are synthesized and used successfully in various processes [64].

The AATCC Technical Manual has some test procedures that are most frequently used, the agar-based zone of inhibition and the bacteria counting tests. The tests are summarized in Table 20.3 [65, 66].

A more rapid test method, developed by the British Textile Technology Group in the late 1980s, is based on adenosine triphosphate (ATP)

Table 20.3 Different antimicrobial tests methods by AATCC.

AATCC test methods	Comments
Antibacterial activity of textile materials: Parallel Streak Method; Test Method 147 (agar plate method)	It is a rapid and qualitative method to determine the anti-bacterial activity of treated textile materials against bacteria. Herein, test textile material is kept on nutrient enriched agar and streaked with test bacteria. Antibacterial activity is seen by zones of inhibition on and around the textile material.
Antibacterial finishes on textile materials, assessment of: Test method 100	This is quantitative test method to check the antibacterial activity wherein the test specimen is kept in solution containing either gram positive or gram negative bacteria for specified time and the bacterial growth or inhibition was measured by serial dilution and subsequent inoculation of sterile agar.
Assessment of antifungal activity on textiles: Mildew and rot-resistance of textiles; Test method 30	It contains a set of four methods for determining the antifungal properties of treated textiles. In the first method, properties of treated textiles are tested after burial in soil that contains fungi. In the second method, the cellulose fabricis exposed to *Chaetomium globosum* in an agar plate and the subsequent growth is visually determined. The third method exposes textiles to *Aspergillus niger* in an agar plate and visually determines any fungal growth. The fourth method uses a humidity jar to expose textiles to mixtures of fungi spores. Any growth on the textile is visually determined.
Assessment of antimicrobial activity of carpets; Test Method 174	This test is set for carpet materials. The quantitative and qualitative measurement of antimicrobial activity of carpets is evaluated by tests similar to those in the above test methods.

luminescence. The growth of microorganisms is assessed by firefly bioluminescent detection and ATP analysis [67].

20.2.8 Textile Detergent

Since 1961 when Bio40 was introduced with Novo's Alcalase (a proteolytic enzyme), detergent enzymes have proceeded on a great growth track. In the early 1980s, lipase enzyme was identified for fat splitting, and in 1987 in Japan, Kao had achieved great success with the first alkaline cellulase for detergents. Later on, α-amylase was found to be very useful towards cleaning starch based stains [68].

20.3 Influence of Textile on Biotechnology

20.3.1 Filtration

Many fatal infectious diseases, such as tuberculosis, acute lower respiratory infections, and severe acute respiratory syndrome, are caused by bacteria or viruses. The spread of these causative microorganisms is mainly via airborne particles and water [69]. Lei Yang *et al.* worked with multilayer deposition of hydroxyapatite on cotton fabric for filtration of bacteria. Hydroxyapatite is investigated for its excellent biocompatibility and nontoxic hypostasis with organic tissues and its adsorbability of bacteria and replication-competent human virus [70]. Blood filtration devices contain particular kind of fabrics. Phosphorylcholine is reported to be used as a coating on blood filtration fabrics as the polymer reduces the platelet adhesion and activation during contact with blood in dry state [71].

20.3.2 Immobilization

In biological systems, enzymes are predominantly intracellular or associated with cell membranes. This enables them to perform their activity in a particular environment, be stored and protected in a stable form, take part in multi-enzyme reactions, acquire cofactors, etc. They are, in general, quickly inactivated under conditions such as high temperature, high or low pH, the presence of organic solvents, and even conditions suitable for many catalytic reactions (Table 20.4). The recovery of these enzymes from the spent reaction mixture is another problem when biocatalysts are used in the free form. Immobilization is one way of overcoming these problems. In general, immobilized catalysts are stable and can be utilized either repeatedly in

Table 20.4 Hydrolase enzymes and their substrate.

Enzyme classification	Substrate	Natural source	Reaction catalyzed
Protease	Proteins, polypeptides	Proteinaceous food, milk, meat products, cheese, body soils	Hydrolysis of amide or peptide bond
Lipase	Tri, di and monoglycerides	Natural amides and plant fats, margarine and oils	Ester bond hydrolysis
α-Amylase	Amylose, amylopectin	Starch-based soils, flour, potato and gravy	Hydrolysis of α-1,4-glycosidic bonds
Cellulase	Cellulose	Amorphous cellulose, vegetable, fruit and grains, and cereals	Hydrolysis of β-1,4-glycosidic bonds

a series of batch-wise reactions or continuously in flow systems. In practice, sometimes microorganisms, instead of enzymes, are also immobilized to apply them directly onto the reaction and recover for further use.

Immobilization is a fascinating field of research for the last two decades, with the result that it has been transformed from a novelty to a fully accepted and used technology. Different textile materials are proved to be the best efficient immobilizing supports for these enzymes or microorganism both economically and ecologically.

Polyamides are suitable immobilizing supports in both woven, nonwoven, membrane, and gel form. Laccase is immobilized in nylon 6,6 woven fabric with glutaraldehyde as a cross-linking agent [72]. Insulin and heparin immobilized on non-woven polyester fabric discs were developed for L929 cell growth in the low-serum media [73]. Polyester fleece is also used as supports to immobilize trypsine [74]. Polyacrylate copolymers are reported to be used as immobilizing aminoacylase by adsorption from *Aspergillus oryzae* [75]. When extracellular laccases produced by three different wood-rotting fungi, *Cerrena unicolor*, *Heterobasidionannosum*, and *Trametesersicolor*, were immobilized via covalent bonds formation on acrylic careers, immobilized laccase exhibited the highest enzymatic activity at slightly acidic pH environment and showed more resistance over native enzymes to thermal decay [76]. Macroporouspolystyrene-based polymers were used for immobilizing *Citrobacter freundii* for the anaerobic production of trimethylene glycol from glycerol [77]. Natural polysaccharides such as cellulose, chitosan, alginates are readily used for immobilization in different cases as reported [78–82]. Silk fiber is also used for the same purpose in many cases for the application as biosensors [83, 84].

20.3.3 Protective Textile

It is one of the main concerns of biotechnologists and microbiologists while working with pathogens and other harmful microorganisms and chemicals to take proper protection. The protection can be achieved by using proper garments, masks, and other textile products. Protective textile refers to clothing and other fabric related items designed to protect the wearer from harsh environment effects that may result in injuries or death. These materials are modified both structurally and chemically to withstand pathogens and harmful chemicals. There are mainly four types of Chemical-Biological (CB) Protective Material.

20.3.3.1 Air Permeable Material

This type of fabrics generally consists of an outer woven fabric, a layer of sorptive material such as activated carbon impregnated foam or a carbon loaded non-woven felt, and a liner fabric. Sorptive material layer absorbs toxic chemical vapors. Outer shell fabric is treated a liquid repellent finish by fluorocarbon polymers.

20.3.3.2 Semipermeable Material

These materials are, by their structure may be the porous or solution-diffusion type. Large molecules are excluded by their size. In the case of the solution-diffusion membrane, it follows Fickian Permeation through the nanoporous membrane where gas dissolves into the membrane, diffuses across it and desorbs on the other side based on concentration gradient, time, and membrane thickness. Polytetrafluoroethylene and Polyurethane are common materials for creating this kind of protective material.

20.3.3.3 Impermeable Material

Impermeable material such as butyl, halogenated butyl rubber, neoprene, and other elastomers have been commonly used over the years to provide

CB agent protection. They provide excellent protection against liquid, vapor, and aerosol forms. The main problem with these materials is that body moisture cannot go through the fabric, materials are heavy as well as bulky and finally costly.

20.3.3.4 Selective Permeable Membrane

This is an extremely thin, lightweight and flexible protective barrier material allowing selective permeation of moisture vapor from the body to escape through the clothing layers while protecting from damaging chemicals and pathogens. The protective mechanism of selectively permeable fabric relies on a selective solution-diffusion process [85].

20.4 Conclusion

Throughout the history of mankind, human race has depended on textile as much as they depended on food and shelter. In this modern age of civilization, demand of newer, better, and more colorful textile has increased and reached to the sky. Meeting these demands without hampering the lives of our future generation is a great responsibility. Therefore, sustainable development is the need of the day. Textile industries are not in the place where it was said as one of the most pollution generating industries due to the healthy support it received from biotechnology. At the same time, textile materials also supported in advancement of biotechnology by providing its unique features. In a nutshell, we can conclude that textile and biotechnology are going hand in hand for many days and will serve humankind in future. The fusion of these two fields will surely show a synergistic effect for creating and betterment of a greener world.

References

1. Purohit, S.S., *A Laboratory Manual of Plant Biotechnology*, Agrobios, Jodhpur, India, 2004.
2. *Kirk-Othmer Encyclopedia of Chemical Technology,* John Wiley & Sons, New York, 2005.
3. Ribeiro, T.P., Arraes, F.B.M., Lourenço-Tessutti, I.T., Silva, M.S., Lisei-de-Sá, M.E., Lucena, W.A., Macedo, L.L.P., Lima, J.N., Santos Amorim, R.M., Artico, S., Alves-Ferreira, M., Mattar Silva, M.C., Grossi-de-Sa, M.F., Transgenic cotton expressing Cry10Aa toxin confers high resistance to the cotton boll weevil. *Plant Biotechnol. J.*, 38, 42–49, 2017.

4. Snow, A.A., Palma, P.M., Commercialization of transgenic plants: Potential ecological risks. *BioSci.*, 47, 86–96, 1997.
5. Hails, R.S., Genetically modified plants–the debate continues. *Trends Ecology Evol.*, 15, 14–18, 2000.
6. Tabashnik, B.E., Evolution of resistance to Bacillus thuringiensis. *Ann. Rev. Entomol.*, 39, 47–79, 1994.
7. Hilbeck, A., Moar, W.J., Pusztai-Carey, M., Filippini, A., Bigler, F., Toxicity of *Bacillus thuringiensis* CrylAb toxin to the predator *Chrysoperla carnea* (Neuroptera: Chrysopidae). *Environ. Entomol.*, 27, 1255–1263, 1998.
8. Liu, W., Effects of Bt transgenic crops on soil ecosystems: Areview of a ten-year research in China. *Front. Agricul. China*, 3, 190–198, 2009.
9. Eco-friendly textiles through application of bio-technology, http://textileinformation.blogspot.in/2007/10/ecofriendly-textiles-through.html. (Accessed on 12.12.2016)
10. Orford, S., Delaney, S. and Timmis, J., The genetic modification of cotton, in: *Cotton: Science and Technology*, S. Gordon and Y.L. Hsieh (ed.), pp.103–129. Woodhead Publishing Ltd, Cambridge, 2006.
11. Zhu, S.-W., Gao, P., Sun, J.-S., Wang, H.-H., Luo, X.-M., Jiao, M.-Y., Wang, Z.-Y., Xia, G.-X., Genetic transformation of green-colored cotton. *In Vitro Cellular Developmental Biol.-Plant*, 42, 439–444, 2006.
12. Sekhri, S., Sardana, C., Enhancing the consumer appeal of naturally coloured cottons through blending and mordanting. *Colourage*, 55, 77–80, 2008.
13. Chen, J., Wang, Q., Hua, Z., Du, G., Research and application of biotechnology in textile industries in China. *Enzyme Microbial Technol.*, 40, 1651–1655, 2007.
14. Franceschi, E., Cezaro, A. de, Ferreira, S.R.S., Kunita, M.H., Muniz, E.C., Rubira, A.F., Oliveira, J.V., Biopolymers based on renewable resources A review. *Open Chem. Engg. J.*, 5, 11–20, 2014.
15. Shahid, M., Mohammad, F., Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers: A review. *Ind. Engg. Chem. Res.*, 52(15), 5245–5260, 2013.
16. Lim, S.H., Hudson, S.M., Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals. *J. Macromol. Sci. Part C: Polym. Rev.*, 43, 223–269, 2003.
17. Younes, I., Rinaudo, M., Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Marine Drugs*, 13, 1133–1174, 2015.
18. Pang, F., He, C., Wang, Q., Preparation and properties of cellulose/chitin blend fiber. *J. Appl. Polym. Sci.*, 90, 3430–3436, 2003.
19. Qin, Y., Alginate fibers: An overwiew of the production processes and applications in wound management. *Polym. Int.*, 57, 171–180, 2008.
20. Fenoradosoa, T.A., Ali, G., Delattre, C., Laroche, C., Petit, E., Wadouachi, A., Michaud, P., Extraction and characterization of an alginate from the brown seaweed Sargassum turbinarioides Grunow. *J. Appl. Phycol.*, 22, 131–137, 2010.

21. Zhang, Y.Q., Applications of natural silk protein sericin in biomaterials. *Biotechnol. Adv.*, 20, 91–100, 2002.
22. Auras, R., *Poly(lactic acid). Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New York, 2010.
23. Gupta, B., Revagade, N., Hilborn, J., Poly(lactic acid) fiber: An overview. *Prog. Polym. Sci.*, 32, 455–482, 2007.
24. Persson, M., Cho, S.W., Skrifvars, M., The effect of process variables on the properties of melt-spun poly (lactic acid) fibres for potential use as scaffold matrix materials. *J. Mater. Sci.*, 48, 3055–3066, 2013.
25. Zinn, M., Witholt, B., Egli, T., Occurrence, synthesis and medical application of bacterial polyhydroxyalkanoate. *Adv. Drug Deliv. Rev.*, 53, 5–21, 2001.
26. Lenz, R.W., Marchessault, R.H., Bacterial polyesters: Biosynthesis, biodegradable plastics and biotechnology. *Biomacromol.*, 6, 1–8, 2005.
27. Pouton, C.W., Akhtar, S., Biosynthetic polyhydroxyalkanoates and their potential in drug delivery. *Adv. Drug Deliv. Rev.*, 18, 133–162, 1996.
28. Nair, L.S., Laurencin, C.T., Biodegradable polymers as biomaterials. *Prog. Polym. Sci.*, 32, 762–798, 2007.
29. Zyga, L., Scientists breed goats that produce spider silk, https://phys.org/news/2010–05-scientists-goats-spider-silk.html (Accessed on 11.03.2017)
30. Rogers, G.E., Genetic engineering for novel fibres. *J. Text. Institute*, 91, 24–31, 2000.
31. Lange, N.K., Lipase-Assisted Desizing of Woven Cotton Fabrics. *Text. Chemist Colorists*, 29(6), 23–26, 1997.
32. Opwis, K., Knittel, D., Kele, A., Schollmeyer, E., Enzymatic recycling of starch-containing desizing liquors. *Starch-Stärke*, 51, 348–353, 1999.
33. Etters, J.N., Husain, P.A., Lange, N.K.: Alkaline pectinase: An eco-friendly approach to cotton preparation. *Textile Asia*. 5, 83–85 (1999).
34. Tzanov, T., Calafell, M., Guebitz, G.M., Cavaco-Paulo, A., Bio-preparation of cotton fabrics. *Enzyme Microbial Technol.*, 29, 357–362, 2001.
35. Bankar, S.B., Bule, M. V, Singhal, R.S., Ananthanarayan, L., Glucose oxidase—an overview. *Biotechnol. Adv.*, 27, 489–501, 2009.
36. Betcheva, R.I., Hadzhiyska, H.A., Georgieva, N.V., Yotova, L.K., Biobleaching of flax by degradation of lignin with laccase. *BioResources*, 2, 58–65, 2007.
37. Paul, R., Pardeshi, P.D., Enzymes: The marvellous molecular machines. *Asian Text. J.*, 11, 29–35, 2002.
38. Ramachandran, T., Karthik, T., Application of genetic engineering and enzymes in textiles. *J. Inst. Eng. Part TX: Text. Engg. Division*, 84, 32–36, 2004.
39. Tsatsaroni, E., Liakopoulou-Kyriakides, M., Effect of enzymatic treatment on the dyeing of cotton and wool fibres with natural dyes. *Dyes Pigm.*, 29, 203–209, 1995.
40. Vankar, P.S., Shanker, R., Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments. *Desalination*, 230, 62–69, 2008.
41. Vankar, P.S., Shanker, R., Verma, A., Enzymatic natural dyeing of cotton and silk fabrics without metal mordants. *J. Clean. Prod.*, 15, 1441–1450, 2007.

42. Dawson, T.L., Biosynthesis and synthesis of natural colours. *Color. Technol.*, 125, 61–73, 2009.
43. Kim, D.H., Kim, J.H., Bae, S.E., Seo, J.H., Oh, T.K., Lee, C.H., Enhancement of natural pigment extraction using Bacillus species xylanase. *J. Agricul. Food Chem.*, 53, 2541–2545, 2005.
44. Cho, Y.J., Kim, S.Y., Kim, J., Choe, E.K., Kim, S.I., Shin, H.J., One-step enzymatic synthesis of blue pigments from geniposide for fabric dyeing. *Biotechnol. Bioproc. Engg.*, 11, 230, 2006.
45. Cho, Y.J., Park, J.P., Hwang, H.J., Kim, S.W., Choi, J.W., Yun, J.W., Production of red pigment by submerged culture of Paecilomyces sinclairii. *Lett. Appl. Microbiol.*, 35, 195–202, 2002.
46. Dikshit, R., Tallapragada, P., Comparative study of Monascus sanguineus and Monascus purpureus for red pigment production under stress condition. *Int. Food Res. J.*, 20, 1235–1238, 2013.
47. Evans, P.J., Wang, H.Y., Pigment production from immobilized Monascus sp. utilizing polymeric resin adsorption. *Appl. Environ. Microbiol.*, 47, 1323–1326, 1984.
48. Vazquez, M., Santos, V., Parajo, J.C., Effect of the carbon source on the carotenoid profiles of Phaffia rhodozyma strains. *J. Ind. Microbiol. Biotechnol.*, 19, 263–268, 1997.
49. Chattopadhyay, M.K., Jagannadham, M. V, Vairamani, M., Shivaji, S., Carotenoid pigments of an antarctic psychrotrophic bacteriumMicrococcus roseus: temperature dependent biosynthesis, structure, and interaction with synthetic membranes. *Biochem. Biophys. Res. Commun.*, 239, 85–90, 1997.
50. Guyomarc'h, F., Binet, A., Dufossé, L., Production of carotenoids by Brevibacterium linens: variation among strains, kinetic aspects and HPLC profiles. *J. Ind. Microbiol. Biotechnol.*, 24, 64–70, 2000.
51. Molouba, F., Lorquin, J., Willems, A., Hoste, B., Giraud, E., Dreyfus, B., Gillis, M., de Lajudie, P., Masson-Boivin, C., Photosynthetic bradyrhizobia from Aeschynomene spp. are specific to stem-nodulated species and form a separate 16S ribosomal DNA restriction fragment length polymorphism group. *Appl. Environ. Microbiol.*, 65, 3084–3094, 1999.
52. Poplawsky, A.R., Urban, S.C., Chun, W., Biological Role of Xanthomonadin Pigments inXanthomonas campestris pv. Campestris. *A Appl. Environ. Microbiol.*, 66, 5123–5127, 2000.
53. Lu, Y., Wang, L., Xue, Y., Zhang, C., Xing, X.-H., Lou, K., Zhang, Z., Li, Y., Zhang, G., Bi, J., Production of violet pigment by a newly isolated psychrotrophic bacterium from a glacier in Xinjiang, China. *Biochem. Engg. J.*, 43, 135–141, 2009.
54. Lenin, V., Kandasamy, N., Karthick, S., Kanipriya, M., Enzymes in textiles finishing. *Man-Made Text.* India, 52, 7–10, 2009.
55. Roda, D., Garment value addition. *Colourage*, 56, 91–93, 2009.
56. de Aragao Umbuzeiro, G., Freeman, H.S., Warren, S.H., De Oliveira, D.P., Terao, Y., Watanabe, T., Claxton, L.D., The contribution of azo dyes to the mutagenic activity of the Cristais River. *Chemosphere*, 60, 55–64, 2005.

57. Silveira, E., Marques, P.P., Silva, S.S., Lima-Filho, J.L., Porto, A.L.F., Tambourgi, E.B., Selection of Pseudomonas for industrial textile dyes decolourization. *Int. Biodeterior. Biodegrad.*, 63, 230–235, 2009.
58. Sumathi, S., Manju, B.S., Uptake of reactive textile dyes by Aspergillus foetidus. *Enzyme Microbial Technol.*, 27, 347–355, 2000.
59. Balan, D.S.L., Monteiro, R.T.R., Decolorization of textile indigo dye by ligninolytic fungi. *J. Biotechnol.*, 89, 141–145, 2001.
60. Fiechter, A., Biosurfactants: moving towards industrial application. *Trends Biotechnol.*, 10, 208–217, 1992.
61. Van Dyke, M.I., Lee, H., Trevors, J.T., Applications of microbial surfactants. *Biotechnol. Adv.*, 9, 241–252, 1991.
62. Montoneri, E., Boffa, V., Savarino, P., Tambone, F., Adani, F., Micheletti, L., Gianotti, C., Chiono, R., Use of biosurfactants from urban wastes compost in textile dyeing and soil remediation. *Waste Manage.*, 29, 383–389, 2009.
63. Zouboulis, A.I., Matis, K.A., Lazaridis, N.K., Golyshin, P.N., The use of biosurfactants in flotation: application for the removal of metal ions. *Minerals Engg.*, 16, 1231–1236, 2003.
64. Slade, P.E., *Handbook of Fiber Finish Technology*, Marcel Dekker, New York, 1997.
65. Test methods. AATCC – Technical Manual, Vol. 82., USA, 2007.
66. Schindler, W.D., Hauser, P.J., Textile, I., *Chemical finishing of textiles*, Woodhead Publishing Ltd., Cambridge, UK, 2004.
67. Dring, I., Anti-microbial, rotproofing and hygiene finishes, in: *Textile finishing*, D. Heywood (ed.), pp. 351–371, Society of Dyers and Colourists, Bradford, 2003.
68. Peter, F.P., Deborah, S., Enzymes: Their Applications and Biochemical Characterization. *Enzymes Detergen.*, 69, 23, 1997.
69. Concha-Barrientos, M., Nelson, D.I., Driscoll, T., Steenland, N.K., Punnett, L., Fingerhut, Mar. A., Prüss-Üstün, A., Leigh, J., TAk, S., Corvalan, C., *Selected occupational risk factors. Comparative quantification of health risks: global and regional burden of disease attributable to selected major risk factors.* World Health Organization, Geneva, 1651–1801, 2004.
70. Yang, L., Ning, X., Chen, K., Zhou, H., Preparation and properties of hydroxyapatite filters for microbial filtration. *Ceramics Int.*, 33, 483–489, 2007.
71. Iwasaki, Y., Yamasaki, A., Ishihara, K., Platelet compatible blood filtration fabrics using a phosphorylcholine polymer having high surface mobility. *Biomater.*, 24, 3599–3604, 2003.
72. Silva, C., Silva, C.J., Zille, A., Guebitz, G.M., Cavaco-Paulo, A., Laccase immobilization on enzymatically functionalized polyamide 6, 6 fibres. *Enzyme Microbial Technol.*, 41, 867–875, 2007.
73. Saşmazel, H.T., Aday, S., Gümüşderelioğlu, M., Insulin and heparin co-immobilized 3D polyester fabrics for the cultivation of fibroblasts in low-serum media. *Int. J. Biol. Macromol.*, 41, 338–345, 2007.

74. Nouaimi, M., Möschel, K., Bisswanger, H., Immobilization of trypsin on polyester fleece via different spacers. *Enzyme Microbial Technol.*, 29, 567–574, 2001.
75. He, B., Li, M., Wang, D., Studies on aminoacylase from Aspergillus oryzae immobilized on polyacrylate copolymer. *React. Polym.*, 17, 341–346, 1992.
76. Al-Adhami, A.J.H., Bryjak, J., Greb-Markiewicz, B., Peczyńska-Czoch, W., Immobilization of wood-rotting fungi laccases on modified cellulose and acrylic carriers. *Process Biochem.*, 37, 1387–1394, 2002.
77. Griffiths, M.S., Bosley, J.A., Assessment of macroporous polystyrene-based polymers for the immobilization of *Citrobacter freundii*. *Enzyme Microbial Technol.*, 15, 109–113, 1993.
78. Li, F.-Y., Xing, Y.-J., Ding, X., Immobilization of papain on cotton fabric by sol–gel method. *Enzyme Microbial Technol.*, 40, 1692–1697, 2007.
79. Bora, U., Kannan, K., Nahar, P., A simple method for functionalization of cellulose membrane for covalent immobilization of biomolecules. *J. Memb. Sci.*, 250, 215–222, 2005.
80. Chiou, S.H., Wu, W.T., Immobilization of *Candida rugosa* lipase on chitosan with activation of the hydroxyl groups. *Biomater.*, 25, 197–204, 2004.
81. Altun, G.D., Cetinus, S.A., Immobilization of pepsin on chitosan beads. *Food Chem.*, 100, 964–971, 2007.
82. Reischwitz, A., Reh, K.D., Buchholz, K., Unconventional immobilization of dextransucrase with alginate. *Enzyme Microbial Technol.*, 17, 457–461, 1995.
83. Liu, Y., Zhang, X., Liu, H., Yu, T., Deng, J., Immobilization of glucose oxidase onto the blend membrane of poly (vinyl alcohol) and regenerated silk fibroin: morphology and application to glucose biosensor. *J. Biotechnol.*, 46, 131–138, 1996.
84. Demura, M., Asakura, T., Nakamura, E., Tamura, H., Immobilization of peroxidase with a Bombyx mori silk fibroin membrane and its application to biophotosensors. *J. Biotechnol.*, 10, 113–119, 1989.
85. Scott, R.A. (ed.), *Textiles for Protection*, Woodhead Publishing Ltd., cambridge, UK, 2005.

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