Sustainable Textiles: Production, Processing, Manufacturing & Chemistry

Subramanian Senthilkannan Muthu
Miguel Angel Gardetti *Editors*

Sustainability in the Textile and Apparel Industries

Production Process Sustainability

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Preface

The dyeing and printing sector has taken a major hit because of the devastating effects of hazardous dyes and discharge of waste water, etc. This volume addresses these important topics and the sustainable options for dyeing and printing. It also deals with the environmental issues from conventional production, finishing processes and the sustainable options in the textile sector in terms of technologies, machines, and chemicals to make finishing a sustainable process. The book begins with the work titled "Printing with Sustainable Natural Dyes and Pigments" developed by Fatma Filiz Yıldırım, Arzu Yavas, and Ozan Avinc, which presents detailed information about various eco-friendly prints and printing techniques which were applied to different kinds of fibers and fabrics using sustainable natural dyes and natural pigments.

The second chapter, "Sustainability in Textile Dyeing: Recent Developments," written by Aravin Prince Periyasamy and Jiri Militky explores different dyeing techniques and processes such as modified chemical pretreatments, plasma-induced coloration, supercritical carbon dioxide dyeing process, microwave-assisted dyeing, ultrasonic dyeing and electrochemical process to reduce negative impacts of dyeing in the textile industry.

Then, S.K. Sahoo, B.P. Dash, and A. Khandual develop the chapter titled "Sustainable Yarn Sizing," which presents the history and development of yarn sizing processes and emerging sustainable alternatives.

Subsequently, Hüseyin Aksel Eren, İdil Yiğit, Semiha Eren, and Ozan Avinc, in their chapter titled "Ozone: An Alternative Oxidant for Textile Applications," present the potential uses of ozone as an alternative oxidant for textile applications. They also focus on ozone utilization as chemical substitution, waste reduction, and energy conservation in textile processes leading to a more sustainable world for future generations.

Moving on to the next chapter, Dr. Faith Kane, Prof. Jinsong Shen, Dr. Laura Morgan, Dr. Chetna Prajapati, Prof. John Tyrer, and Dr Edward Smith present "Innovative Technologies for Sustainable Textile Coloration, Patterning and Surface Effects." They study emerging advances in technology that facilitate new methods of textile coloration, pattern, and surface effects which could help toward sustainable development. They focus on methods such as plasma processing, supercritical carbon dioxide dyeing, ultrasonic dyeing, and digital printing that have begun to be adopted within various industrial contexts.

The following chapter titled "Sustainable Finishing Process Using Natural Ingredients," by M Gobalakrishnan, D Saravanan, and Subrata Das, presents and analyzes sustainable preparatory processes, finishing practices for flame retardant finish based on bio-based flame retardants, antimicrobial finish, bio-finish, and UV protection finish.

Later, R. Ramachandran and P. Kanakaraj, in the chapter entitled "Cellulose Textile Colouring with Clay Particles: and Enviro Safe Process," analyze innovative natural dye which could replace the harmful chemical dyes by reducing the toxic dye effluents. They present an analysis using clay as a natural-colored material, the usages, and different reactions.

In the next chapter, "Sustainability in Dyeing and Finishing," P. Senthil Kumar and G. Janet Joshiba present and elaborate a set of strategies to follow in sustainable dyeing and finishing process in the textile industry.

Following, Hüseyin Aksel Eren, İdil Yiğit, Semiha Eren, and Ozan Avinc in "Sustainable Textile Processing with Zero Water Utilization Using Supercritical Carbon Dioxide Technology" explore supercritical carbon dioxide (scCO2) technology usage in textile scouring, surface modification, desizing, bleaching, dyeing, and finishing processes leading to waterless sustainable textile wet processing. Moreover, they present recent commercial and technological developments regarding scCO2 technology.

Finally, P. Senthil Kumar and G. Janet Joshiba, in their chapter "Sustainability in the Spinning Process," explore the key issues for sustainability, review the mechanism of the spinning process in textile production, and also explain the various sustainable approaches implemented in the spinning process.

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Contents

Printing with Sustainable Natural Dyes and Pigments

Fatma Filiz Yıldırım, Arzu Yavas, and Ozan Avinc

Abstract Natural dyes and pigments could be obtained from insects, plants, and animals. Natural dyes have been utilized in the dyeing of wool, cotton, and silk since the prehistoric ages. The first applications of natural dyes on textile fibers are estimated to have started in Mesopotamia and India in 4000 BC. In these first dyeing trials, it is thought that pigments were used for dyeing process and these pigments could be easily removed from fabrics by friction and washing because of their weak mechanical bonding onto the fibers, and therefore, dyeing process was not really successful. It is thought that mordant dyeing method may have been accidentally discovered. In many countries, such as India, Egypt, Anatolia, and China, many historical natural dyed fabrics were found. One of the first synthetic dyes, mauveine (also known as aniline purple), was accidentally synthesized by W.H. Perkin (at the age of 18) in 1856 during attempts to make quinine. The discovery of the first synthetic dye changed the natural dyeing habits and synthetic dyes replaced almost all natural dyes. However, it is known that the wastewater produced in the production steps of synthetic dyes and the chemicals used in the textile dyeing process can have toxic and pollutant effects on human and environmental health. Nowadays, the effects of environmental awareness, organic products, and the tendency toward healthy lifestyle also reflect on the textile sector. Disagreements on the risks of the usage of synthetic dyestuffs and increasing environmental awareness result in an enhanced interest in natural resources, environmentally friendly products, and new strategies. That is one of the reasons why the use of natural dyes came back to the agenda due to an increased ecological and sustainable awareness. Unlike non-renewable raw materials of synthetic dyes, natural dyes are mostly renewable and sustainable. Natural dye sources are agriculturally renewable sustainable vegetable-plant-based colorant sources. In terms of sustainability, synthetic dyes are produced from non-renewable resources; however, natural dyes are extracted from renewable sources. The ability to obtain the dye from renewable natural sources

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makes natural dyes an attractive dye class for more sustainable world. Natural dyes can be applied on the fibers not only with dyeing method but also with printing method. Textile printing is one of the most important and versatile methods among the methods used to design and colorize textile fabrics. Ancient men and women mixed the colorants such as coal or soil paint with oils and used them with their fingers in lines on various materials. The staining of the plant extracts and fabrics has provided different approaches. The patterns can be produced by the wax applications to provide resistant dye liquor, or the surrounding areas provide a tightly attached and reserved area. The word of print is referred to a process that uses pressure to impart colorant to the material. And there is no doubt that the first textile printing was occurred by the blocks with embossed printing surfaces, then these blocks were inked and printed on the fabric. Some of the first blocks were made of clay or terracotta, while others were made of carved wood. In this chapter, the information about various eco-friendly prints and different printing techniques which were applied to different kinds of fibers and fabrics using sustainable natural dyes and natural pigments are given in detail.

Keywords Sustainable · Printing · Natural dye · Pigment · Natural printing · Sustainability

1 Introduction

Printing is generally a coloring technique that can be applied on many natural and man-made fibers. In the printing process, the dyestuff usually added to the printing paste is transferred to the fabric surface by various methods (block, rotation, stencil, etc.) and the fabrics pass to the fixing stage. After the fixation process, printed fabrics are generally washed, and unfixed dyestuffs are removed. The type of dyestuff varies according to the type of fiber and the printing technique differs accordingly. The printing paste, technical and fixing conditions used are important for proper and successful printing. In the printing process, natural products can be used when preparing the printing paste. In addition, natural dyes were used in the printing process before the synthetic dyes were invented.

In ancient times, ancient civilizations had used natural dyes to colorize their clothes. They printed their clothes by using wooden blocks. In the block printing method, making wooden blocks were very hard and needed special talent and handcraft. Reserved printing is another ancient printing technique. In this method, some parts of the fabric reserved with wax or wax like materials and then dyed with natural dyes. Over thousands of years, civilizations used these methods for printing their garments. Industrial revolution affected ancient printing methods as it affected many sectors. After industrial revolution, firstly, blocks were integrated to the machines and first block printing machines were invented.

After industrial revolution, another industrialized ancient printing method was screen printing. This method had been developed in Japan and human hair or silk threads were used. In 18th's, first gauze was used, and it was the first step of industrial flat screen printing. In industrial flat screen-printing method after preparing flat screen, printing paste put on the screen and then rubber doctor blade pushed through the screen template. Semi-automatic screen printing was provided by driving squeegee mechanically. Moreover, fully automatic flat screen-printing machines were developed as an alternative to semi-automatic printing systems. However, fully automatic printing systems could not be defined as continuous machines. Thus, cylindrical printing machines had been invented for providing continuous printing. Cylindrical (rotary) printing method is considered one of the most used and efficient printing methods among other traditional printing methods. Furthermore, nowadays this method can be regarded as predominant by the influence of low-cost equipment and productivity. However, this method has various disadvantages. One of these disadvantages is longer template preparing times. These day's short-term full-color market and customer demands force manufacturers for producing small amounts. Therefore, rotary printing method becomes bulky due to its long preparing times. New technology research has been conducted to develop new printing techniques such as digital printing.

In all this industrial printing history, synthetic dyes have been used due their low cost and the colors they provide. Recently, natural dyes have become popular due to the environmental awareness and the negative and hazardous effects of chemicals on human body. There is an enhanced interest in natural resources. This chapter reviews the textile printing with sustainable natural dyes and pigments. In other words, the information about various eco-friendly prints and different printing techniques which were applied to different kinds of fibers and fabrics using sustainable natural dyes and natural pigments are given in detail. First of all, history of printing, traditional printing techniques, block printing, and screen-printing techniques are introduced. Thereafter, printing with natural dyes and pigment printing technique are reviewed in detail. Finally, information regarding innovative and digital printing systems and abrasion, reserved printing, and special printing types are given.

2 History of Printing and Traditional Printing

Textile printing is one of the most important and versatile methods among the methods used to design and color textile fabrics [1, 2]. Ancient women and men mixed colorants, such as coal or earth colorants with oil, which they could find, and used them first by applying them as streaks on various materials with their fingers. The staining of fabrics with plant extracts also provided different approaches. Understanding the use of colorless materials called mordants to fix some plant dyes is a vital step in understanding the history of printing. The discovery of different mordants, when applied for the first time, to give different colors and shades with the same dyestuff, must have seemed magical and has been proposed as a type of printing that has become very important. It is not clear whether the origin of this type of printing is India, Egypt, or China [1]. Traditionally, various wooden blocks have been used primarily for the printing process, which have been adapted to various commercial machines. In addition to this technique, techniques such as screen printing have been developed and thus more production is possible. The screen-printing technique was further developed, and the rotary printing technique used for mass production in conventional textile printing was developed. Nowadays, these techniques are ungainly to meet the demands of small production quantities of the customers, and this has led to the development of new technologies in printing processes. Textile printing, which gained a new perspective with the development of digital printing machines, continues its adventure to achieve more sustainable production by using less water and chemicals. This part of this chapter provides brief information about the block printing technique and its development, template printing techniques and its development, and innovative printing techniques.

2.1 Block Printing

The word "printing" refers to a process that uses pressure. And there is no doubt that the first textile printing technique is a technique in which blocks with an embossed printing surface are used, which are then inked and then printed onto the fabric. The first blocks are thought to be made of clay or terracotta or carved wood. Patterned tree blocks are known to be found in tombs near a historic village in Egypt. A children's grave in the same area also contained tunics (shirts) of white rectangular printed fabrics, each with a blue background surrounding floral motifs [1, 3]. Wood blocks for printing in the fourteenth century was certainly used in France, Italy, Germany, and the craftsmen experienced in the prints used mineral pigments instead of dyes. The first use of blocks in Europe can be seen in the production of cliche wallpaper products, which are very expensive imitation of glazed brocade fabrics and tapestries [1, 4]. In the fifteenth century, Portuguese merchants discovered the potential to trade with India, which could produce beautiful cotton fabrics that could meet the demands of Europe. There was a famous printed fabric center in India, where the use of root dyes was a long tradition [1, 5]. In the prints made during this period, the fabric was wetted with milk and polished to obtain a smooth surface. The patterns were transferred from paper through holes drilled on paper by rubbing with charcoal [1]. The fabric was waxed after the outlines were drawn. The fabric was then dyed in a reduced indigo bath, and the wax was then removed by scraping or washing. After drying, the reds, pinks, lilacs, browns, and blacks were dyed, aged, and washed in the bath with the appropriate metal acetate mordant. The unfixed dyes were removed by washing and then the printed fabrics were bleached by leaving them under the sun. The importance of repression in European trade increased considerably in the eighteenth century, and the growth of the textile industry was revived as demand for pressures increased [1]. Wooden blocks are not very difficult to make, but it can be quite time consuming to find suitable thickeners. Senegal gum and gum were found to be useful and starch was added to the pastes to increase color yield. One of the biggest problems encountered with this printing technique was to obtain bright and fast colors. Root dyes were the most important dye and could meet the needs [1]. In Fig. 1, examples of printing and various printing blocks which are performed using blocks are given. In the nineteenth century, some blocks were made of brass [1].

Block printing required a very hard table (Fig. 2). These tables were prepared using a blanket and waterproof material on stone or iron slabs. In addition, a raw cotton fabric would be stretched around the table to absorb increasing dyes and would be pinned to the fabric to fit the printed patterns (Fig. 3) [1]. The printing paste should be applied to the block surface attentively [1].

The printing blocks used in block printing were produced from teak or 'sisum.' Poor village printers used second-hand wood prints from rich printers (in India) [17]. Today, it is possible to perform printing with natural dyes. Although these studies are now used in more niche areas, it is possible to come across both commercially and academically. 100% cotton and polyester fabrics were printed using kikar (*Acacia nilotica*) and bhangra (*Eclypta prostrate*) fruits. In this study, firstly, cotton and polyester fabrics were boiled with 2 g/ml soap and soda ash for 45 minutes and then washed and dried under running water. Applied printing pastes are given in Table 1 [18]. Wooden blocks were used for printing. In addition, the printing process was carried out by conventional methods. The polyester fabrics were then heat-treated in an oven at 110 °C for 10 minutes, washed in water and allowed to dry under ambient conditions. Then, the color and fastness properties of the fabrics were examined. The results showed that the dyestuff was more permanent in cotton fabrics and the highest loss in polyester fabrics was in fabrics printed with bhranga dye. The results also showed the effect of mordanting. Colors are more permanent in mordanted fabrics. Potassium bichromate provides brown, iron sulfate gray shades. According to the results of the study, un-mordanted prints displayed

Fig. 1 Block printing block examples [6–12]

Fig. 2 Hard printing table [13]

Fig. 3 Block printed fabrics [14–16]

weaker fastness properties than mordanted prints. In addition, in general, color fastness results displayed moderate-to-good level of fastness (in the range 3–5) [18].

Jute fibers were printed using *Terminalia chebula* dye (commercial dye C.I. Natural Brown 6) in the presence of copper sulfate ($CuSO_4$), iron sulfate ($FeSO_4$), and tin chloride ($SnCl_2$). In the printing process, gum arabic was used as a thickener. In this study, printing process was carried out with wooden blocks. Fixation was carried out at 102 °C under 25 lbs. of pressure for 15 minutes. After all treatments, the fabrics

Table 1 Printing paste recipe [18]

Printing paste	Recipe
Dyestuff (ml)	100
CMC (carboxyl methyl cellulose)	4.6 g
Mordant (potassium dichromate, iron sulfate)	1 g

were washed with non-ionic detergent at 60 ° C for 15 minutes. It was then rinsed, dried, and ironed [22]. The results of the study showed that jute fabrics can be printed with *Terminalia chebula* dye. The highest color yield values were obtained in iron sulfate mordanted fabrics. In addition, the fastness values of fabrics showed values in the range 4–5 [18].

Ajrakh is one of the other block printing methods. It has traditionally undergone some changes in the production of double-sided durable block-printed cotton fabric, in the maintenance of motifs and in the care of colors used [3, 20]. The blocks used in this printing, danda (mixer), ghod (wooden stand), printing table, and budho (wood beater) are traditional and made of wood. However, equipment such as indigo maat (clay paint tank), kundi (tank for harda process), and tari (tray) are made of clay (mud). In addition, equipment such as rangchul (paint tank) is made of brick and cow droppings. Charu (dish inside the paint tank) is made of aluminum. Chappri, bamboo sticks, are placed on the bottom layer of the tray (tari) [3]. The traditional color combinations of Ajrakh can be from blue to red of all possible permutations with the palette of natural dyes [20]. Besides Ajrakh, another known type of fabric is Nandana, which is used by tribes and produced entirely by an ecological printing technique. During the process, the main fabric is treated with soap clay, soaked in turmeric, and printed with beautiful patterned wooden blocks. In addition, natural coloring dyes such as turmeric, pomegranate peel, dried flowers, and indigo are used to add colorful motifs and designs on the fabric [21]. Akrajh method is used in new studies. Resistant natural printing was applied to fabrics by the well-known Ajrakh method in Anjar and Dhamadka in Kutch and these textile materials were examined [3, 19]. In this study, Ajrakh printing is documented in detail and the changes that occur between printing production process, colors, and motifs were examined.

In Anatolia, there is a traditional block printing method. For teaching this old traditional method to youth, one researcher explained the art of creating printed scarf via block printing method, the one of the oldest handicrafts of Anatolia. In addition, the patterning techniques used in the art of scarf were examined. In writing, fabrics are drawn by hand or printed using wood molds. It is known that this technique was first used by Hittites in Anatolia and it was seen in Central Asian Turks between 1000 BC and 100 AD. Some excavations yielded seal-shaped molds (baked clay) dating back to 7000 BC. Examining the examples of scarfs to date, it is possible to see that manuscripts are single and multi-colored. In both groups of writing types, wood molds are dipped in paint and printed onto the fabric or the paint is brushed onto the fabric. Kastamonu, Ankara, Tokat, and Elazıg can be mentioned as the important centers where the scarf is done in Anatolia. Some mold carvers in Tokat made from linden wood are sold in the Grand Bazaar. Besides, it is known that more than 200 writing patterns are preserved in Kastamonu Museum today. In Turkey, recently, sample print studies were conducted with the leadership of Cemil Kızılkaya, one of the masters of the art of scarf, which is gradually decreasing [23]. A less precise form of block printing has been applied to the production of African prints, an example of which is the use of large plywood blocks with polyurethane foam on the printing surfaces [1]. Other African block printing techniques are given below (Fig. 4).

Adinkra: This garment is a hand-printed fabric made in Ghana. This fabric is patterned with traditional Ashanti symbols using a dark brown or black dye made of a shell and iron slag called *Adinkra aduru*. Using the dye, the fabric is divided into squares, then the symbols are carved into the gourd, the gourd is pressed into the dye and then these symbols are applied to the fabric. Adinkra garments were traditionally made for the royal family to be worn in religious ceremonies such as funerals. Over the years, people have used these clothes to tell stories or express their ideas or feelings [24]. In a study, this type of print (*Adinkra*) belonging to Ghana was examined. This type of printing is made using natural dyes. The dye used to achieve this type of printing is obtained from the Badie (*Bridelia ferruginea*) plant grown in the savannah of Ghana [24, 26]. After a long boiling chain, the paint turns into a paste and is used in printing with traditional symbols to design Adinkra garments. Another plant used in this edition is Kuntunkuni (*Bombax brevicuspe*) [26].

Bagru technique is another method used in printing fabrics by blocks. The printing process is carried out with unique methods from the preparation of the fabric to the finished printed fabric. Motifs with some features are transferred to the light-colored fabric surface with two types of wooden blocks, direct and reserved style. Bagru printing steps are usually easy; in the first step, the raw fabric is prepared, in the second step the dyes are prepared, in the third step, different printing processes are performed, and in the last step, mixed dyeing techniques are developed for reserved printing. Two days are required for the preparation of the printing paste: animal (cow) manure, sodium carbonate (soda ash), and sesame oil are mixed. The fabric is washed with the mixture, this step is called washing, and traditionally this

Fig. 4 *Adinkra* printing [25]

process is called “Hari Sarana [27]. The washed and dried fabric is ready for “Harda” process. Harru plant Bagru is the most important element of printing and dyeing process. Harda contains tannic acid and can produce black prints if iron is used as mordant. The fabric treated with harda is squeezed and laid under the sun. At almost every stage, the garment needs to be washed with water and dried under the sun. Then, direct or reserve printing is applied to the fabrics. In each procedure, the blocks are first soaked in mustard or refined oil overnight and then washed [27]. Colors commonly used in Bagru printing are red (derived from root dye or Aahl tree), black (from fermented Hard seeds), blue (from indigodan), yellow (from dried pomegranate bark, turmeric, and leaves of Dhabaria trees) [27]. In a study, gum extracted from mango seeds and *Cassia tora* seeds and block printing was made on paneled fabrics using *Butea monosperma* flowers. In the study, CIELAB values and fastness values of printed fabrics were examined and evaluated. The results of the study showed that good block printed fabrics were obtained. Fastness values were also found to be good [28].

Block printing on flat surfaces is done manually. Even today, many fabrics can still be produced by manual block printing in India and many local areas. However, at the beginning of the 1800s, various machines were produced which can perform the block printing process mechanically. These printing machines used cylindrical forms of printing using block printing molds. The most primitive machines that perform this process are briefly described and illustrated below. In 1805, a machine using a rotating (cylindrical) woolen cloth strainer was introduced and this machine was successfully used (Fig. 5) [1, 29]. In 1834, Perrot invented a machine that would automatically perform all these processes of block printing (Perrotine machine) [1, 29]. This machine was limited to three colors and only a maximum of 15 cm repetition, and only three colors could be printed simultaneously (Fig. 5, Perrtoine

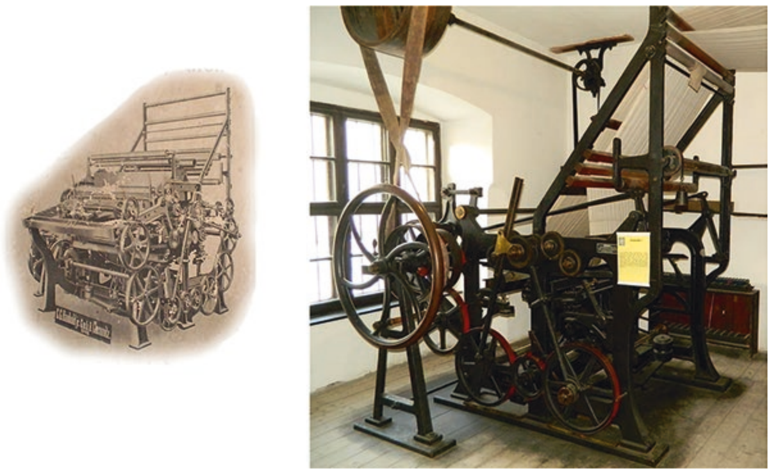


Fig. 5 Perrotoine machine [30, 31]

machine picture) [1, 5, 29]. The operating principle of this machine is slightly different from that of the above machine.

By 1805, a new way of making blocks was developed and mold or stereotype blocks were evolved [29]. Thanks to the production of these machines, a step has been taken to achieve a development for the machine-based industry instead of traditional block printing. Another technique used in printing is the template printing technique and is one of the old techniques.

2.2 Screen-Printing Technique

The screen-printing technique was initially used for simple patterns and writings on the walls and became a complex craft for Japanese fabric printing [1, 32]. Centuries ago, when the Japanese developed the stencil technique for textile printing, human hair or silk threads were used to bind the stencils. This method of printing fabrics in the nineteenth century spread well beyond Japan and was used worldwide [1, 4, 29]. In 1850, the first silk gauze in Lyon was used as a supporting template base, and later, this technique became known as template printing. It has become an ideal method for these fibers in the period 1930–1954 as a result of the growth of the use of hand stencil printing and the increase in the use of knitted fabrics and man-made fibers. The successful mechanization of flat screen printing had eventually expanded the use of cylindrical printing machines [1]. To provide the best result in template printing, the support fabric is stretched to a frame and this system is known as the template [1, 29]. The following is an example of the principle of manual screen printing (Fig. 6).

After the fabrics in the templates are stretched to the template, a photo-sensitive coating is coated on top of this template fabric and dried in a non-light environment. After drying, the template is then coated on the other side and dried. Then, black paper masks are made in the form of patterns and placed in areas where light is not desired. The template is then exposed to light and the template is washed immediately in warm water. The important thing is that this wash is not more than 3–4 minutes [29]. After the template is prepared, the printing process consists of pushing a flexible and synthetic rubber doctor (check) through the open areas of the template. A rubber or rubber support containing a metal or wooden support is pulled down steadily along the template with a constant angle and pressure [1]. The manual process is made semi-automatic by attaching the template to a carrier and driving the squeegee mechanically through the template [1]. In addition to semi-automatic screen-printing systems, there are also fully automatic screen-printing systems. Fully automatic flat screen-printing machines cannot be defined as continuous machines because their printing process is a stopping and reprocessing action. Rotation printing machines have been achieved more easily and economically in order to achieve continuous movement of the fabric [1, 2]. In rotation screen printing, the continuous (continuous) rotation of the cylindrical screen while in contact with the fabric provides a true continuous screen printing. The printing paste is fed

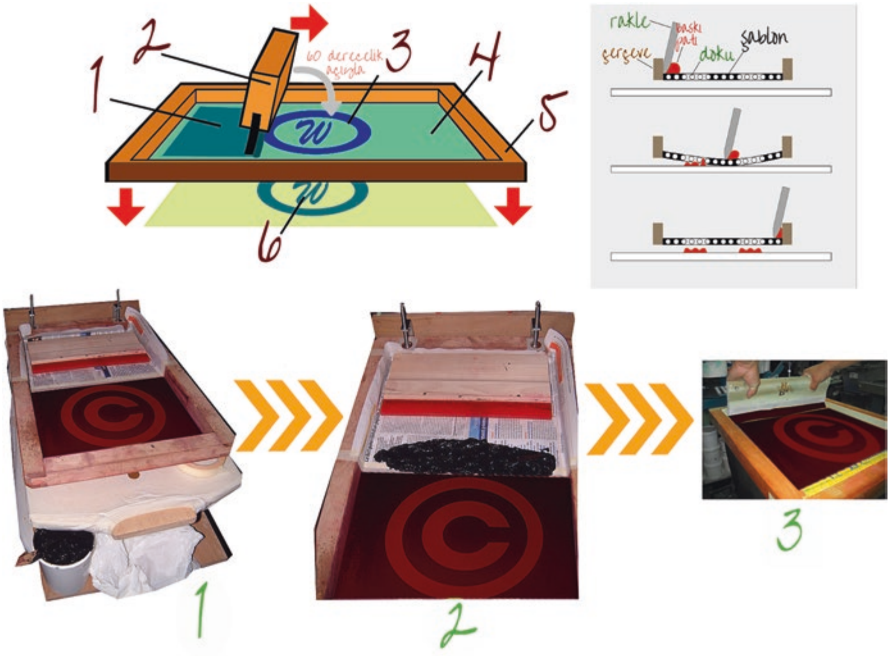


Fig. 6 Flat screen-printing mechanism; (1) Print paste, (2) doctor knife, (3) Pattern or texture (this part is blank and print paste can pass to the fabric), (4) Gauze cloth, (5) Frame, (6) Pattern on fabric [33–35]

into the stencil and is forced to come out of the pattern areas during printing with the help of a fixed (still) squeegee [1, 2]. Two types of colorants are used in textile printing. These are pigments and dyes [2].

2.2.1 Printing with Dyes

Although many printers agree that pigment printing is the easiest method, dye printing continues to hold 50% of the market. Dye printing or wet printing has many advantages. Wet printing covers many different classes of dyestuffs and each dyestuff has an affinity to a different textile fiber. Rotational printing is one of the most commonly used methods in wet printing [2]. The number of researches on the use of natural dyes for template printing is limited. Today, many conventional thickeners [such as rice starch, potato starch, carob, and seaweed (sodium alginate), as well as gum arabic, ash, and tragacanth (gum)] can be used in textile printing processes. These thickeners can be combined with vegetable oils, honey, glycerin, glucose, and molasses as decelerators or plasticizers [36, 37]. Natural thickeners could be described as products produced from natural sources such as plants, seeds, seaweeds, and microorganisms [38]. The most commonly used natural polymers as thickeners in printing are polysaccharides [38–41]. Sources of polysaccharides and plant seeds: guar gum, moss, alginate, plant gums, arabic gum, jhinguh gum, tragacanth gum (tragacanth), goat horn gum, and so on [39–41]. In addition, other natural thickeners have also been studied. Some of these are starches found in plants such as wheat, potatoes, corn, and rice [39, 40]. It has also been used in other natural polymers. Some studies have pointed out that the color of the tracery does not change or the quality of the printed fabric. When arabic gum or goat horn gum was used as a thickener, it was observed that the final colors became dull or changed. Sodium alginate is preferred for reactive and acid dyes, which can coagulate when natural dyes are added [36]. Sodium alginate is one of the most commonly used thickeners in printing with reactive dyes [42].

In a study about natural thickeners, guar gum was used instead of alginate in printing with bifunctional reactive dyes. The results of the study showed that guar gum and alginate mixtures can be used in reactive printing and these mixtures can provide high color yield and fastness properties [42]. Again, in the reports about the printing of fibers with natural dyes, it was observed that many natural and synthetic fibers were used [43]. Meyrpo used as a thickener has been reported to provide good results. Additionally, the results showed that steaming-fixed printed fabrics provide slightly higher color yields than their thermodynamically fixed counterparts. In addition, the printing of cotton with henna-reactive cyclodextrin was also evaluated [43]. In the recent years, the usability of chitosan for many textile applications has been investigated. Chitosan has found various applications in textile, dyeing of artificial fibers, cotton, silk, wool and polypropylene, permanent finishing processes, wool finishing processes, antimicrobial, antistatic, and deodorizing finishing processes, sizing, printing and ink-jet printing [41, 44, 45]. In addition, the usability of aloe vera gel as new thickeners in the printing of polyesters with disperse dyestuffs was also investigated. The printing paste prepared in the study: 30 g/kg disperse dyestuff, 50 g/kg urea, 15 g/kg citric acid, and 500 g/kg Aloe vera thickener. The fabrics were dried for 3 minutes at 100 °C after printing and then exposed to steam fixation at 180 °C for 6 minutes. The printing paste is given in Table 2 [46].

The results of the study showed that the properties of the printed fabric (color yield, fastness properties, etc.) depend on the concentration of the gel. It also depends on the type and concentration of additives (urea or citric acid, etc.) and on the fixing conditions [46]. In a study on flat screen printing with natural dyes, wool fabrics printed with 2-hydroxy-1–4 weeks of quinquine (main colorant of henna)

Table 2 Printing paste recipes [46]

Printing paste	Recipe 1
Dyestuff (disperse dye)	30 g
Urea	75 g
Thickening agent	500 g
Citric acid	10 g
Water	385 ml
Total weight	1.000

were fixed using different fixing methods. These methods can be given as microwave heating, steaming, and thermosetting. The effects of dye concentration on printing, mordant type and thickener have also been investigated [47]. It was stated that fabrics fixed at pH 3 with a printing paste containing 0.3% dye and 3% glycerin, CMC thickener and microwave heating for 4 minutes showed the highest color yield values without any drying step. Printed fabrics exhibit brown red tones when fixed by conventional fixation methods, and orange tones when fixed by microwave. The color yield and fastness values of microwave-fixed fabrics were found to be good and these samples showed a soft handle [47].

In the study conducted by Hakeim et al., chitosan was applied to cotton fabrics by pad-dry method. Chitosan pre-treated fabrics were printed with curcumin (turmeric). The pre-treated cotton fiber fabric was printed with natural coloring matter, curcumin. The printing paste is prepared according to the following recipe: 3 g of curcumin dye, 80 g of carboxymethyl cellulose (CMC), 30 g of glycerin, 887 g of water, and a total of 1000 g of printing paste were formed. The printing paste is prepared by mixing until the required curcumin starting with the mixing of water with CMC is added, then glycerine is added and homogeneity is ensured [19, 48]. In this study, printing process was applied by using template printing method. After drying, the fabrics were fixed at 125 ° C for 45 minutes and dried by various washing processes. The whiteness, color yield, washing, and rubbing fastness and stiffness values of the fabrics were measured [48]. The results exhibited a rise in absorbance with increasing concentration regardless of the use of chitosan samples. The increase in absorbance by decreasing the average molecular weight of chitosan can be attributed to the increment in the amount of terminal aldehyde groups [48]. In another study, kilmora roots, walnut shells, hamelia leaves, and jatropha flowers were obtained for printing silk and cotton fabrics with natural dyes. In this study, potassium aluminum sulfate, copper sulfate, and iron sulfate were used as mordants and tragacanth was used as thickener [36, 49]. The mixture of printing paste, natural dye, thickener, and mordant was prepared in a beaker and rested for 12 hours. The printing was carried out by stencil printing technique and the fabrics were then fixed. Then the color fastness of the fabrics was evaluated. The results of the study showed that printed fabrics generally exhibited values in the medium-to-good range [36, 49].

Hebeish et al. have tried to improve the printability properties of cotton fabrics by chemical modification with reactive cyclodextrin (R-CD) at different concentrations. Reactive dyestuff and natural dyes (henna, *Lawsonia inermis Linn Lythraceae*) were used for printing before and after modification of cotton fabric [19, 50]. The traditional pad-dry-thermofixation method was used in the reaction of cotton fabric with R-CD and the pad bath comprising R-CD and the catalyst (sodium hydrogen carbonate) was prepared as follows [50]: 100 g of henna powder, 25 kg/kg of Ciba Alco print synthetic thickener, 100 g of Printofix MTB binder, 12.5 g of ammonium phosphate, 40 g of urea, and varying amounts of water are added to complement the total recipe of 1000 g. Fixation process was done either by steaming method or by heat treatment and then washed under ambient conditions and color yield and fastness values were investigated [50]. As a result, the amount of the modification reaction increases with increasing R-CD concentration and the color yields (K/S) of the printed samples also increase with the concentration regardless of the dye used. Again, the results showed that the K/S of R-CD modified cottons were higher than that of the unmodified products regardless of the time before printing and the fixation method. On the other hand, the combination of R-CD with reactive dyes in the printing paste had negative effects. This was probably because of the increased viscosity of the paste and / or the interaction of the reactive dye with the hydroxyls of the R-CD [50].

Agarwal et al. printed cotton fabric with marigold. First, marigold was dried in the shadow, grounded into powder, and then used as a natural dye for printing paste [51]. After the printing process was carried out with the printing paste prepared from plant dyes, the cotton fabrics were dried and after 24 hours, printed fabrics were then steam-fixed at 100 ° C. The steamed fabrics were then rinsed with cold water to remove residual printing paste [51]. Aluminum sulfate, copper sulfate, iron sulfate, lead acetate, potassium dichromate, tin chloride, and zinc chloride were used as mordant. In order to determine the optimum mordant concentration with copper sulfate, potassium dichromate mordants, 3, 5, 7% amounts were also tested; 3% and 5% were found to be optimum mordant amounts [51]. In this study, the mordanting method was also selected and the mordants were added to the printing paste at the required weight. The colors obtained from the marigold vary depending on the mordant used. When un-mordanted printing is carried out, the color of the samples is beige, while mustard with potassium dichromate and olive green with copper sulfate are obtained. High mordant concentration is not chosen because it is not ecological, but as the mordant concentration increases, the brightness of the colors increases as well [51].

Printing silk fabrics using *Malvaviscus arboreus* plant was another study concluded by researchers. Different mordants (alum, copper sulfate, iron sulfate, tin chloride, pomegranate peel, and harda) were used in this study. The fibers were printed as a result of the study. Fabrics printed using natural dyestuffs have often been found to produce soft color tones [52]. Boonroeng et al. made a printing from a mahogany tree bark (Neem tree, *Azadirachta indica*) with a natural dye to improve cotton fabrics. Pre-mordanting method was applied in this study. Mordanted fabrics and un-mordanted fabrics were subjected to reactive printing method. The steaming process, which was first carried out for 45 minutes, was extended to 60, 90, and 120 minutes. Color yields of pre-mordanted fabrics are higher than those of un-mordanted fabrics. Pre-mordanting samples with alum and copper sulfate are considered to have poor light fastness and good rubbing fastness. The increase in steaming time and the increase in color yield were statistically significant. Optimum steaming time: it is determined to be 90 minutes for the sample mordanted with copper sulfate and 120 minutes for the sample mordanted with alum [53].

Rekaby and his colleagues printed wool, silk, cotton, and linen fabrics using air-mercury (alkanet, *Alkanna tinctoria*) and rhubarb (rhubarb, *Rheum emodi*), which are the natural dye sources. In this study, they investigated the effects of different factors such as dye concentration, structure of thickener, fixation method, concentration, and mordant type. In addition, color yield (K/S) values of the samples were measured and all fastness properties were evaluated [54]. In the study, as mordant, aluminum ammonium sulfate ($NH_4Al(SO_4)_2 \cdot {}_{12}H_2O$), two tin chloride ($SnCl_2 \cdot {}_2H_2O$), magnesium sulfate ($MgSO_4 \cdot {}_7H_2O$), iron trichloride ($FeCl_3$), iron sulfate ($FeSO_4$), and tannic acid were used. All pastes were applied to the fabrics by flat screen printing. After printing and drying, the fabrics were exposed to fixation either by steam at 130 °C for 30 minutes or by thermofixing at 160 °C for 4 minutes. The fabrics were then subjected to various washing processes and dried [54]. The highest color yield (K / S) values are obtained when Meyprougm NP-16 is used as a thickener. This may be attributed to the higher stability and fixation conditions of Meyprogum paste to the printing paste components [54]. As the printing paste increases from 10 g/kg to 40 g/kg, it is observed that the color yield (K/S) values increase. Further increases in concentration, for example, from 40 g/kg to 50 g/kg, result in either a slight increase or a slight decrease in K/S. An increase in the K/S value with increasing dye concentration in the printing paste is expected because the number of color particles in the printing film is increased. The possibility of migration of the dye component from the film layer toward the surface of the printed fabric increases until the optimum concentration is reached (40 g/kg in the printing paste) [54]. It was stated that printed samples fixed with steam fixation have better color yield (K/S) values than thermofixed printed samples. This can be attributed to the condensation of water vapor on the surface of the printed fabrics during the steaming process in the steam fixation, and to accelerate the penetration of the dye molecule into the fabric. Thus, the K/S values of these printed fabrics can provide higher values than the K/S values of the fabrics obtained by thermosetting. Optimum temperatures for steam fixing: for silk and wool it is 115 °C, and for cotton and linen it is specified to be 120 °C [54]. In addition, the effect of mordants on color development was also studied in this study. As is known, mordants can be used to fix the dye, to obtain a range of colors, to retain the paint against fading, to improve fastness properties and/or to lighten, darken, or dull a color. In addition, dye is better bonded to fabric by using mordant [54–56]. Air-mercury (alkanet) dye was selected as the sample for this research and the best results were obtained by using mordant with a concentration of 20 g/kg printing paste. Color fastness results were found to range from very good to excellent [54]. It is stated that products of different colors can be obtained by using different mordants [43, 54]. Iron salts, magnesium salts, aluminum and tin salts, and tannic acid were used as mordant [54].

Patel and Chattopadhyay studied the process development for the printing of cotton fabric with natural dye extracted from black halile (*Terminalia chebula*, C.I. Natural Brown 6) in their study [57]. They printed cotton fabrics with *Terminalia chebula* natural dye extract with different mordant presence (copper sulfate, iron sulfate, and tin). Simultaneous mordanting (printing and mordanting at the same time) and post-mordanting (mordanting after the printing process) were applied as two different mordanting methods. Thickener (gum tragacanth) and gum arabic (gum acaia) were used as thickeners [57]. The effect of mordants on the color strength (K/S values) and color shades of the printed samples was evaluated and the fastness properties (light, washing, and rubbing) of the samples were examined. Mordant concentrations: iron sulfate was used in concentrations of 1%, 2%, and

3%, tin two chlorides 1%, 2%, and 3%, copper sulfate 1%, 1.5%, and 2%. The highest color yield is measured in samples in which iron sulfate is used as mordant. It is stated that fastness levels of printed samples are good enough [57]. In another study, it was aimed to produce natural dyed fabrics with thermoregulation (heat regulation) properties. The microcapsules comprising n-octadecane and n-eicosane (individually and in a 50/50 mixture) were applied to natural indigo dyed cotton fabrics by flat screen-printing technique. Even after 20 washes, 94% latent heat (heat that changes the physical state of a substance without changing the temperature) is retained in the fabrics. The colors of the fabrics have changed negligibly. The latent heat was kept at 70–89% after the rubbing test and 92–96% after the ironing test [58]. The results of the study displayed that thermoregulated fabrics can be developed by using flat screen-printing technique on natural dyed fabrics. These fabrics possess heat storage capacity and they are resistant to the effects of washing, rubbing, and ironing [58].

Tragacanth and gum arabic were used as thickeners for screen printing. It is possible to carry out various prints with them. In a study, viscosity of thickeners was measured and their reflections on fabric attitude were examined and light fastness levels were also evaluated [36]. Abd – El Thalouth isolated the environmentally friendly galactomannan and natural dye from carob seeds (*Ceratonia siliqua* L.) with a single processing step and used the colored paste as a natural printing paste. In this study, the rheological properties of this paste were investigated in the presence and absence of different mordants in cotton, wool, and silk printing. (a) Cyanoethylation, (b) reaction with reactive cyclodextrin, and (c) the effect of chemical modification of cotton by processes such as cationization were investigated [59]. In this study, pre-mordanting process was applied. In this process, the fabrics were soaked in 2% aqueous solution and then allowed to dry at room temperature. The mordanted fabrics were then printed by stencil printing, dried, fixed, and washed. Screen printing of wool, cotton, and silk fabrics was applied by using natural dye printing paste. The printed fabrics were steam-fixed for 15 minutes at 100 ° C, then washed, and dried in various ways [59]. In many cases, the color yield (K/S) values of protein fibers such as wool and silk are relatively higher than those of cellulosic fabrics such as cotton. This is expected because tannins found in locust-bean as previously reported are high molecular weight components containing phenolic hydroxy groups that help them form effective cross-links with proteins [59]. It is noteworthy that although high K/S values are achieved with the use of iron sulfate, this leads to degradation of cotton fibers. Fe^{+2} reacts with oxygen in the atmosphere to form Fe^{+3}. Fe^{+3} reacts with water to give free hydroxyl radicals (OH). These free hydroxyl radicals are responsible for the deterioration of textile materials. Therefore, iron mordant is not recommended because of its effect on textile fibers [59]. A striking observation is that the strength of wool fibers is not affected by iron sulfate like cotton. Not surprisingly, wool fabrics may be more resistant to the effect of iron sulfate used as mordant when compared to cotton fabrics. Silk fiber shows the lowest K/S values with alum mordant compared to wool and cotton. Although silk is a protein fiber, its weight, absorbance, resilience, and reactivity differ from wool. All these parameters may be the cause of the drop in K/S when alum was used as a mordant [59].

100% cotton and silk fiber fabrics were printed with lacquer and harda extracts in the presence of alum and iron sulfate. After printing, the fabrics were exposed to steaming for 30 minutes at 102–110 ° C. Then the color fastness values of the fabrics were examined [27]. The washing and dry rub fastness values of the fabrics were good. Wet rub fastness levels were moderate. The results of the study also showed that the color depth and wash fastness values of rope fiber fabrics were higher than those of cotton fabrics [27]. Klachoi et al. examined the printability of plain cotton fabric samples by using reactive printing technique utilizing pseudo-acacia (*Acacia catechu* Willd). The effect of urea, thickener, and sodium bicarbonate in printing paste on color yield was investigated. In addition, sodium alginate was used as thickening agent. The color yield (K/S) values of the printing presses were measured and the fastness properties of the samples were examined. Printing was performed using film-druck printing technique. The printed samples were washed, then rinsed, and dried at room temperature [60]. According to the results of the research, the highest color yield (K/S) values are reached with prints. Fastness values are reported to be in the range 3–4 gray scale ratings. The results show that this plant can be used as a natural dye for the printing of cotton fabrics [60].

The potential usability of annatto plant colorant as a natural dye in traditional and innovative textile applications was also investigated by researchers [61]. In this study, alum was used as mordant. In addition, a wide variation in different mordanting techniques and dyeing recipes has been applied to achieve optimization and improve color fastness properties [61]. The printing process on cotton fabric was made by using annatto flat screen-printing technique. The measurement of the rheological and physical characteristics of the annatto printing paste confirms its stability and suitability for conventional printing. A new water-based digital printing ink was prepared using Annatto and applied to cotton fabrics using digital printing applications. In conventional printing process, thermosetting was done at 150 °C for 4 minutes. Fixation has not been made to prevent digital printed fabrics from being affected. Washing, light, and abrasion fastness properties of digitally printed fabrics were determined and compared with fastness characteristics of fabrics produced by conventional printing method. Annatto acts as a typical water-soluble dye rather than an insoluble pigment [61]. Conventionally, Annatto printed fabrics were found to have excellent dry cleaning, dry heat, and rubbing fastness properties (level 5), but light fastness values were slightly lower. It is known that light fastness values can be increased by adding mordants such as alum; again, it is possible to increase the light fastness values by adding UV absorbers to the printing paste. All fastness values of digital printed fabrics are higher than traditional printed fabrics, because the color yield (K/S) values of digital printed fabrics are lower than traditional printed fabrics. The results are promising for the use of annatto as a natural dye. This may provide a way for the development of a new range of dyes that are environmentally friendly [61].

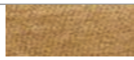
Rutin (a phenolic component found in invasive plants such as *Carpobrotus edulis*) is another natural dye used in printing fabrics. The name comes from the *Ruta graveolens* plant containing rutin, morin (*Maclura pomifera, Maclura tinctoria, and Psidium guajava*), and the use of laccase instead of harmful mordants in the fixation of flavonoid dyes called quercetin. In addition, optimum conditions for the best results in printing of fabrics were determined. The results showed that the optimum conditions for routine dyeing in the printing of cotton fabrics were 60 g/kg printing paste enzyme concentration, pH 4.5, 60 minutes treatment time, and 60 °C treatment temperature. Laccase provides enzymatic oxidative polymerization of flavonoids to give colored pigment. With this technique, these three types of flavonoids can be used as in pigments to print all fabrics and provide color fastness to perfection [134]. Cotton (bleached and mercerized), wool, nylon-6, viscose / polyester (80/20), wool / polyester (70/30) and cotton / polyester (60/40) fabrics were used in the study [62]. When K/S values of the study were investigated, Viscose/polyester > cotton/polyester > cotton > nylon > wool > wool/polyester values were obtained. This may be due to the difference in physicochemical properties of these fibers and therefore the affinity difference between the natural dye and the material to be printed. Morin and quercetin dyes were successful in printing. In addition, all fabrics exhibited very good color fastness values. Differences in K/S values can be attributed to the difference in their chemical structure and position and number of hydroxyl groups [62].

Developing antimicrobial printings on cotton and silk fabrics was investigated by using low, grass, and high molecular weight chitosan and pharaoh natural dyes at different concentrations. The results of the study showed that the molecular weight and concentration of chitosan affect the size of antimicrobial activity and color yield. It was reported that 2% concentration of medium and high molecular weight chitosan solutions inhibited the growth of bacteria and reached the highest color yield values [63]. According to the results of the study, chitosan-treated cotton and silk fabrics showed antimicrobial efficacy, and high chitosan concentration provided high color yield values [63]. In a study, a new natural mordant such as chitosan was applied on cotton fabrics at different concentrations (10% and 20% owf) and then cotton fabrics printed with natural dyes of pseudoacacia (katechu), turmeric, and calendula (marigold) by screen-printing technique. All dyes were used in powder form and were added to the printing paste in concentrations of 1%, 5%, and 10%. According to the results of the study, color yield values of chitosan used fabrics as mordant showed equal values with color yield values of fabrics mordanted with alum exhibiting very good antibacterial activity against gram-positive and gram-negative bacteria [64].

Silk, wool, and soybean fabrics were printed with red beet (*Beta vulgaris* L.) extract [65]. The effect of mordants in the printing process and the effects of the fixings made after printing were also examined. After the printing process on all fabrics, the effect of these processes was investigated by applying fixation process at different temperatures and times. Colors and color yield values of printed fabrics are given in Table 3 [65].

The results showed that the mordanted fabrics exhibited a higher color yield (*f(k)*) than the mordanted ones. The highest color yield value was reached mordanting with potassium bichromate and steam fixing process for 60 minutes woolen fabrics (60.81). In general, mordanted fabrics exhibited colors in beige tones and mordanted fabrics exhibited colors in brown tones. In addition, dry and wet rubbing

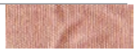
Table 3 Colorimetric values of printed samples [65]

Samples	*f(k)*	Appearance
Wool, un-mordanted, 30 minutes steam fixation	7.33	
Wool, un-mordanted, 60 minutes steam fixation	6.73	
Wool, potassium bichromate 30 minutes steam fixation	42.42	
Wool, potassium bichromate, 60 minutes steam fixation	60.81	
Silk, un-mordanted, 30 minutes steam fixation	3.68	
Silk, un-mordanted, 60 minutes steam fixation	3.71	
Silk, potassium bichromate 30 minutes steam fixation	38.00	
Silk, potassium bichromate, 60 minutes steam fixation	29.95	
Soybean, un-mordanted, 30 minutes steam fixation	4.39	
Soybean, un-mordanted, 60 minutes steam fixation	4.68	
Soybean, potassium bichromate 30 minutes steam fixation	26.65	
Soybean, potassium bichromate, 60 minutes steam fixation	23.71	

fastness of the fabrics were average–good, washing fastness excellent and light fastness showed average color fastness values [65]. The color fastness values of the fabrics are generally good [65]. Pre-mordanted soybean, wool, silk, and cotton fabrics were printed with root dye (Rubia tinctorum) extract. Pre-mordanting process was applied to the fabrics with 20% alum mordanted and then printing process was performed. The fabrics were steamed at 102 ° C for 30 minutes and 60 minutes. The fabrics were then washed [66]. Colors obtained from printed fabrics and color yield values are given in Table 4.

When the printed fabrics were evaluated in terms of color yield, it was observed that the highest color yield values were attained in woolen fabrics, and the lowest color yield values are reached in cotton fabrics [66]. When the fastness values of printed fabrics were examined, the washing and rubbing fastness values of soybean fabrics increased above 4 and were commercially acceptable. However, the 60- and 90-minute steaming process provides better light fastness values. The washing and rubbing fastness properties of silk fabrics were above 4 and steaming for 60 minutes showed the best light fastness value. When the woolen fabrics were examined, the washing and dry rubbing fastness values of the printed woolen fabrics were higher than 4, but the wet rub fastness values were between 3 and 3–4. These fabrics have the highest color yield values and therefore may cause a little more staining on the

Table 4 Colorimetric values of printed samples [66]

Samples	Streaming time	$L*$	$a*$	$b*$	h^o	$C*$	$f(k)$	Appearance
Wool	30	74.59	9.16	18.97	64.23	21.07	11.59	
	60	72.91	10.84	19.48	60.92	22.29	13.41	
	90	72.47	10.82	20.62	62.31	23.29	15.22	
Silk	30	73.82	8.67	16.05	61.62	18.25	7.57	
	60	70.19	10.78	20.50	62.26	23.16	11.35	
	90	70.96	11.18	20.19	61.02	23.08	10.61	
Cotton	30	68.77	12.69	17.21	53.59	21.38	4.87	
	60	67.59	13.42	19.54	55.52	23.70	5.06	
	90	66.65	14.21	21.70	56.78	25.94	4.73	
Soybean	30	77.23	9.58	11.05	49.07	14.62	7.76	
	60	76.89	8.88	11.23	51.68	14.32	9.00	
	90	77.71	8.74	11.54	52.86	14.48	9.63	

friction. Washing and rubbing fastness of cotton fabrics is close to the values of soy and silk fabrics, but light fastness values are around 1–2 [66].

The applicability of root dye by printing various natural fibers was examined in the recent studies. The effects of printing, dye and urea concentration, fixation time, and temperature, as well as fixation type and mordant, were examined and the color values and fastness properties of the printed fabrics were also evaluated. The results show that K/S values increase with increasing natural dye concentration (15–45 g/kg) in printing paste. Cotton, woolen, and silk fabrics were printed with or without mordant and the highest K/S values were reached in the presence of mordant. As a result of the use of mordant, color fastness values showed good, very good, and excellent values, as well as the rootstock also exhibits some superior fastness properties [68]. In studies conducted in Turkey, wool, soybean, and silk fabrics were screen printed with the black cabbage (*Brassica oleracea*. *capitata* f. rubra) extract, accompanied with mordant (potassium dichromate) and un-mordanted. The results of the study show that the overall fastness values of the fabrics are good. Colors and color yield values of printed fabrics are given in Table 5 [67]. The fabric samples exhibit various shades of color from beige to brown. The highest color yield value was achieved by mordanting with potassium bichromate and silk fabrics which were fixed for 30 minutes. When the results are examined, it is observed that the use of mordant provides a color enhancing property [67].

The use of lac (*Laccifer lacca* Kerr.) natural dye as a colorant in the printing process was investigated. Cotton and silk fabrics were used as natural fabrics. In this

Table 5 Colorimetric values of printed samples [67]

Samples	*f(k)*	Appearance
Wool, un-mordanted, 30 minutes steam fixation	7.43	
Wool, un-mordanted, 60 minutes steam fixation	27.61	
Wool, potassium bichromate 30 minutes steam fixation	43.79	
Wool, potassium bichromate, 60 minutes steam fixation	24.74	
Silk, un-mordanted, 30 minutes steam fixation	3.62	
Silk, un-mordanted, 60 minutes steam fixation	11.05	
Silk, potassium bichromate 30 minutes steam fixation	45.98	
Silk, potassium bichromate, 60 minutes steam fixation	30.91	
Soybean, un-mordanted, 30 minutes steam fixation	3.99	
Soybean, un-mordanted, 60 minutes steam fixation	7.75	
Soybean, potassium bichromate 30 minutes steam fixation	4	
Soybean, potassium bichromate, 60 minutes steam fixation	21.31	

study, alum, tartaric acid, or tannin was applied by pre-, post-, and simultaneous mordanting methods. The color yield and fastness values of the fabrics were also investigated. In general, pre-mordanting process provided high color yield values in cotton and silk fiber fabrics. The fastness values of the fabrics were also good [69]. The printing was carried out as flat screen printing and the printed fabrics were dried at room temperature and then exposed to steam fixation at 102–105 °C for 40 minutes. The fabrics were then washed and dried. The results of the study show that cotton and silk fiber fabrics can be printed with lacquer dye. The improvement in color yield and fastness depends on the mordanting method and the type of mordant used. In cotton fiber fabrics, mordanting with alum followed by pre-mordanting with tannin gave the best results. Similar results were obtained in silk fiber fabrics. In alum mordanted fabrics, the highest color yield values in all mordanting methods have been reached with recipes used from 25 g/kg mordant [69]. Dai et al. investigated the effect of sinapic acid on sorghum printed silk fiber fabrics in order to improve fastness properties of silk fiber fabrics printed with natural dyes. Silk fiber fabrics were printed with guar gum paste and sorghum red dye in the presence of sinapic acid adjuvant. The printed fabrics were subjected to steaming with saturated steam for 15 minutes at 100 °C. The results of the study displayed that the light and wash fastness properties of the fabrics improved with the addition of sinapic acid [70].

Some natural dyes or substances are known with their antibacterial properties. Therefore, Teli MD, Javed Sheikh and Pragati Shastrakar (2014) used chitosan, a functional biopolymer, as a mordant for the printing of woolen fabric with natural dyes [71]. Natural dyes prepared for printing (false acacia, turmeric, and calendula (or marigold)) were first powdered. The most suitable non-ionic structured guar gum is used for textile printing. The colorimetric values, wash and light fastness and antimicrobial properties of treated fabrics (according to the AATCC 100–2004 test method) were investigated [71]. Natural mordant chitosan and standard mordant alum were compared, and it was found that both mordants gave similar color values. The fabrics printed without mordanting showed very light color tones and most of the dye flowed after washing. However, pre-mordanted fabrics with alum or chitosan produced darker prints, and even chitosan-treated fabrics provided darker colors than alum-treated fabrics. It is stated that this method may be suitable for environmentally friendly printing and antibacterial finishing of woolen fabrics [71].

Nano particles are new developed materials and exhibit interesting properties. Wool, wool/polyester, and polyester fabrics were printed with this interesting nano particle rhubarb dye [72]. Dyes, such as rhubarb, contain molecules having the characteristic of a typical disperse dye, and these molecules are quinone based. These molecules exhibit a very small and hydrophobic nature that makes them substantive to hydrophobic fibers [72]. Wool and wool/polyester fabrics were mordanted before printing with tartaric acid and potassium bichromate. Printing was performed by applying the screen-printing technique. The dye nanoparticles were combined with urea at the acidic pH values in the printing paste, the fabric was printed, and finally, the prints were fixed and washed. The K/S values of wool and wool/polyester fabrics mordanted with tartaric acid are increased with increasing mordant concentration compared to the K/S of non-mordant fabrics. Again, when the fabrics are mordanted with potassium bichromate at the same concentrations, it is seen that the K/S values increase tremendously compared to un-mordanted fabrics [72]. Cotton/wool (50/50%) blended fabrics were printed by other three natural nanoparticle dyes such as turmeric, root dye, and rhubarb. The dye powders were sonicated for 6 hours and milled for 30 days. In addition, cotton−/wool-blended fabrics were subjected to pre-mordanting with tartaric acid and alum separately. All color and fastness values of fabrics have been examined [73]. The results of the study showed that the best K/S values were reached at pH 5, 6, and 6.5. The results also show that fastness values are good to excellent. This indicates the presence of strong bonds between the dye molecules and the fibers. On the other hand, the printing process with dye nanoparticles showed a remarkable improvement in fastness values compared with printing with regular dyes. The study showed that these nanoparticulate natural dyes can be applied successfully in printing applications [73]. In a study, the printability of nanoscale particles and silk and nylon 6 fiber fabrics were investigated. The dried plants were ground and exposed to ultrasound waves. It was then combined with urea at acidic pH and printed on pre-treated fabrics. Finally, the printed fabrics were fixed and washed. In this study, color yield and fastness values of printed fabrics were examined. The results have shown that the use of nanoparticles in printing has improved the color yield and fastness properties of printed fabrics [74].

The applicability of root dye to various natural fibers was tested by some researches using the printing technique. The fastness and color yield properties of the printed fabrics were evaluated. In addition, the effect of mordant on these properties was examined. The results showed that the highest K/S value was reached by using mordants. It is thought that the application of root dyeing on fabrics with printing technique will present a different and ecological alternative. Since the exposure of the fabric to high steaming temperatures for a long time poses a risk of yellowing of the fabrics, the optimum fixing conditions were determined as 10 minutes at 102 ° C in this study. In addition, it was observed that steaming fixed fabrics exhibited higher K/S values than thermofixed fabrics [75]. In addition, mordanted fabrics exhibited good and close fastness values, indicating that mordanting has a positive effect on fastness properties [68].

2.2.2 Pigment Printing Technique

The colorants used in printing were certainly mineral pigments, although the form of printing was already used. Today, the great availability of excellent organic pigments and reliable pigment binders has led to an increase in the importance of pigment printing. In the 1990s, more than 50% of world textile prints were pigment printed. Increasing importance of polyester / cellulose mixtures and the complexity of printing with dyes on these substrates increased the use of pigment printing. Although it does not eliminate the extra risks associated with the general use of paints due to steam fixation and post-wash requirements, pigment printing has been shown to reduce these risks [1, 76]. Pigment printing allows manufacturers to print blended fabrics in one step without sacrificing permanence and color. Like many simple processes, there are very few disadvantages compared to pigment printing in pigment printing. The pigment particles are chemically stable and insoluble. Therefore, these particles do not have a natural affinity to textile fibers and require an external fixation [2]. In 1984, a 50-year period was reported to effect the change of paints. Reactive dyes account for 25% of printing colorants, 10% for disperse dyes, 9% for vat dyes, and 3% for azoic dyes [1, 2, 76]. However, rigid pigment prints limit their use [2].

In the literature, the use of chitosan as a thickener and binder combination for pigment printing has been studied. In this way, as a result of the use of chitosan, color yield decreases and fabric hardness is increased [41, 44, 48, 77, 78]. The chitosan printing paste may be produced by dissolving the chitosan in dilute acetic acid and adding the pigment then mixing to prepare homogeneous pigment dispersion. Then the fabrics (PET and PET cotton) were printed with chitosan printing paste and dried at 150° C for 6 minutes. The biggest problem with chitosan printing paste includes poor color yields and fabric hardening [77, 78]. In a study on wool printing made with natural dyes, printing was performed with root dye (*Rubia cordifolia*) using pigment printing technique. The aim of this study was to determine the optimum values of dye concentration, pH, binder concentration, and selection of suitable thickener. The washing and light fastness values of the samples were tested. The results show that woolen fabrics can be printed with root dye using pigment printing technique. The color strength (K/S) of the sample which was pressed at pH 5 with the synthetic thickener and fixed by steam was measured as 4.7. Wash and light fastness have been reported to vary from moderate to excellent [79].

Some researchers tried to apply turmeric powder on cotton, polyester, and their blends by using pigment printing technique. Color concentration, thickener structure, fixation type, and pH of printing paste were also examined. Printed fabrics were evaluated according to color yield and fastness properties. The K/S value increases as the turmeric concentration increases and/or the pH drops to 6.3, regardless of the nature of the fabric used, the type of fixation, or the time before printing begins. The results also show that thermosetting provides better results than steam fixing. In this case, turmeric was applied with its head as a natural dye source [80]. In another study conducted in 2012, Yavas and Avinc used henna (*Lawsonia spinosa* L.) to print on woolen fabrics. In this study, the effects of pre-mordanting, binder in printing paste, different fixing conditions, durations, and temperatures on color properties were investigated [81]. Henna was added to the paste without any extraction in powder form and the printing was carried out according to the binder and pigment printing method. The prescriptions in the table were used for printing and the printed fabrics were dried at 100 ° C for 3 minutes and fixed with steam, thermosetting, and microwave [81]. Steam fixing provides the highest color yield values for both wool and cotton fabrics. In addition, thermosetting provides higher color yield values than microwave fixation. Color yields of pre-mordant woolen fabrics are generally higher than those of un-mordanted fabrics. This shows that pre-mordanting increases the color yield of woolen fabrics. The presence of binder in henna printing paste leads to an increase in the color yield of woolen fabrics pre-mordanted with alum. Microwave energy fixation method gives the lowest color yield values compared with the other two fixation methods [81]. Four different natural dyes (walnut shell, madder, buckthorn, and indigo) were used for pigment printing on wool fiber and cotton fiber fabrics. No mordant was used in the study [82]. This study shows how easy pigment printing can be done with natural dyes without using any mordant. The highest K/S value was obtained in cotton walnut shell printed fabrics. In general, fastness values of fabrics vary from poor to good [82]. Also the application of four eugenol-substituted metallophthalocyanine (M:Zn) (Fig. 7) containing extracts from clove (*Eugenia caryophilis*) on cotton fabrics and its antimicrobial properties were investigated. Eugenol is known to be active against many pathogenic bacteria, fungi, or viruses. It is also known that metal members such as zinc and copper exhibit antibacterial properties. For this reason, eugenol and zinc metal ions were combined as phthalocyanine pigment (green color). Then, cotton fabrics were printed with pigment by using pigment printing technique and color fastness performances were examined. Antibacterial test (against *Staphylococcus aureus* and *Klebsiella pneumoniae*) was also applied to the printed

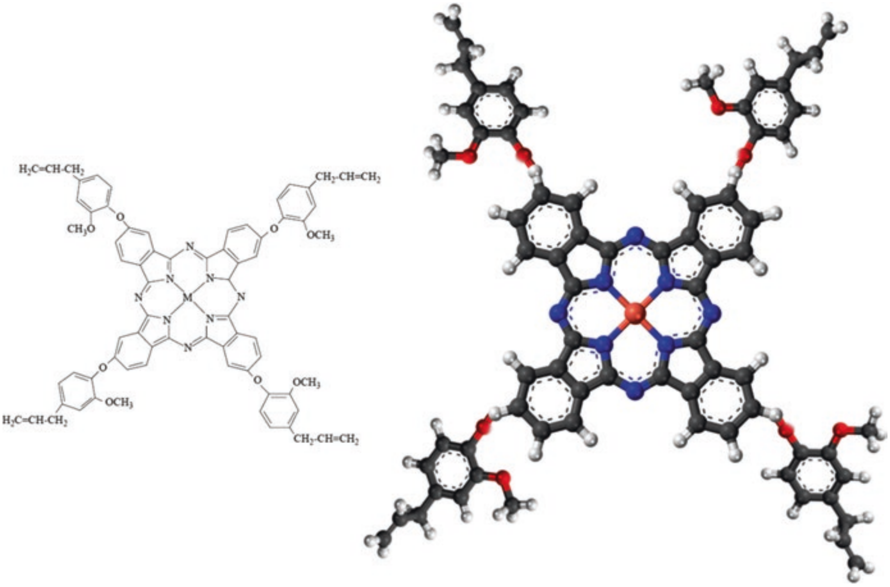
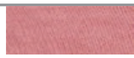
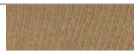
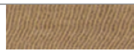


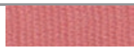
Fig. 7 Four eugenol-substituted metallophthalocyanine [83–85]

Table 6 CIELab values of the soybean fabrics printed by using pigment printing technique [86]

Samples	$L*$	$a*$	$b*$	$C*$	h^o	K/S	
Soybean, red bet extract printed, *un-mordanted*	73.5	5.3	17.3	18.1	72.9	1.3	
Soybean, red bet extract printed, *mordanted*	56.2	1.5	18.6	18.7	85.6	4.6	
Soybean, red onion extract printed, *un-mordanted*	76.8	4.0	18.3	18.8	77.8	1.5	
Soybean, red onion extract printed, *mordanted*	58.0	3.1	20.3	20.5	81.3	4.3	

fabrics. The results of the study exhibited that the obtained dye showed activity against *S. aureus*, but did not show activity against *K. pneumoniae*. When examined in terms of the general characteristics of pigment printing, it was stated that the dye provided better rubbing fastness levels but resulted in lower light fastness results [83]. Yildirim et al. printed soybean and wool fabrics by pigment printing technique using red beet (*Beta Vulgaris* L.) and red onion peel (*Allium cepa* L.) extracts. Color and fastness properties of the printed samples were also investigated. The results of the study displayed that the highest color yield values were found in mordanted woolen fabrics printed with red beet extract. Printed fabrics exhibited various color tones from to pink to brown. CIELab values for printed fabrics are given in the following two tables (Tables 6 and 7) [86].

Table 7 CIELab values of the woolen fabrics printed by using pigment printing technique

Samples	*L**	*a**	*b**	*C**	*h°*	*K/S*	
Wool, red bet extract printed, *un-mordanted*	70.8	6.5	16.4	17.6	68.4	1.4	
Wool, red bet extract printed, *mordanted*	51.1	3.3	23.7	23.9	82.1	9.9	
Wool, red onion extract printed, *un-mordanted*	72.6	5.5	16.7	17.6	71.9	1.8	
Wool, red onion extract printed, *mordanted*	50.8	5.1	24.2	24.7	78.0	8.9	

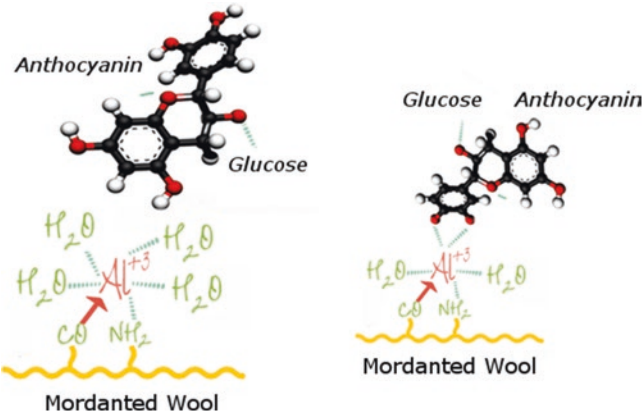


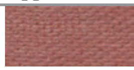
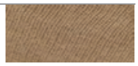
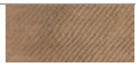
Fig. 8 Bonding between anthocyanin and wool via aluminum [87, 88]

In another pigment printing study carried out by same researchers, wool and soybean fiber fabrics were printed extracts using black cabbage and carrot extracts with and without mordant presence. Black carrot and black cabbage contain anthocyanin pigments which were sensitive to pH and temperature. In this study, the prescription used for pigment printing process: 4 g Tubivis VP681, 15 g Tubivis Binder 450, and 100 grams of printing pastes were prepared using 2% potassium bichromate and extract as mordant. Mordants are generally required for fiber fixation of natural dyes without substantivity to textile fibers. Figure 8 shows the bond of mordant wool with natural dyes [87]. The colorimetric values and appearances of the printed fabrics used in this study are given in Table 8 [87].

The results of the study show that the color yield values of printed fabrics vary between 2.3 and 13. In addition, both soybean and woolen fabrics decreased color yield values after washing. When the rubbing fastness values of the fabrics are examined, it is observed that wet rubbing fastness values are lower than dry rubbing fastness values. Again, when the results of water fastness tests of fabrics were examined, it was observed that the values were generally good [87].

Pigment dyeing was applied to silk fiber fabrics using natural paint obtained from red mangrove shells. Three different types of thickeners were used in the study: syn-

Table 8 The colorimetric values of the unwashed and washed wool and soybean fabrics [87]

	Process	Wool fabrics		Soybean fabrics	
		K/S	Appearance	K/S	Appearance
Un-washed	Printed with black carrot extract, *unmordanted*	6.3		3.5	
	Printed with black carrot extract, *mordanted*	11.7		6.3	
	Printed with black cabbage extract, *unmordanted*	12		3.9	
	Printed with black cabbage extract, *mordanted*	13		5.7	
Washed	Printed with black carrot extract, *unmordanted*	2.6		1.9	
	Printed with black carrot extract, *mordanted*	9.2		4.8	
	Printed with black cabbage extract, *unmordanted*	5.3		2.3	
	Printed with black cabbage extract, *mordanted*	8.9		4.2	

thetic thickener, sodium alginate, and tex gum. In addition, the effects of dye concentration and fixation time on color yield values were investigated [89]. Nowadays, screen printing (especially rotary screen printing) is dominant [1, 2, 90]. Much more printing paste can be carried on the surface in the flat screen-printing process compared to block printing. Compared to digital printing techniques, stencil printing has low capital cost equipment compared to weekly or monthly investment income, and these machines can work productively for decades. This shows that the developing regions and countries of the world have the power to establish natural dyeing and printing organizations. However, it may not compete with large ink-jet printing machines used for short-term full-color market because it is labor-intensive as template printing [2, 36]. This is because there is no need to modify or produce patterned rollers or stencils in jet printing systems; in addition, it has the potential for sudden sample change or long operation [1, 2, 90]. The trend toward digital dominance in textile materials in recent years has negative effects on the screen-printing industry in many countries that do not have capital for these new technologies [1, 2, 36, 90].

2.3 *Innovative and Digital Printing Systems*

Digital technology has greatly affected many areas in the textile industry. This technology not only introduced the textile printing market to full-width jet printing machines, but also influenced all stages of traditional printing production from the design stage to coloring and recipe preparation, from template production to printing paste preparation and final electromechanical control of printing machines. Jet-printing machines on textile fibers started to be used at least 25–30 years ago and were limited to the carpet industry [1]. The main objective of the printing process is to obtain sharp bounded colored patterns on the textile material without moving any dye beyond the boundaries of the designed motif [2, 39, 91]. This can be achieved by using suitable thickeners which act as a means of transporting dyes, chemicals, and other printing auxiliaries on the textile material during the printing process. The printing thickener holds the dye particles in the desired location on the fabric until the printing and subsequent fixing processes are completed, where the dye is permanently attached [39]. Thickeners utilized in textile printing are high molecular weight compounds that give thick pastes in water [37–40].

The usability of sodium alginate as a pre-treatment printing paste for digital ink-jet printing was a mystery. For solving this mystery, some researchers impregnated the cotton fabric with a pre-treatment printing paste containing sufficient amounts of sodium bicarbonate, urea, and chitosan with 80% wet pick-up [44, 92]. The fabric was then ink-jet printed using a Mimaki Tx2–1600 digital ink-jet printing machine with a reactive dye-based four-color ink system. The printed fabric was then dried under ambient conditions and steam-fixed at 110° C for color fixation. The outcomes of the study displayed that while the color fastness values of printed fabrics were quite satisfactory, the outline sharpness of prints improved with chitosan pre-treatment. However, the color yield values were not as good as those obtained by the ones pre-treated with the sodium alginate [44, 92]. In another study, chitosan was used in pre-treatment before digital printing process [44, 93]. The neutralizing effect may have reduced the amount of sodium bicarbonate and increased the amount of neutralization products such as water. Thus, during the steaming process, water poses a high risk for reactive dye hydrolysis, while the decreased amount of sodium bicarbonate reduces the fixation of dye to the fiber. And so, this led to the reduction on the color yield. The pre-treatment method was modified to increase the color yield and chitosan was separately applied for reactive dyestuffs and digital ink-jet printing on cotton fabrics [44, 93].

There is a recent study conducted by researchers who have previously investigated whether it is possible to use chitosan in the pre-treatment printing paste for the printing of cotton fabrics by digital ink-jet method and as a result, the final color was not as good as expected. In their new study, researchers applied chitosan separately to cotton fabrics for digital ink-jet printing. It was stated that the two-bath method provided better color yield values. Nevertheless, the utilization of chitosan slightly reduced the strength of digital ink-jet printed fabrics [44, 94]. In this study, chitosan was applied with a post-treatment method as a binder for fixing the digital printing of pigment-based inks on cotton fabrics, unlike the pre-treatment methods of chitosan. It was assumed that chitosan post-treatment can fix the pigment inks printed on cotton fabrics by forming a film layer on the fabric surface. Thus, the pigments will be captured or encapsulated. The study has two objectives: to develop and examine a chitosan-based post-treatment for fixing with ink-jet ink-based pigments digitally printed on cotton fabrics, plus formulating encapsulated nanoparticle ink-jet pigment inks using chitosan for pigment applications and one-step binder [44]. It has been observed that cotton fabrics pre-treated with chitosan have almost 85% fixed pigment even after 50 washes. This shows that chitosan post-treatment could be utilized as a permanent finishing process and there is a strong chemical interaction between chitosan and cotton. The poor washing resistance of chitosan-treated cotton fabrics indicates a strong lack of bond between chitosan and cotton fabrics. In the study, chitosan was also applied to different fiber types. These fibers are 50/50% polyester cotton blends, wool, silk, and viscose. The chitosan post-treatment of these fibers with pigment-based inks is almost 80% or greater. However, the amount of fixation in polyester fabrics is about 28%. The reason for this low pick-up is the hydrophobic nature of the polyester and the lack of reactive groups to be cross-linked with chitosan [44].

Chitosan can be utilized as a chemical in the preparation of printing media for digital ink-jet printing of cotton fabrics. Recently, the low temperature plasma (LTP) treatment has provided an effective pre-treatment process to improve the coating process by altering the surface characteristics of the material without substantially altering the dimensional properties. Therefore, the aim of this study was to examine the feasibility of applying LTP as a pre-treatment process to increase the coating of printing media such as sodium alginate, chitosan, and mixtures by improving the final properties of digital ink-jet printed cotton fabrics. Reactive yellow ink was used for digital printing. The patterns are prepared with a pattern size of 80 mm $*$ 80 mm and 360 dots per inch. After printing, the fabrics were treated in 110 $°$ C superheated steam for 5 minutes. The steamed fabrics were washed with 10 g/l non-ionic detergent and dried [45]. Experimental results showed that the maximum color yield was achieved with all printing media, but the color yields decreased as the exposure time increased. In general, printing media with sodium alginate/chitosan mixture reached 85% of color yield of printing media containing only alginate, but color fastness, external sharpness measures, and antibacterial evaluations showed that sodium alginate/chitosan mixture gave better results than only alginate [45].

Ink-jet printing is one of the fastest growing printing technologies and compared to traditional techniques, it has unique advantages such as simplicity, low production costs, reduced waste, and reduced water and energy consumption [61, 94]. Four natural dyes [annatto (*Bixa orellana),* pomegranate peel (*Punica granatum*), acacia (*Acacia catechu*), and golden dock (*Rumex maritimus*)] were utilized as colorants in the preparation of water-based ink-jet inks for digital textile printing. The results showed that the inks were suitable, and the inks were utilized for printing cotton fabrics. Color fastness and colorimetric values of printed fabrics were examined. The results showed that fastness and colorimetric values were comparable to synthetic dyes [91]. The outcomes of the study displayed that the washing and rubbing fastness properties of natural dyes were comparable to the washing and rubbing fastness properties of low-molecular weight direct dyes. The results are promising, which may allow the production and use of environmentally friendly ink-jet inks in digital printing [91].

2.4 Abrasion, Reserved Printing, and Special Printing Types

Abrasion and reserve printing styles have been important since the earliest times of textile printing. In the direct printing style, the final effect is achieved by an operation under fixation and washing is also required. In fact, the term “direct” means that there is no need for a preliminary or subsequent step, such as pre- or post-mordanting. In the abrasive style, the fabric should first be dyed with a dyestuff, and then this dye should be destroyed by a selected abrasive [1]. With appropriate recipes and process recommendations, it is possible to apply abrasive stress to many substances. These materials can be given to cellulosic fibers (by wetting), wool and silk, secondary cellulose acetate and triacetate, polyester fibers, nylon, acrylic fibers, and polyester–cellulose mixtures [1]. The suitability of the environmentally friendly laccase enzyme instead of harmful reducing agents utilization in order to make abrasive printing on natural fabrics (cotton, wool, and silk) with different natural dyes (henna, turmeric, and leucaena) under various conditions was an interesting issue and needed to be investigated. Enzyme concentration, fixation time, and temperature were also investigated. The outcomes displayed that by increasing the concentration of laccase enzyme in the printing paste, the color yield of printed fabrics decreased. Optimum conditions were determined to obtain color etching using laccase enzyme [95]. Abrasion printing of natural fibers dyed with different natural dyes was carried out using laccase enzyme. The results of this study indicated that the increase on laccase enzyme concentration in the printing paste from 50 to 200 led to the decrease in the color yield of printed fabrics and the color fastness properties of the dyed fabrics were good to very good. Optimum fixing time was 5 minutes at 102 ° C. The regions where the abrasion prints used the laccase enzyme gave a different color from the background color. Therefore, different shades could be obtained that prohibit attractive and beautiful features [95]. It can be used to create a similar effect in reserve printing, but in this method, the fabric is first printed with a reserved material and then dyed. Background colors can therefore be obtained with non-corrosive dyestuffs. It prevents the absorption of a physical reserve dyestuff and prevents a chemical reserve fixation. If the background color does not appear too dark, the desired effect can be achieved by overprinting. This is a simple direct printing process on a pre-dyed fabric. For example, blue dyes can be printed on yellow fabric to produce green areas [1]. In another study, a color-resistant material from taro (a tropical plant) flour for reserve white printing and *Acacia catechu* as a natural dye for batik technique were used. The paste, obtained from taro flour for color-resistant material, was prepared with 20% taro flour, 36% water, 30% sodium chloride (chloride), 10% calcium hydroxide, and 4% vegetable oil. Printed fabrics were fixed using hot air at 120 ° C for 3 minutes. Reserved printed areas provided sharpness and whiteness. The results of the study showed that the fastness of fabrics against rubbing and light showed good values. However, washing, water, and sweat fastness values were found to be poor [96].

3 Conclusion

Natural dyes and pigments could be extracted from insects, plants, and animals. Natural dyes have been used in the dyeing of wool, cotton, and silk since the prehistoric ages. However, the discovery of the first synthetic dye changed the natural coloration habits and synthetic dyes replaced almost all natural dyes. However, it is known that the wastewater produced in the production steps of synthetic dyes and the chemicals utilized in the textile printing/dyeing process could have toxic and pollutant effects on human and environmental health. Nowadays, the effects of environmental awareness, organic products, and the tendency toward healthy lifestyle also reflect on the textile sector. Disagreements on the risks of the usage of synthetic dyestuffs and increasing environmental awareness result in an enhanced interest in natural resources, environmentally friendly products, and new strategies. That is one of the reasons why the use of natural dyes came back to the agenda due to an increased ecological and sustainable awareness. Unlike non-renewable raw materials of synthetic dyes, natural dyes are mostly renewable and sustainable. Natural dye sources are agriculturally renewable sustainable vegetable-plant-based colorant sources. In terms of sustainability, synthetic dyes are produced from non-renewable resources; however, natural dyes are extracted from renewable sources. The ability to obtain the dye from renewable natural sources makes natural dyes an attractive dye class for more sustainable world. Natural dyes can be applied on the fibers not only with dyeing method but also with printing method. Textile printing is one of the most important and versatile methods among the methods used to design and colorize textile fabrics.

Printing technique for fabrics dates back to ancient times. Over thousands of years, civilizations used natural dyes for this technique. Industrial revolution affected these ancient printing methods, as it affected many sectors. Firstly, blocks were added to the machines and then semi-automatic and fully automatic screen-flat machines were developed. For increasing productivity, rotary printing machines were produced. Nowadays, this method can be regarded as a predominant method. It has low-cost equipment and productivity. However, this method has various disadvantages that include longer template preparing times. Short-term full-color market and customer demands force manufacturers for producing small amounts. Therefore, the rotary printing method becomes bulky and new research studies have been conducted to develop new printing techniques such as digital printing. In parallel with the development of these machines, the development of synthetic dyes had continued. Synthetic dyes are used instead of natural dyes in these automatic machines. Synthetic dyes have many advantages, but also have disadvantages. Recently, natural dyes have become popular, thanks to the increasing environmental awareness and deserve second chance.

For companies to increase their competitive power, they must be able to produce high-value designed products in accordance with legal restrictions, official rules, and changing customer demands. Increased environmental awareness makes customers to be more selective and cautious. This approach has recently led to the revival of studies about the natural dyes. It can easily be said that natural dyes, which have been used for dyeing and printing purposes since ancient times and are still in use, will continue to be the subject of many different research studies in the near future. Considering the importance of innovative and functional products, the usability of natural dyes and pigments in textile printing and their protective properties that give functionality justify the increasing interest in natural dyes. It can also be expected that textile products printed with natural dyes will be much more involved in niche and special applications (such as baby products).

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Sustainability in Textile Dyeing: Recent Developments

Aravin Prince Periyasamy and Jiri Militky

Abstract The textile industry is one of the largest contributors to environmental threats globally, producing 60 billion kilograms of fabric annually and using up to 9 trillion gallons of water. During coloration, large volumes of unfixed dye are released into water bodies, and approximately 10–15% of dye is lost into the environment as wastewater. In addition, because of competitiveness in textile industry production, an increase in the use of combinations of synthetic dyes has contributed to dye wastewater, creating an even larger volume of effluent. Dye can remain in the environment for an extended period of time because it has high thermal photostability and resists biodegradation. The release of dye effluent into seawater and river water is very destructive to living organisms, including humans and other animals. Therefore, it is important to study and raise awareness of alternative processes that reduce pollution loads. This chapter discusses recent developments that reduce unfixed color loads in effluent by use of various dyeing techniques such as modification of chemical pretreatments, the nanodyeing process, plasma-induced coloration, supercritical carbon dioxide dyeing, microwave-assisted dyeing and ultrasonic dyeing to the next level.

Keywords Chemical modification · Plasma process · Ultrasound-assisted dyeing · Electrochemical

1 Introduction

The Earth is considered to be an exceptional planet among other planets in our solar system because it offers life-sustaining conditions. Numerous types of organisms, from microbes to human beings, live on the Earth. The biosphere is the environment that sustains life and withstands the impacts of various human activities. The term "environment" refers to our surroundings and has also been defined as "the totality

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of social, economic, biological, physical or chemical factors establishing the surroundings of man whose mission is to manage the environment." When compared with the total size of the Earth, the biosphere is a narrow layer only 20 km thick, extending from the bottom of the ocean to the highest point in the atmosphere at which humans can survive without suitable man-made equipment. The Earth is inhabited by humans, and our accomplishments—such as agriculture and the industrial revolution, followed by the more recent sophisticated world of synthetic and man-made materials—have had undesirable influences on the environment and biodiversity. The main impacts of humans on our surroundings are described below. The life-spans of humans have been increased by the development of medicines, reducing childhood mortality, and our birth rates are now 2–3 times higher than our death rates. Thus, by 2050, the world's human population is predicted to be around 9.8 billion; the current figure is 7.6 billion [1]. The majority of environmental devastation is due to population stress, which, in turn, affects land habitation and increases demands on resources such as water, minerals, fossil fuels, food, etc. Exploitation of resources such as surface water, natural wealth, fossil fuels, forests, greenery, and species diversity has occurred, since much of the land is occupied enormously by humans, and this exploitation has now became a threat to both humanity and the environment. Deforestation is expanding exponentially, leading to soil erosion, plant loss, and species extinction, accompanied by global warming and climate change. A lot of species have become endangered or extinct since deforestation, hunting, urbanization, and agricultural land reformation came into existence. The natural ecosystem is facing a threat from loss of biodiversity, since each species plays its own role in maintaining the harmony of nature. Numerous industries have arisen since the industrial revolution, and the textile industry is one of them. The textile industry has two divisions:

- Dry processing, in which the majority of processes performed for engineering and assembly of fabric practically do not consume water (e.g., the blowroom, carding, weaving, etc.)
- Wet processing, in which water is used either in its raw state or in solutions used in processing, or both (e.g., chemical processing of textiles, such as coloration, printing, and garment washing)

In chemical processing of textiles, there are various processes were involved to removal of impurities, coloration, and finishing. In reality, the most frequently used process is dyeing. Because of the enormous consumption of energy and water involved, and the resulting pollution, these processes are costly and non-eco-friendly. Additionally, they involve a huge number of different fabrics, which seems to be unnecessary and has a negative impact on the overall performance of the industry. Chemical processing is now being replaced by sustainable coloration techniques because of the toxicity of the former and the health hazards it causes. The process of dyeing involves huge consumption of water and energy, and the used water is then released into the environment as a pollutant, along with greenhouse gases (GHGs). Globally is approximately for one year, 10000 tonnes of dyes were produced worldwide, among it 7000 tonnes of dye is utilized in the textile industry

[2]. The chemical reagents that are used vary in their composition, ranging from simple organic and inorganic compounds to various polymers and complex synthesized organic products [3]. Hence, in-depth research is being done to introduce sustainable dyeing techniques as a replacement for conventional dyeing processes. Figure 1 provides an overview and the consumption and emissions that cause ecological concern. Hence, efforts are being made to evaluate sustainable dyeing methods such as plasma, ultrasonic (US), laser, and supercritical carbon dioxide dyeing, which can enrich specific properties of fabrics without causing adverse effects on the environment.

1.1 Air Pollution

The dyeing of fabric requires use of energy, and burning of fossil fuels is often used to accomplish it. In the meantime, emissions of various GHGs (such as carbon monoxide, carbon dioxide, and nitrogen), sulfur, and carbon particles occur, creating global warming potential. The chief concerns regarding air pollution in the dyeing industry are due to the use of boilers and power generators, and the transportation of goods from one place to another. Air is contaminated by textile factories, posing threats to the environment and causing human health problems [4]. In general, volatile organic compound (VOC) fumes are generated by textile factories, and the problem can be wide ranging and unquantifiable, extending in all directions from these locations [5–10]. Figure 2 shows typical air pollution caused by the textile-dyeing industry near Erode, India.

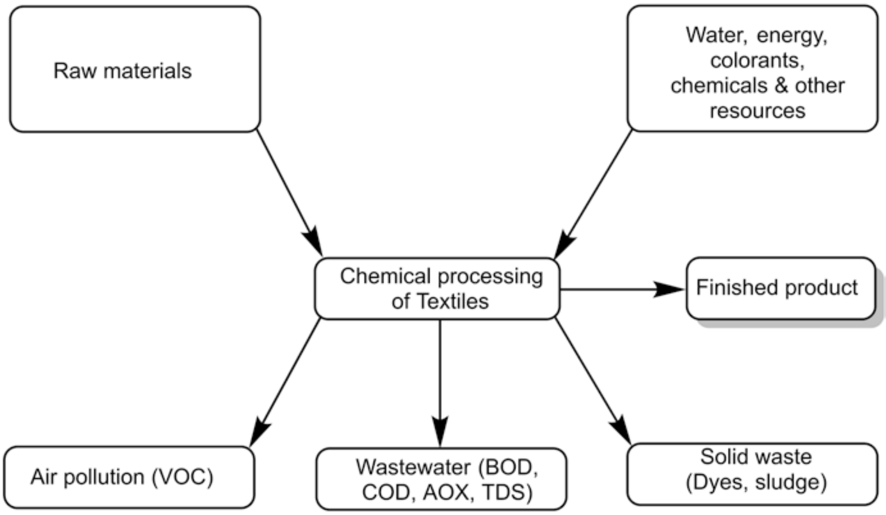


Fig. 1 The pollution route in the textile industry

Fig. 2 Air pollution caused by the denim industry near Erode, India

1.2 Water Pollution

Water resources are contaminated by activities performed to meet the domestic, agricultural, and industrial needs of humans. Water, which provides fundamental support to the majority of abiotic elements, is contaminated by organic, mineral, toxic, bacterial, and physical pollution. The water is thus made unfit for consumption through modification of its physical, chemical, and biological properties. Pollution of water makes it unpotable and unsafe for human or animal health, and for use in industry, aquaculture, agriculture, and recreation, with additional effects on the land, thermal pollution, and marine pollution [11]. Table 1 shows the World Health Organization (WHO) and International Organization for Standardization (ISO) quality criteria for raw water used as a drinking water source and for bathing. Table 2 shows the parameter limits for process wastewater and domestic sewage. Production of 1 kg of product generally produces 40–65 L of wastewater in the textile industry; however, this varies with the type of fiber being colored (Table 3). Figures 3 and 4 show the utility of water and the overall consumption of the textile wet processing industry, respectively [13]. Textile processing causes 20% of global water pollution, according to the prominent nongovernmental organization (NGO) Greenpeace International, and the most populated nations in this regard are China, India, and Bangladesh [14]. The environment is constantly under attack from the wastewater that is generated, which contains an extensive diversity of dangerous and toxic chemicals used throughout processing. The major cause of textile industry pollution is coloration using dyes, dyeing additives, and other chemicals. Dyes containing heavy metals are highly toxic [15, 16]. These pollutants have aquatic toxicity and include various toxic elements such as salts, surfactants, ionic metals and their complexes, formaldehyde, toxic organic chemicals, biocides, toxic anions,

Table 1 World Health Organization (WHO) and International Organization for Standardization (ISO) raw water quality criteria for inland surface water used as drinking water

Parameter	Maximum value	
	WHO	ISO
pH	6–9	6–9
TDS (mg/L)	1500	–
Iron (mg/L)	50	–
Nitrogen [expressed as NO_3 (mg/L)]	45	–
Fluoride (mg/L)	1.5	1.5
BOD (mg/L)	6	3
COD (mg/L)	10	–
Phenolic substances (mg/L)	0.002	0.001
Cyanide (mg/L)	0.2	0.1
Chromium (mg/L)	0.05	0.05
Lead (mg/L)	0.05	0.10
Arsenic (mg/L)	0.05	0.02
Chlorides (mg/L)	–	600

BOD biological oxygen demand, *COD* chemical oxygen demand, *TDS* total dissolved solids

Table 2 Parameter limits for process wastewater and domestic sewage

Parameter	Maximum value
pH	6–9
BOD (mg/L)	50
COD (mg/L)	250
Oil and grease (mg/L)	10
TSS (mg/L)	50
Total heavy metals (mg/L)	10
Total cyanide (mg/L)	1
Chlorine (mg/L)	0.2
Sulfide (mg/L)	1

BOD biological oxygen demand, *COD* chemical oxygen demand, *TSS* total suspended solids

Table 3 Water requirements for dyeing processes used for different fibers [12]

Process	Water requirement (Liters /1000 kg of product)					
	Cotton	Viscose rayon	Lyocell	Nylon	Acrylic	PET
Dyeing	10,000–300,000	17,000–34,000	17000–34000	17,000–34,000	17,000–34,000	17,000–34,000

PET polyethylene terephthalate

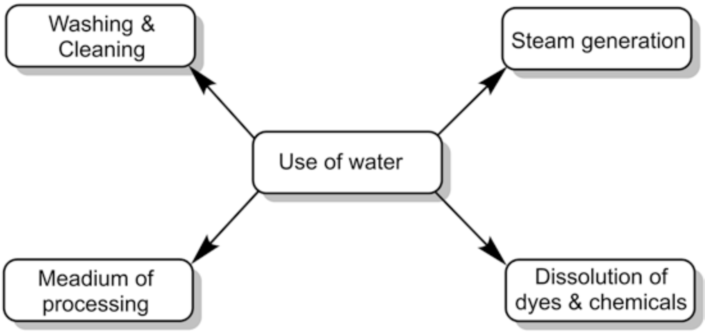


Fig. 3 Water consumption in chemical processing of textiles

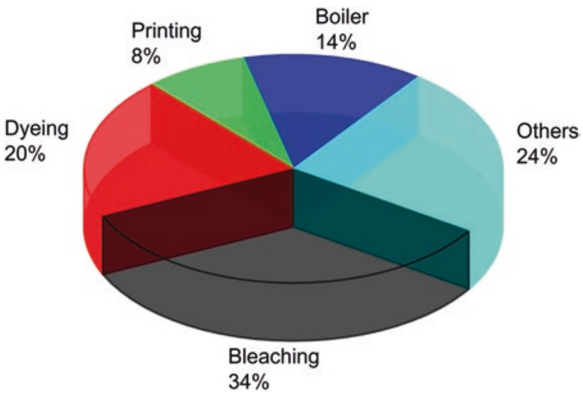


Fig. 4 Water consumption in wet processing of textiles

detergents, emulsifiers, and dispersants [17]. Thus, the textile industry produces wastewater that is highly polluted and dangerous, especially when it gets mixed with other chemicals and disposed of without treatment. Many places have been spoiled in terms of agriculture and everyday life by untreated pollution from the textile-dyeing industry. Since this spoils the groundwater, it is thereafter not possible to use such affected water for any other purpose (see Fig. 5). The wastewater that is produced possesses the characteristics of a high pH; a high biological oxygen demand (BOD); a high chemical oxygen demand (COD); and high concentrations of total dissolved solids (TDS), total suspended solids (TSS), chlorides, sulfates, and phenols (see Tables 2 and 4). This causes severe health problems because these chemicals and dyes are not readily biodegradable [3, 17]. The sludge produced by textile treatment plants contains chromium and other heavy metals, which are highly toxic; consequently, it should be treated and disposed of in a secure landfill.

Fig. 5 Effects of polluted water from the dyeing industry near Erode, India, on groundwater (**a**, **b**) and on agricultural land (**c**)

1.2.1 Impact of Dyeing Wastewater Pollution on the Environment

The dyeing industry bears a huge responsibility for environmental pollution caused by discharge of wastewater. It plays a major role in changing the environment [18–23]:

- Generally, colored water reduces dissolved oxygen (DO) levels and increases the BOD, resulting in the deaths of many aquatic organisms.
- Wastewater from the dyeing industry increases eutrophication-related problems.
- Some dyes contains toxic metals.
- Most dyeing wastewater contains toxic contaminants such as heavy metals, acids, alkalis, phenols, cyanides, pesticides, and pentachlorophenol (PCP).

Table 4 Characteristics of dyeing wastewater according to the dyes and materials used

Process	pH	Color (ADMI)	TSS (mg/L)	TS (mg/L)	TDS (mg/L)	COD (mg/L)	BOD (mg/L)	Chlorides [expressed as Cl^- (mg/L)]
PET with disperse dyes	5–10	1450–4800	n/a	500–14,100	50	1100–4600	10–1800	n/a
Cotton with reactive dyes	6.3–10.7	12000–18000	72–956	500–16400	258–1970.6	258–1970.6	70–300	48–601

ADMI American Dye Manufacturers Institute unit, *BOD* biological oxygen demand, *COD* chemical oxygen demand, *PET* polyethylene terephthalate, *TDS* total dissolved solids, *TS* total solids, *TSS* total suspended solids

- The toxicity of the wastewater causes many diseases, including birth abnormalities and reduced fertility of women.
- The wastewater reduces photosynthesis.

1.2.2 Toxic Waste

Toxic waste of any type can be discharged in water, air, or dust, and may contain toxic organic compounds, phosphates, chlorinated solvents, nondegradable surfactants, etc., initiated from numerous processes such as preparation of fiber, dyeing, printing, bleaching, or cleaning. Because of the emissions that occur from dyeing and finishing in the textile industry, there is a chance of dangerous emissions of toxic substances occurring. Workers involved in dyeing and printing are repeatedly exposed to various forms of acid (e.g., formic, sulfuric, and acetic acids), fluorescent brighteners, organic solvents, and fixatives, while workers involved in finishing operations are repeatedly exposed to crease resistance agents, flame-retardant chemicals, and a number of toxic solvents used for degreasing and spotting. Various skin diseases of a dermatitis type ensue from the impacts of bleaching, dyeing, and finishing processes. Bladder cancer can certainly be caused by exposure to intermediate dyestuffs. The occupational health effects include byssinosis, chronic bronchitis, dermatitis, and bladder cancer among dyers and disorders of the nasal cavity among weavers. With poor management of waste, due to lack of data, these harmful chemicals and solids are dumped in unsafe landfills, creating very dangerous surroundings in terms of the air, soil, and groundwater. Then, in the future, this land may be converted into a residential area.

2 Pollutants Associated with Dyeing Processes

The majority of environmental pollution caused by the textile-dyeing industry is due to discharge of pollutant wastewater. However, there are some possible types of air pollution caused by utilization of energy in the industry (e.g., the operation of boilers and power generators), but this air pollution is less of a problem than the water and land pollution caused by the industry. The dyeing industry consumes huge quantities of water in comparison with other wet processing techniques. This huge consumption of water not only results in a huge quantity of wastewater discharge but also involves utilization of large quantities of chemicals, energy, etc. Together, these cause serious environmental pollution problems. The wastewater generated by the Indian textile industry is shown in Table 5. During the coloration process, it is necessary to add many chemicals such as leveling agents, electrolytes, dispersing agents, defoaming agents, and demineralizing agents [24]. Apart from those, the main ingredient is the colorant (dye or pigment). The majority of colorants contain heavy metals and other toxic substances, posing threats to the environment and to health. Two processes are involved in dyeing operations: exhaustion and fixation. The dyeing efficiency can be determined on the basis of these processes. Usually, there is no possibility of 100% of the dye being exhausted during coloration; in some instances, 80–90% exhaustion can be achieved, and the remaining dye is then discharged as colored wastewater (i.e., with high turbidity). Table 6 lists unfixed dyes percentages, which vary and depend on the type of fiber and the type of dyestuff. Apart from the dyestuff, the dyeing process generates various pollution characteristics such as high TDS and TSS values, affecting aquatic life by increasing the BOD and COD.

Table 5 Characteristics of wastewater generated from Indian textile processing mills, as against the relevant standards [12]

Characteristic	Cotton	Synthetic	Standard
pH	8–12	7–9	5.5–9.0
Alkalinity [expressed as $CaCO_3$ (mg/L)]	180–7300	550–630	220–550
TDS (mg/L)	2100–7700	1060–1080	150–680
TSS (mg/L)	35–1750	50–150	100–600
BOD at 20 °C (mg/L/5 days)	150–750	150–200	30–350
COD (mg/L/day)	200–2400	400–650	250
Phenols (mg/L)	0.030–1.00	0.028–1.02	0.018–1.093
Oils and grease (mg/L)	4.5–30.00	4.4–31.9	10–20
Chlorides (mg/L)	80–1500	100–200	75–280
Sulfates (mg/L)	30–350	50–100	50–100

BOD biological oxygen demand, *COD* chemical oxygen demand, *TDS* total dissolved solids, *TSS* total suspended solids

Table 6 Pollutants associated with various type of dye [12]

Dye class	Fiber	Type of pollution
Direct dye	Cotton, regenerated cellulose	Fixing agents, high TDS, unfixed dye (5–20%)
Reactive dye		Alkalis, high TDS, unfixed dye (15–30%)
Vat dye		Alkalis, oxidizing and reducing agents, unfixed dye (5–8%)
Sulfur dye		Alkalis, oxidizing and reducing agents, unfixed dye (20–30%)
Chrome dye	Wool	Acids, high TDS, metals, unfixed dye (5–7%)
1:2 metal complex dye		Acids, heavy metals, high TDS, unfixed dye (2–8%)
Reactive dye	Nylon/wool	Alkalis, high TDS, unfixed dye (5–20%)
Basic dye	Acrylic	Acids, alkalis, unfixed dye (2–7%)
Acid dye	Wool	Acids, unfixed dye (7–20%)
Disperse dye	Polyester	Acids, carriers, reducing agents, unfixed dye (5–20%)

TDS total dissolved solids

3 Steps Toward Environmentally Friendly Processing

To address the need for sustainability, processing of textiles with use of limited amounts of water and energy and also with chemicals that are eco-friendly is a logical approach. Figure 6 provides a classification of developments in sustainable processing.

3.1 Use of Toxic and Nonbiodegradable Products

As noted by Kumar et al. [25], more than 8000 different chemicals are used in wet processing, and dye is the major one. Every year, the world consumes and produces approximately 80 billion new garment items [26], most of which are colored. In the case of reactive dyes, many studies have been conducted on salt-free dyeing [27–32] and alkali-free dyeing [31, 33], which reduce pollution loads. As discussed earlier, most of the chemicals used in dyeing are toxic and hazardous; however, there are some alternatives (see Table 7), which can help to reduce the pollution load.

3.2 Enzyme-Assisted Dyeing

As a result of the industrial biotechnology revolution, there is vast application of enzymes in textile production. The main advantage of enzymatic processing is sustainable and environmentally friendly processing. Use of enzymes has been studied

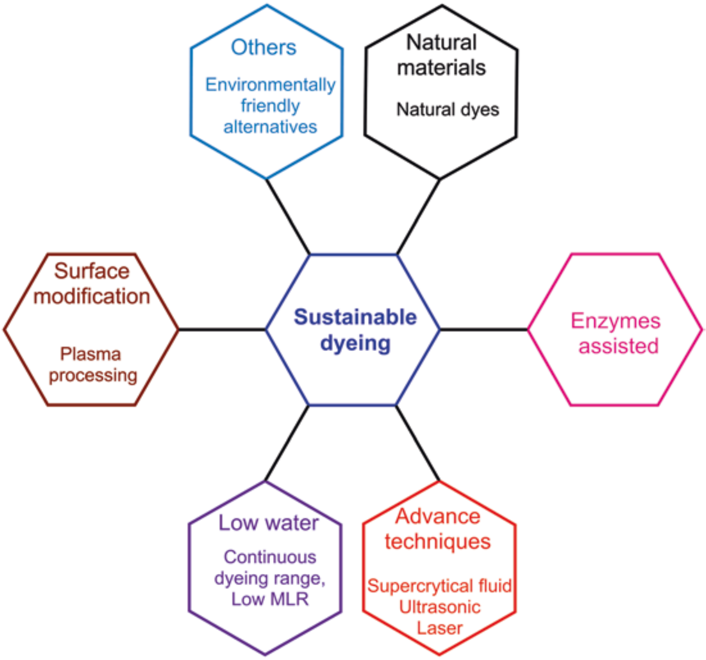


Fig. 6 Sustainable approaches in textile dyeing

Table 7 Environmentally friendly alternative chemicals and processes used for textile coloration

Process/agents	Chemicals	Alternatives	References
Reduction of sulfur dyes	Na_2SO_3	β-Mercaptoethanol, glucose	[34, 35]
Reduction of vat dyes	$Na_2S_2O_4$, NaOH	Electrochemical method	[36–40]
Oxidation of sulfur and vat dyes	$K_2Cr_2O_7$	Hydrogen peroxide, sodium perborate	[35, 40, 41]
Sulfur and vat dyes	–	Prereduced dyes	–
Hydrotropic agents	CH_4N_2O	Dicyanamide	[42]
Neutralizing agents	CH_3COOH	Formic acid	[42]
Wetting agents	Alkylphenol ethoxylates	Fatty alcohols	[42]

in different textiles such as cotton [43], wool [44], and silk [45, 46]. As described by Liakopoulou-Kyriakides et al. [47] and Tsatsaroni et al. [48], α-amylase, amyloglycosidase, and trypsin enzymes have been applied during preparation of cotton and wool textiles for the dyeing process. After application of the above enzymes, the treated fabric shows shrink resistance properties and better dye uptake than untreated fabric. Kumbasar et al. [49] applied alkali proteases to wool and silk to enhance their properties when they were dyed with tannin-based natural dyes, and found that alkali protease treatment significantly improved dye uptake. Vankar et al. [43, 45, 46] applied four enzymes (lipase, diesterase, protease, and amylase) and studied dyeing characteristics. They concluded that these enzymatic treatments increased dye penetration in comparison with conventional coloration techniques. Zhang et al. [50] studied the dyeability of wool fabric after application of protease. The color strength was increased with the protease treatment, but there was no significant change in fastness properties. Although there are only limited studies in the scientific literature regarding use of enzymes in natural textile dyeing, these techniques have been applied extensively in process improvement, enhancing the quality of the finished fabric, increasing the consumption of resources, and, in turn, reducing the environmental impact of dyeing. This has resulted in the introduction of a large number of industrial enzymes. The recent trend toward enzyme application has encouraged exploration of the feasibility of developing new enzymes for natural and eco-friendly dyeing in the textile industry. Furthermore, thorough research is required in order to evaluate the compatibility of dye enzymes with specific dyes and to develop a methodology for this type of dyeing on a commercial scale. Table 8 lists different studies of enzymes in textile dyeing.

El-Khatib et al. [53] studied the efficiency of dyeing bamboo fabric and bamboo/cotton blended fabric with use of a brewer's yeast enzymatic treatment (containing protease, amylase, and lipase). In this work they first carried out pretreatment in different pH conditions (from 5 to 9) and at different temperatures (40–80 °C). Later, the pretreated fabrics were dyed with natural dyes. Once the dyeing was finished, the fabrics were rinsed and soaped to remove the unfixed dyes, then they were rinsed again. Table 9 provides information on dyeing efficiency without and with enzymatic treatment. The color strength was linear and depended on the enzyme concentration.

Table 8 Application of enzymes in textile dyeing

Enzyme class	Substrate	Output	References
Protease	Wool	Better dyeability	[51]
Protease	Wool	Better colorability	[50]
Transglutaminase		No significant improvement in fastness properties	[50]
Laccase	Wool		[44]
Protease	Wool		[52]
Protease	Wool and silk		[49]
Protease	Cotton and silk		[43, 45, 46]
Amylase			[43, 45, 46]
Lipase			[43, 45, 46]
Diesterase			[43, 45, 46]

Table 9 Dyeing efficiency with different concentrations of enzymatic treatment and without treatment

Concentration of yeast suspension	Bamboo fabric		Bamboo/cotton blend fabric	
	K/S	% increase in K/S	K/S	% increase in K/S
No treatment	0.73	–	1.26	–
25%	1.96	168.49	1.79	42.06
50%	2.76	278.08	2.76	119.05
75%	2.86	291.78	2.96	134.92
100%	3.17	361.24	3.01	138.89

Reproduced from El-Khatib et al. [53], with kind permission from Elsevier

3.3 Continuous Dyeing

In 1940, DuPont developed the continuous-dyeing process for dyeing military uniforms with vat dyes. Continuous dyeing is usually defined as a method in which a relatively concentrated dye solution is applied evenly across the entire width of the fabric passing through it in a continuous manner. Application of the colorant solution is usually accomplished by padding but may also be done by other means. Padding is followed by subsequent fixation of the dye by chemical or thermal means. Continuous dyeing is predominantly used for woven fabrics. However, machinery is also available for both open-width and tubular knit fabrics. During processing of knit fabric, the fabric must be subjected to low and uniform tension to maintain the desired aesthetics. Padding techniques must be altered to properly handle tubular knit goods, because edge lines can occur if good dye penetration is not obtained or if the hardness of the pad rolls is not correct. In the pad batch method, the fabric ready for dyeing is impregnated with dye liquor, excess liquor is squeezed out on a mangle, the fabric is batched onto rolls or held in boxes for 2–12 hours, and then the fabric is covered with plastic film to prevent adsorption of carbon dioxide from the air or evaporation of water. Subsequently, the fabric is washed in one of the conventional ways, depending upon the available equipment [54]. Continuous dyeing offers several advantages over batch-dyeing methods; the primary one is a reduction in the pollution load, particularly for dyeing of cotton with reactive dyes. A comparison of continuous and batch dyeing is shown in Table 10.

3.3.1 Pad Batch Dyeing

This method is most suitable for cellulosic fibers such as cotton and lyocell. In this process, the fabric is dipped in dye liquor (in the case of reactive dyes) containing an alkali. Later, the padded fabric is mangled with suitable expression and wound onto a roller without any further drying. The fabric is then covered with a polyethene sheet to avoid drying. In the industry this is usually called a batch, and the batch

Table 10 Comparison of continuous and batch-dyeing processes using the same concentration of reactive dye

Continuous dyeing	Batch dyeing
Water utilization: ~25 L for 1 kg of cotton fabric	Water utilization: ~50 L for 1 kg of cotton fabric
Steam requirement: ~2.2 kg for 1 kg of cotton fabric	Steam requirement: 5.2 kg for 1 kg of cotton fabric
Power consumption: 0.55 kW for 1 kg of cotton fabric	Power consumption: 0.60 kW for 1 kg of cotton fabric
No salt in the effluent	Large amount of salt in the effluent High TDS Need for frequent changes of the reverse osmosis membrane Need for an evaporator to treat the effluent Resulting higher energy requirement
Waste effluent discharge: Dye liquor effluent: ~50 L for 1000 kg of fabric Washing effluent: ~24,000 L for 1000 kg of fabric	Waste effluent discharge: Dye liquor effluent: ~5000 L for 1000 kg of fabric Washing effluent: ~45,000 L for 1000 kg of fabric
High fixation of dyes and reduced dye bleeding during consumer use	Low fastness properties

TDS total dissolved solids

may be allowed to rotate at 1–5 revolutions per minute (rpm) for 12–24 hours. Since it is a cold pad batch and requires no application of heat, this avoids unnecessary utilization of energy. In addition, it provides better fixation and fastness properties than the batch-dyeing process (i.e., dyeing of fabrics with soft-flow or jet dyeing machines). However, the process can be influenced by the atmospheric temperature during the fixation, and better results are achieved in summer than in winter. A typical cold pad batch–dyeing process is shown in Fig. 7.

The advantages of pad batch dyeing in comparison with soft-flow/jet dyeing are:

- Low water requirements
- Cold process
- Better fixation
- No salt requirement (i.e., for exhaustion of reactive dyes)
- Very low TDS in the dye effluent
- Good productivity

The advantages of pad batch dyeing in comparison with continuous dyeing are:

- Cold process
- Possibility of running small batches
- Economy
- Suitability for knit fabrics and elastane blended fabrics

Fig. 7 A pad batch–dyeing machine

3.3.2 Padding with a Modified Trough Shape

In a conventional padding mangle, the padding trough is bigger and consumes a huge quantity of dye liquor. Frequently, there is a large quantity of dye liquor left over after the dyeing process, creating a large quantity of effluent. Therefore, the volume of dye liquor left in the trough mainly depends on the trough design and its capacity. In the last two decades, a lot of research has been done on reducing the trough capacity. Benninger has developed U-shaped troughs with the smallest capacity (10–14 L), shown in Fig. 8a. This ensures the lowest utilization of dyestuffs and the necessary chemicals. Also, this unit offers roller adjustments, which increase the flexibility of fabric movement. Figure 8a shows a setup of padding with a cleaning spray, which removes unwanted materials (including fibers) from the surface of the fabric, resulting in good color appearance on the surface. The machine can also be used without a cleaning spray, as shown in Fig. 8b. Another development, nip dyeing, is shown in Fig. 8c; however, there are some production and quality issues associated with this method, so it is not very commonly used in the industry.

The advantages of padding with a modified trough shape are:

- Uniformity of color
- Very low pollution load
- Greater efficiency and less energy utilization

3.3.3 The Counterflow Washing Principle

The counterflow washing principle is quite common in continuous dyeing because it offers good potential efficiency and the lowest utilization of water. The principle behind this system is very simple, as water from the next washing zone can be reused, i.e., the washing water from the final zone can be reused in the preceding washing zone, as shown in Fig. 9. Usually, this process is suitable for use in continuous-dyeing or printing machines.

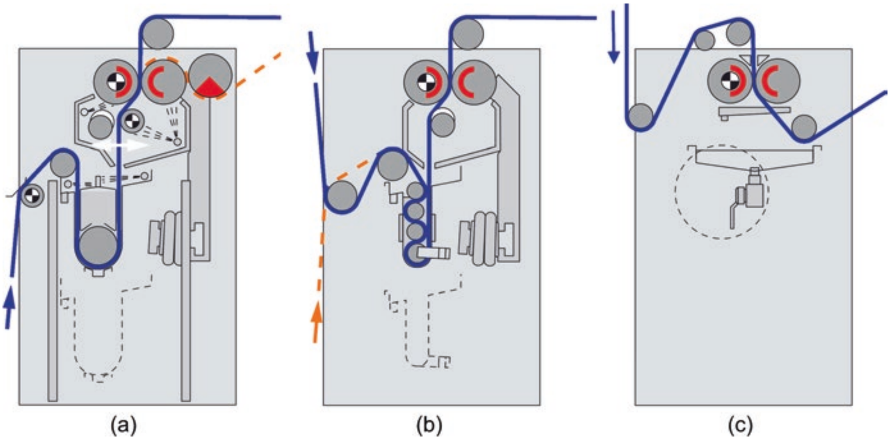


Fig. 8 (**a**, **b**) S-roller technology with quick cleaning (**a**) and without quick cleaning (**b**). (**c**) The nip dyeing method

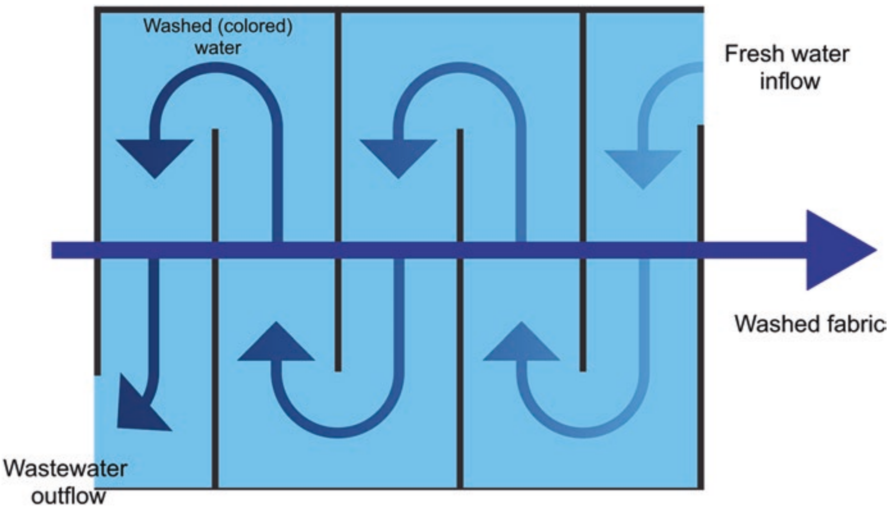


Fig. 9 Counterflow washing technology

3.4 Natural Dyes

Natural dyes are colorants obtained from various natural sources, such as vegetables, minerals, and animals. Vegetables offer plenty of color choice, so they are widely used. More than 500 colorants are obtained from vegetable sources such as the roots, leaves, bark, trunk, or fruit of plants. They have been used to color leather, textile materials, and other crafted products for more than 1000 years. Most natural dyes are cultivated (e.g., turmeric, onion leaves, marigold, annatto, and indigo). There are demands related to the quality of dyestuff used on fabric, particularly with respect to the durability of dyes and their fastness. For these reasons, synthetic dyes have been invented that fulfill the requirements in terms of fastness. On the other hand, synthetic dyes pose huge environmental threats, since colored wastewater blocks generation of dissolved oxygen, resulting in destruction of aquatic life. Moreover, the wastewater contains heavy metals, making it very hazardous and toxic. In the last two decades, there has been a considerable increase in environmental awareness in response to uncontrolled GHG emissions, ozone layer depletion, and pollution of water, air, and land. Therefore, natural dyes could provide a sustainable alternative to conventional dyes. Apart from coloration, they have other potential applications, as shown in Fig. 10. Table 11 provides a classification of natural dyes according to their chemical structure. Table 12 lists the parts of plants that different natural dyes are sourced from.

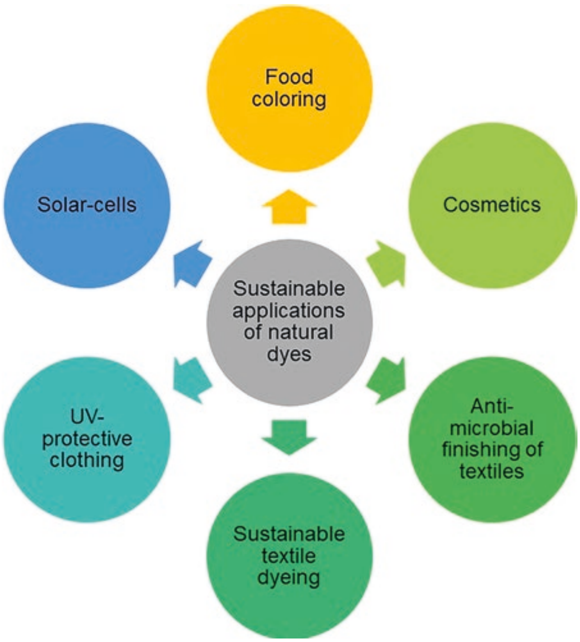


Fig. 10 Important sustainable applications of natural dyes (i.e., without addition of any chemicals)

Table 11 Classification of natural dyes according to their chemical structure

Chemical class	Natural dye source	Substrate	Color produced
Indigoids	Indigo (*Indigofera tinctoria*)	Cotton, silk, and wool	Blue
	Woad (*Isatis tinctoria*)	Cotton, silk, and wool	Blue
	Tyrian purple (*Purpura hoemastroma/Murex brandaris*)	Cotton, silk, and wool	blueish purple/ reddish purple
Anthraquinonoids	Madder (*Rubia tinctorium*)	Silk and wool	Brown, crimson, maroon, orange, pink and red[a]
	Manjith (*Rubia cordifolia*)	Silk and wool	Brown, crimson, orange, pink and red[a]
	Lac (*Laccifer lacca*)	Nylon, silk and wool	Brown, crimson, red and scarlet[a]
	Kermes (*Kermes vermilio*)	Wool	Purple and red[a]
	Cochineal (coccus cacti)	Cotton, silk and wool (printing)	Crimson, pink and scarlet[a]
Alphanaphthaquinones	Henna or lawsone (leaves of *Lawsonia inermis*)	Silk and wool	Yellow to brown
	Juglone (shells of *Juglans regia*)	Silk and wool	Brown
Flavones	Weld (*Reseda luteola*)	Cotton, silk and wool	Olive, orange and yellow
Dihydropyrans	Logwood (compeachy wood, *Haematoxylum campechianum*)	Cotton, leather, silk and wool	Black
	Brazilwood (redwood species, *Caesalpinia echinata*)	Cotton, silk and wool	Black, crimson and purple[a]
	Sappanwood (redwood species, *Caesalpinia sappan*)	Cotton, silk and wool	Black, crimson and purple[a]
Anthocyanidins	Carajurin (leaves of *Bignonia chica*)	Cotton and silk	Orange
	Awobanin (flowers of *Tsuyukusa camellia communis*)	Silk	Blue
Carotenoids	Annatto (*Bixa orellana*)	Silk and wool	Orange and yellow
	Saffron (*Crocus sativus*)	Silk and wool	Yellow

Reproduced from Patel [55], with kind permission from Elsevier
[a]Different colors involve use of different mordants

Table 12 Common natural dyestuffs obtained from different plant parts

Plant parts	Dyestuff
Roots	Beetroot, madder, onion, turmeric
Bark/branches	Khair, purple bark, redwood, sandalwood, sappanwood, shillicorai
Leaves	Cardamom, coral jasmine, eucalyptus, henna, indigo, lemongrass, tea
Flowers	Kusum, marigold
Fruit/seeds	Betel nut, latkant, myrobalan, pomegranate rind

The advantages of natural dyes are:

- Production of soft, lustrous colors
- Production of rare colors
- Extraction from renewable sources
- Nonhazardous nature
- Biodegradability
- Ease of disposal
- Lack of environmental threats
- Reduced carbon emissions

The limitations of natural dyes are:

- Lower reproducibility of colors/shades
- Less availability
- Low color yield
- Inadequate fixation
- Necessity for mordants (with the majority of natural dyes)
- Presence of heavy metals if synthetic mordants are used

3.4.1 Biomordants

A mordant is a metallic compound that helps to make a bond between a natural dye and a fabric, resulting in better fastness properties. Although some natural dyes (e.g., turmeric) do not require a mordant since they have good substantivity properties, the majority of natural dyes do not have good substantivity; thus, utilization of a mordant is important. During dyeing using natural dyes with mordants, there is the possibility that some amounts of the dye and the mordant may be unexhausted and discharged into the environment, resulting in serious environmental and health hazards [56–59]. The safest mordants to use are alum and ferrous sulfate. Examples of toxic mordants are copper and chrome-based mordants. Because of environmental considerations, it is necessary to use sustainable dyeing methods; therefore; use of biomordants could be an alternative to use of toxic metallic mordants. Because of their potential for sustainable use, biomordants have been studied extensively by various researchers. A list of these mordants is given in Table 13.

Table 13 List of plants used as sources of biomordants in natural textile dyeing

Plant	Mordant classification	Reference
Acacia catechu	Tannin mordant	[60]
Emblica officinalis		[61]
Entada spiralis		[62]
Eucalyptus		
Memecylon scutellatum		[63]
Punica granatum		[64]
Quercus infectoria		[65]
Rhus coriaria		[66]
Rumex hymenosepolus		[67]
Tamarindus indica		[68]
Enterolobium cyclocarpum		[69]
Caesalpinia coriaria		[69]
Symplococcus	Alum mordant	[70]
Aporosa		[70]
Baccaurea racemosa		[70]
Xanthophyllum lanceatum		[70]
Eurya acuminata		[43]
Pyrus pashia	Copper mordant	[46]

3.4.2 Popular Natural Dyes

Turmeric

Turmeric dye is a bright yellow powder extracted from the rhizomes of *Curcuma longa*. It is a natural substantivity dye; therefore, it can be applied to cotton and other natural fibers without the need for any other chemicals. In addition, turmeric has natural antibacterial properties and is nontoxic, eco-friendly, and biodegradable. In India, turmeric is used as a spice, food coloring, medicine, cosmetic (in face wash), etc. The active ingredients in turmeric dye are curcuminoids, which mainly consist of curcumin, followed by demethoxycurcumin and bisdemethoxycurcmin [71]. The chemical structure of a curcuminoid (1,7-bis[4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5-dione) is shown in Fig. 11. In the dyestuff library, turmeric is called C.I. Natural Yellow 3. From the chemical structure, it can be observed that turmeric contains a polyphenolic group, which is unique [72]. It is because of the presence of this special group that it shows excellent substantivity toward protein fibers [71].

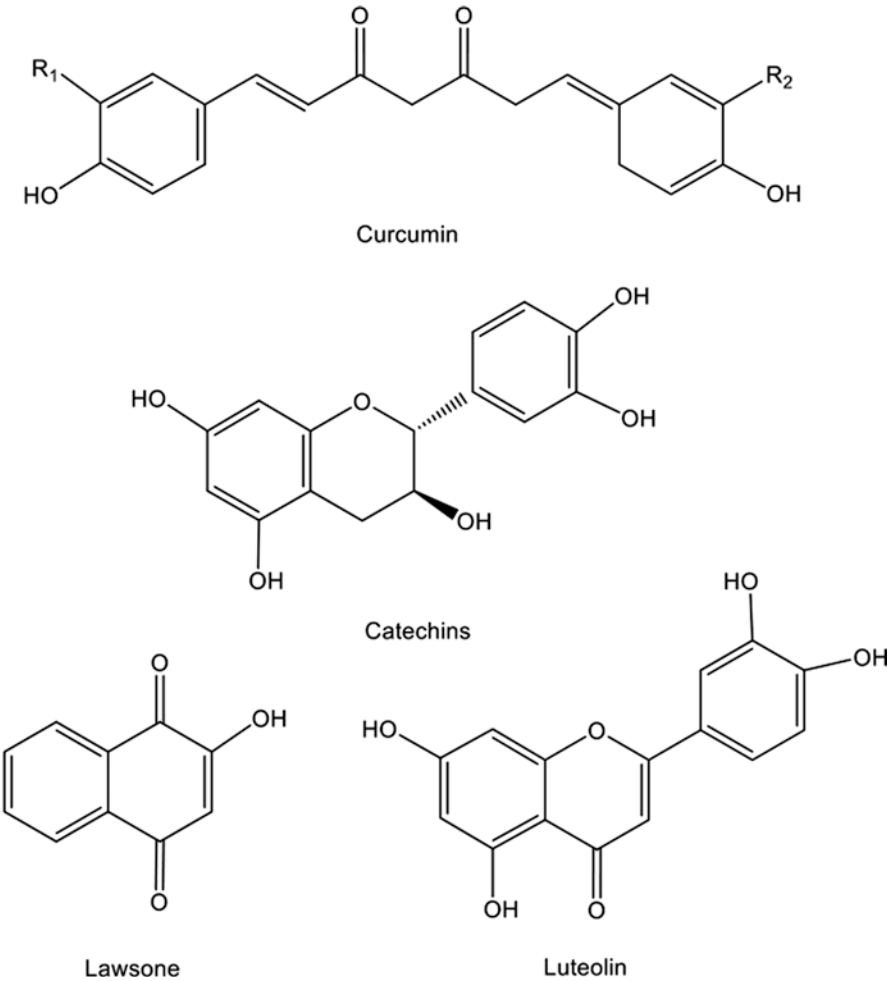


Fig. 11 Structures of curcumin, catechins, lawsone, and luteolin

Tea

Globally, tea (*Camellia sinensis* L.) is one of the most widely consumed beverages. Chemically, it contains various compounds such as caffeine, polyphenols, fluoride, amino acids, and organic acids [73]. The colors of different teas depend on the degrees of fermentation and oxidation of the polyphenols; usually, teas are divided into six colors: black, dark, green, oolong, white, and yellow. The chemical structures of catechins (natural phenol antioxidants found in plants) are shown in Fig. 11.

Henna

Henna is a tropical and subtropical plant, and it grow rapidly in such regions. In India, humans have used henna to make colorful design on the hands and feet for thousands of years. It has also been used to draw paintings on walls and to color textiles with or without the use of a mordant. Henna can be used to color nylon 6.6, silk, and wool [74–76], and it is also used as a sensor [77]. A few reports have concluded that postmordanting could help to improve the washing and light fastness of textiles. Lawsone (2-hydroxy-1,4-naphthoquinone) was identified and isolated from henna in 1920 (Fig. 11) [78].

3.5 *Plasma-Assisted Dyeing*

Globally, plasma is ubiquitous without many people realizing it. Most of the universe is filled with plasma that cannot be seen. The Sun is a burning sphere of plasma, as are other celestial objects that are seen in images of the universe (Fig. 12). Luckily, it is possible to study plasma in various forms and even use it to achieve desired effects on various substrates, including textiles. Plasma is applied to textile fabrics to modify the surface, which helps to enhance the functional properties. Cotton fabric has in-built hydrophilic properties; however, plasma treatment can help to modify the characteristics of the surface, making it hydrophobic in nature. The functional effects on plasma-treated fabric depend on the types of gases used in

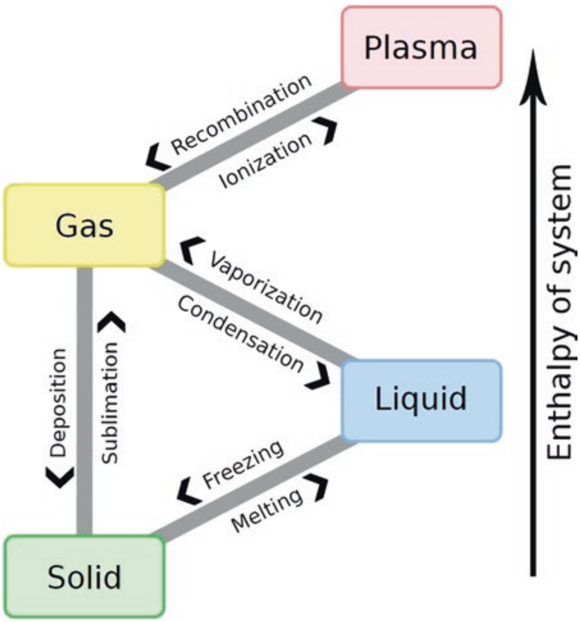


Fig. 12 Different states of matter

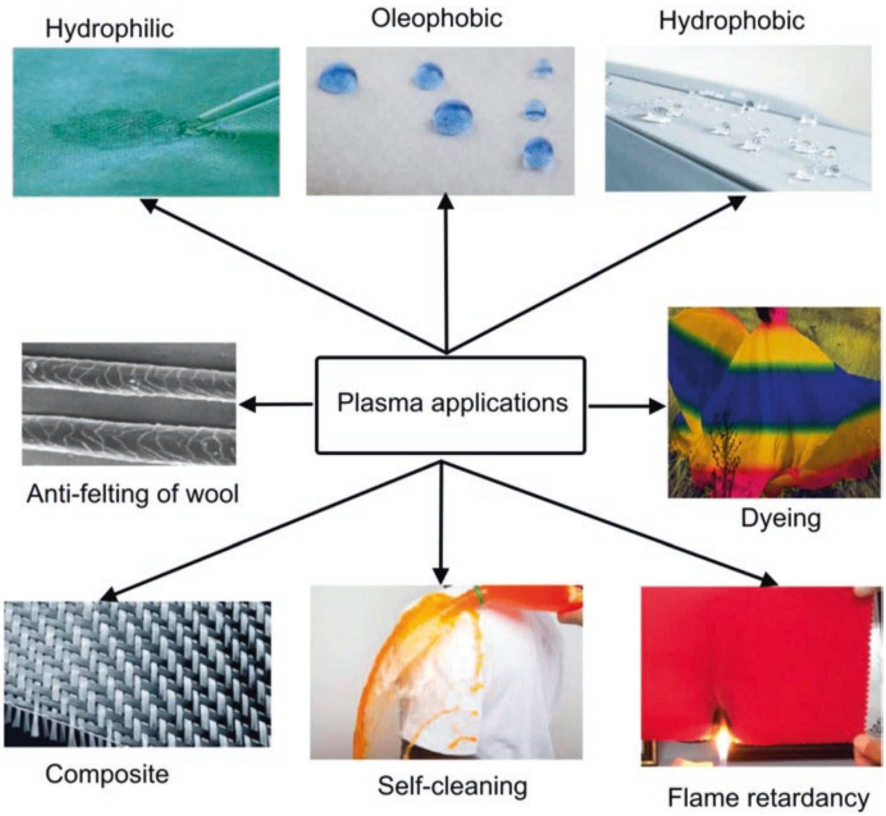


Fig. 13 Different applications of plasma in textiles

the plasma chamber. The main advantage of using this technique is that it modifies the surface properties without affecting the bulk properties. Therefore, it is used to create various functional textile materials (Fig. 13). In addition, it is an environmentally friendly process. As discussed in earlier sections, dyeing normally requires huge amounts of energy, especially during processing of synthetic fibers [79, 80].

The prominent roles involved in refinement of the ability to dye hydrophobic fibers (such as polyethylene terephthalate (PET) and polypropylene) are played by the functional groups that are introduced into the treated textile materials. Water-soluble acid dye can readily dye plasma-treated PET and polypropylene, and this plasma treatment process is considered to be eco-friendly as it has a beneficial effect in forming hydroxyl groups on the PET surface. The color of PET fabric can be deepened by deposition of antireflective coating layers on the surface of the fabric, using two different compounds of organo-silicon—hexamethyldisilazane (HMDS) and tris(trimethylsilyloxy)vinylsilane (TTMSVS)—and atmospheric-pressure plasma. On the surface of the PET, the color intensity is enhanced, and this is because of oxygen promoting decomposition of organic monomers. In addition to treating hydrophobic fibers, plasma can also be employed in treating natural fibers, such as in the dyeing of wool. The dyeing temperature can be reduced, and this is enabled by low-temperature treatment with plasma, which modifies the wool and helps to reduce fiber damage. The color fastness of wool fabric treated with low-temperature air plasma and dyed with acid dye has been assessed [81, 82].

Teli et al. [83] studied low-temperature dyeing of silk fabric, using atmospheric-pressure plasma (a helium and nitrogen gaseous mixture) with a discharge voltage of 5 kV and a frequency of 21–23 kHz. They concluded that plasma-treated samples showed greater color depth than untreated samples. In the same conditions, plasma-treated samples had 27% higher K/S values, which confirmed that the fabric had very good absorbency (Fig. 14). Plasma treatment also reduced the amount of excess dye that was discharged. Plasma treatment makes a combination of both surface and chemical modifications on polymeric materials. This treatment improves functional properties, including water absorption, resulting in better dyeability with minimal time and temperature [84]. Plasma treatment can help in coloration of polypropylene fibers with different dyes, including anionic, cationic, and disperse dyes [85]. Figure 15 shows the dyeing characteristics of polypropylene with anionic dyes. The dyeability is increased when the polypropylene is treated with N_2 under low-temperature conditions, since these treatments create O–H and C=O groups on the surface of polypropylene fabrics.

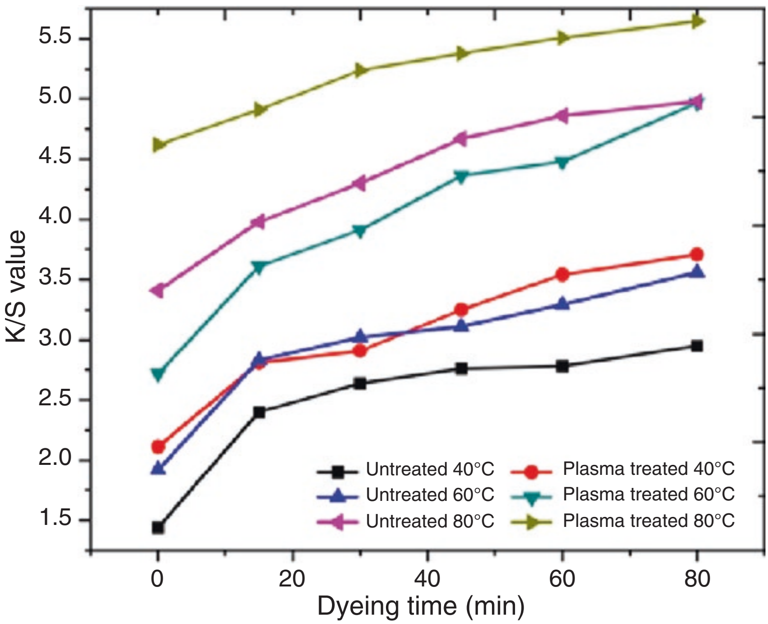


Fig. 14 K/S values of untreated and plasma-treated silk fabrics. (Reproduced from Teli et al. [83], with kind permission from Springer)

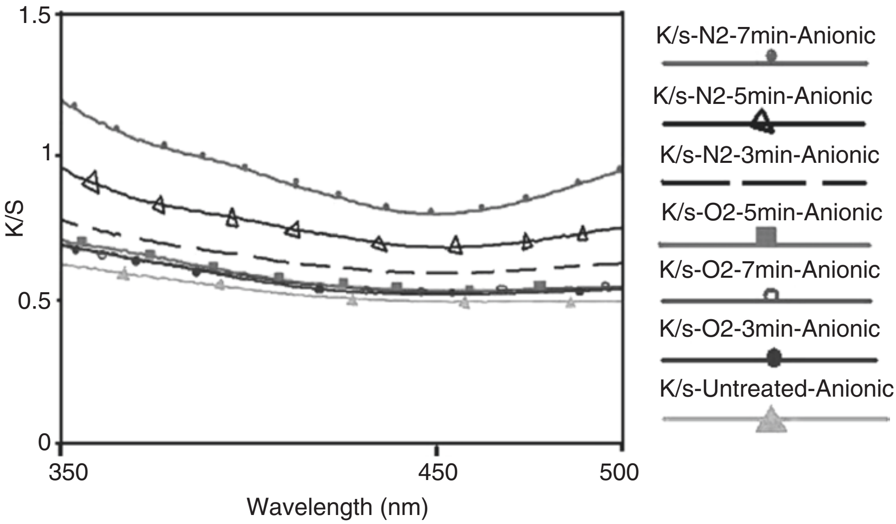


Fig. 15 Reflective spectrophotometry of anionic dyed samples. (Reproduced from Shahidi et al. [85], with kind permission from Springer)

Bulut et al. [86] studied the effects of a corona plasma process on the dyeability of woolen fabric. They concluded that the dyeability also depended on the type of dye used. In the same conditions, monosulfonated acid dyes showed lower color buildup on wool fabric than desulfonated dyes did. In some cases, plasma treatment can help to create a combination of antibacterial and antimicrobial properties when used with some natural dyes [87]. Recently, Zhou et al. [88] studied plasma treatment in a continuous process. First, plasma treatment was carried out to destroy oil and wax substrates, then the fabric was treated with an enzyme to remove other impurities. The authors concluded that this process was much better, in terms of quality and environmental concerns, than a conventional one-bath alkali process with bleaching.

3.6 Laser-Assisted Dyeing

Laser treatment is another method used for physical surface treatment, generating hydrophilic groups on hydrophobic fibers and enriching the dyeing process. Laser irradiation during surface finishing of synthetic fiber fabrics has been the subject of widespread research to explore its possibilities. To irradiate the strongly absorbent spectral region of high polymers, a specific laser type needs to be selected to produce surface restructuring without disturbing the thermal and mechanical properties of the body of the fiber. Particle adhesion, wettability, and optical properties are among the surface characteristics modified by laser treatment. PET can be reformed by a 248 nm KrF excimer laser with high-energy irradiation (above the ablation threshold) and low energy irradiation (below the ablation threshold). With high-energy treatment, the PET surface has a well-oriented intermittent arrangement of hills and grooves, or a “ripple structure.” Irradiation reduces the ripple size to the submicron level of the sample, below the ablation threshold. X-ray photoelectron spectroscopy (XPS) and contact angle studies have been used to characterize the chemical surface changes. With these notable change, the contact angle measurements are in a suitable arrangement when the surface morphology of the PET fibers changes, because of the relation of the laser energy applied. The laser energy and the mean roll-to-roll distance are directly proportional to each other. With approximately 50–200 pulses, the ripple almost approaches parallelism.

Because the segments of the fiber are ellipsoidal, no change in the PET surface is noted with more laser pulses. The dyeing behavior of laser-treated polyester was studied by Kim et al. [89], who observed that with laser treatment the ratio of carboxylic acid groups to ester groups increased, and the relative size of the amorphous regions was directly proportional to the increase in the ratio of oxygen to carbon. With use of the same amount of disperse dye, it was noted that a much deeper shade was achieved on laser-treated fabric than on untreated fabric; thus, less dye was needed to achieve the same shade on laser-treated fabric than was needed for untreated fabric. The effects on the dyeing properties of polyamide (nylon 6) fabric irradiated with a 193 nm argon fluoride excimer laser were examined. Chemical analysis revealed that carbonization had occurred in the laser-irradiated samples. The laser treatment interrupted the long-chain molecules of the nylon, increasing the number of amine end groups and changing the dyeing properties when acid and disperse dyes were used. The results showed that laser treatment could be used to improve the dyeing properties of nylon fabric with a disperse dye. To attain better bonding on laser-treated surfaces, ablation products must be detached. Better dyeability is obtained by stimulating carboxyl group formation on the surface of nylon or polyester. Research has been done on the anomalous surface structure of nylon and polyester fibers and yarns. It was observed that ultraviolet laser radiation caused less damage to nylon yarn than to polyester yarn, which absorbs more radiation and reaches a higher temperature, resulting in a pulse-like action in microscopic areas and causing brief pyrolysis that generates variations in the surface structure.

3.7 Supercritical Carbon Dioxide–Based Dyeing

In a fluid in a supercritical state, the compressed matter behaves like a gas (i.e., it fills and takes the shape of its container), not like a liquid (an incompressible fluid that occupies the bottom of its container). On the other hand, the characteristic dissolving power of a supercritical fluid (SCF) is due to the fact that it has the typical density of a liquid. This is the reason why it cannot be seen as a liquid or as a gas, as it is in a new state of matter. Figure 16 shows the ideal pressure temperature for substances of purity [90–92].

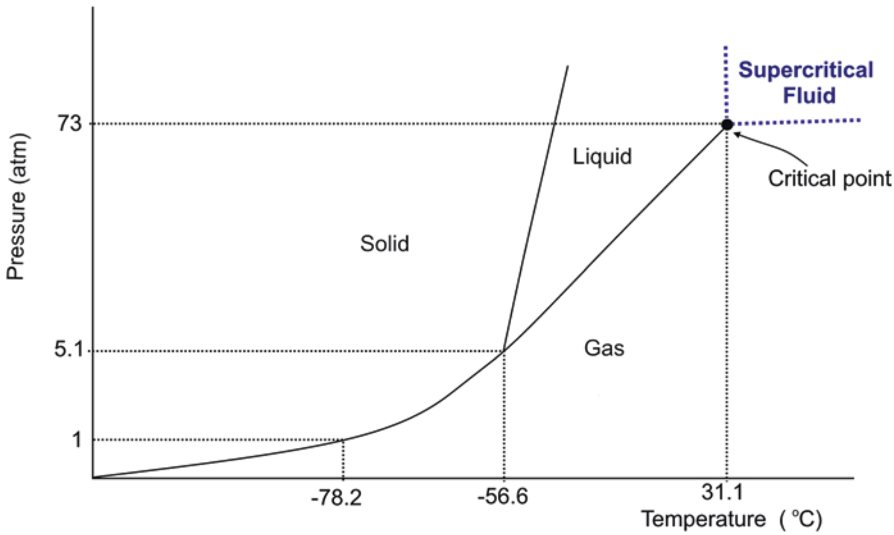


Fig. 16 Phase diagram of CO_2

Above the critical point, there exists a supercritical state of temperature and pressure. In the region of the critical state, a gas substance in a normal condition exhibits liquid-like density, and a greatly increased solvent capacity occurs because the density increases as the mean intermolecular distance decreases, maximizing the number of interactions between the solvent and the solute. Furthermore, the dielectric constant of the system is directly proportional to the pressure, thus imparting dissolving power to the system. A supercritical fluid, however, does not contain two phases (those of a gas and a liquid); it has properties that both a gas and a liquid possess. A supercritical fluid is an excellent solvent since it possesses the special combination of the viscosity of a gas and the density of a liquid. Minor changes in pressure can tune the density of a supercritical fluid effortlessly. A variety of rare chemical possibilities are offered by fluids such as supercritical xenon, ethane, and carbon dioxide in both synthetic and analytical chemistry. Although supercritical fluids possess the property of the density of a liquid, their other properties are mainly possessed by gases. The fact that supercritical fluids can dissolve nonpolar solids is appreciated in various applications ranging from classical extraction to sophisticated industrial processes. Consider the process of impregnation of pharmaceutical products into a polymer matrix. In the past decade, development of supercritical fluid technology for various textile applications has been focused on by many researchers, including extraction of impurities (scouring), bleaching, and dyeing [93–96]. Supercritical CO_2 is a sustainable solvent for chemical processing of textiles; therefore, it is an alternative to conventional solvents such as chlorofluorocarbons. It has several advantages in textile applications, particularly dyeing [91, 92]:

- It is easy to remove the excess solvent (i.e., after processing).
- It is possible to modify the density of the solvent.
- It is a nontoxic and sustainable solvent.
- It is easy to achieve supercritical conditions.
- It has no greenhouse effects.
- It is a good solvent for many nonpolar and low molecules.
- It is possible to modify the functional properties of fibers even in the dyeing process.
- It helps to reduce the glass transition temperature of PET.

For conventional dyeing of PET with disperse dyes, large quantities of dispersing agents, leveling agents, defoamers, demineralizing agents, and leveling agents are required. A comparison of supercritical CO_2 dyeing and conventional dyeing is shown in Table 14.

3.7.1 Dyeing of Textiles with Use of Supercritical CO_2

Supercritical CO_2 dyeing methods are a promising technology. A simple dyeing apparatus is shown in Fig. 17. It has temperature controllers and a heated stainless-steel container with a monometer and a strong cooler. This machine can hold capacity pressure of 350 bars under 100 °C. Disperse dyes can be fed into the machine along with supercritical CO_2 fluid prior to combination with the goods, whereas in conventional dyeing the opposite is the case. In this method, the dyes have a very good diffusion property, which results in high eveness on the surface as well as in the interior structure of the fabric or fiber material. The residual dye can be extracted prior to the dyeing process and collected for reuse.

Generally, color strength is exponentially dependent on the dye concentration; this trend is similar in the case of supercritical CO_2 dyeing methods (Fig. 18). Temperature is another parameter that plays a vital role in dyeing with respect to dye diffusion, followed by color strength. It is evident that a higher temperature can improve dye adsorption because there is greater freedom of molecule movement at a higher temperature (Fig. 19). In the supercritical CO_2 dyeing method, the other

Table 14 Comparison of conventional aqueous dyeing and supercritical CO_2 dyeing

Conventional aqueous dyeing	Supercritical CO_2 dyeing
Produces a large quantity of wastewater (containing dyes and other chemicals)	No water is used Any excess dyes are in a powder form
Chemical recycling is very difficult	The viability of recycling is high
The whole dyeing process takes ~4–6 hours	Coloration occurs rapidly (~2 hours is enough)
Dye efficiency is very poor (~60–85%)	Dye utilization is ~99%
A lot of energy is required, since it takes more time	Less energy is required
The investment is smaller, but the running cost is higher	A huge investment is required, but the process cost is low

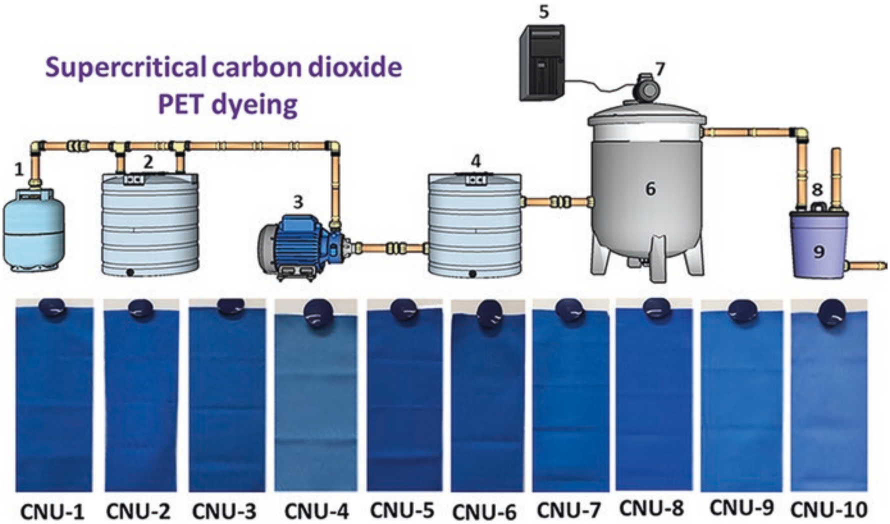


Fig. 17 Typical polyethylene terephthalate dyeing apparatus used in supercritical CO_2 conditions. (1) CO_2 cylinder, (2) circulated cooling bath, (3) CO_2 pump, (4) heating bath, (5) temperature controller, (6) stirrer, (7) dyebath, (8) pressure regulator, (9) separator. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

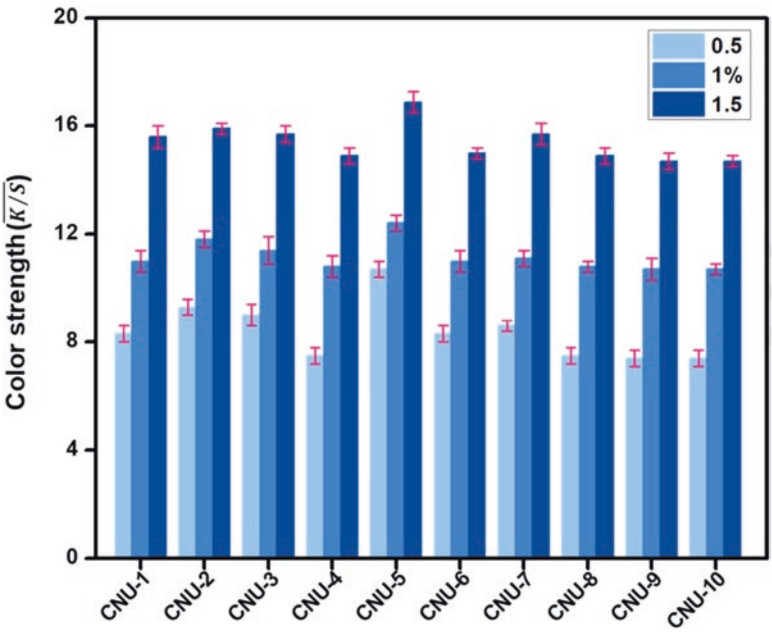


Fig. 18 Effect of dye concentration on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

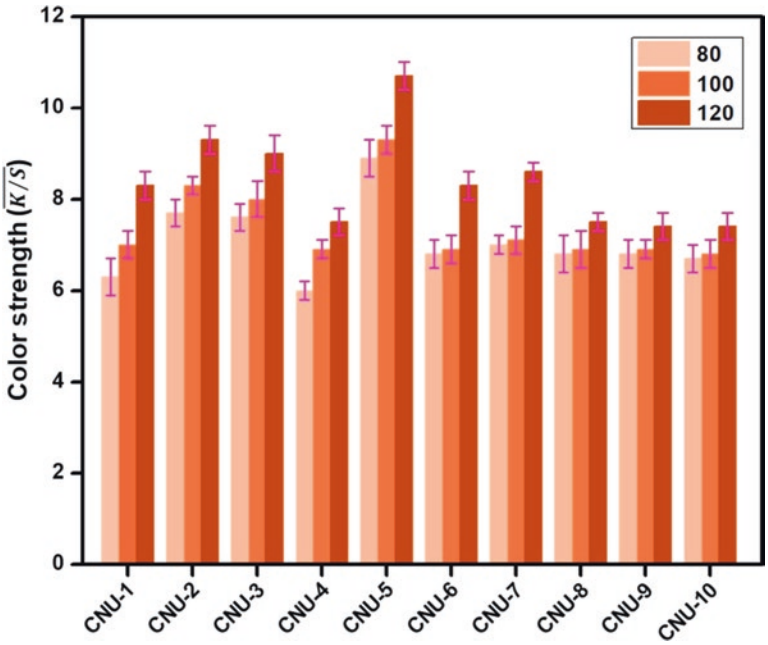


Fig. 19 Effect of process temperature (80, 100, or 120 °C) on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

important parameter is the pressure during dyeing. In this case, the color strength is increased by an increase in pressure, since the increase in pressure simply increases the density of the supercritical CO_2 fluid, resulting in better dye diffusion (Fig. 20).

3.8 Ultrasound-Assisted Wet Processing

Ultrasound was first used commercially in 1917. The frequency of ultrasonic energy is between 20 kHz and 500 MHz (Fig. 21). The oscillation frequency of sound waves in ultrasonic energy is approximately 20,000 per second, creating microbubbles and cavitation. Powerful shock waves can be caused when the bubbles break. The phenomena of bubble formation and collapse (known as cavitation) are generally responsible for most ultrasonic effects observed in solid/liquid or liquid/liquid systems. Figure 22 shows the waves produced by ultrasonic energy [7, 16]. For clean technology and sustainable dyeing, ultrasonic energy can be utilized to perform the coloration process with the least formation of pollutants. The ultrasonic energy creates cavitations in the liquid phase, modifying the surface properties of the treated materials. In addition, it changes the properties of the materials through various processes—namely, dispersion, degassing, diffusion, and intense agitation. Ultrasound causes formation, growth, and implosive collapse of small gas bubbles,

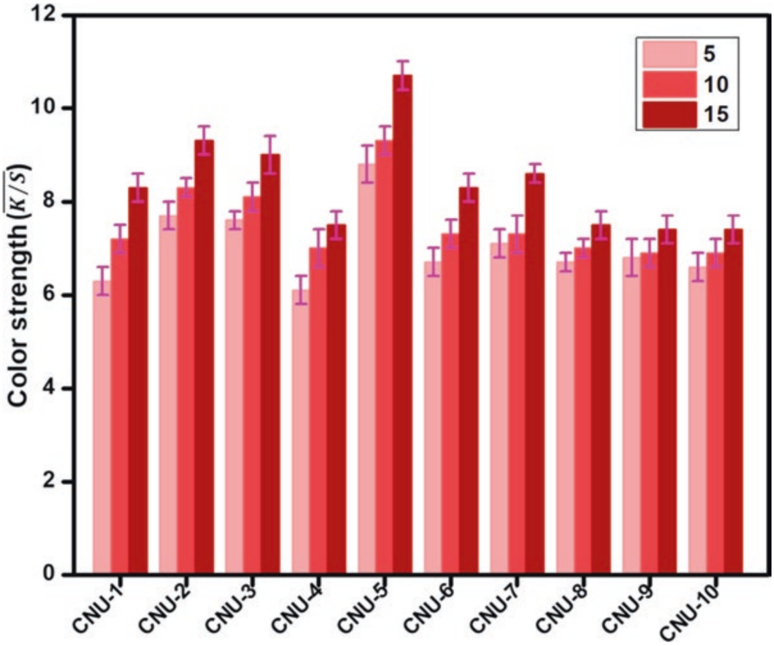


Fig. 20 Effect of process pressure (5, 10, or 15 MPa) on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

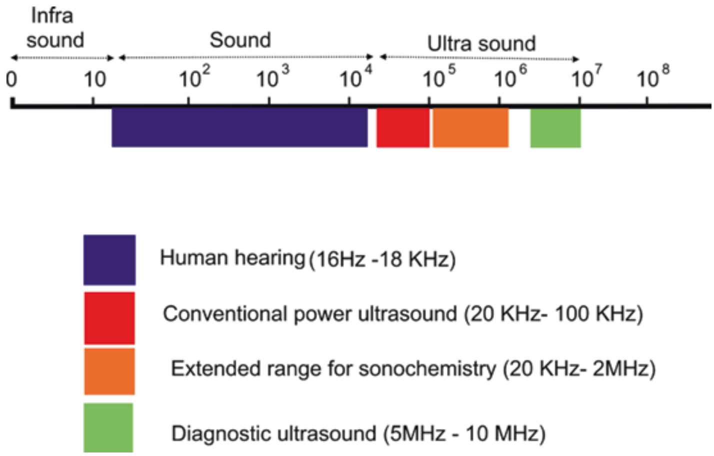


Fig. 21 Classification of sound according to its frequency

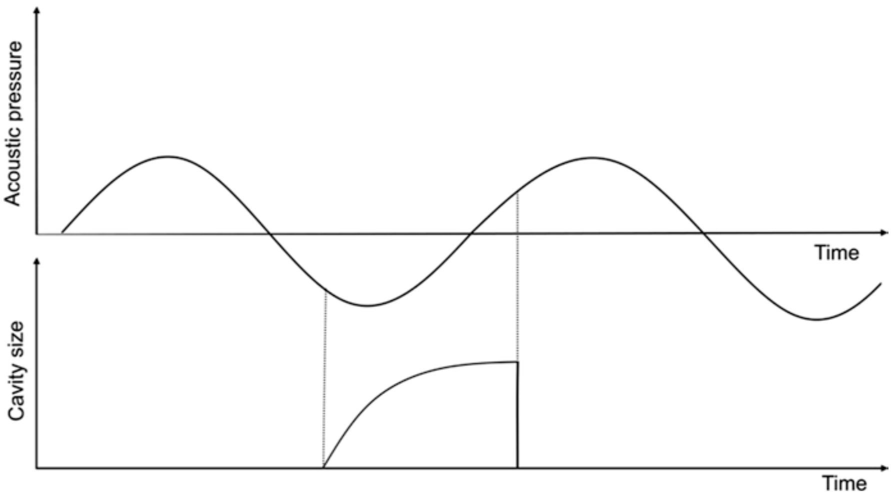


Fig. 22 Characteristics of an ultrasonic wave

inducing alternating compression and rare fraction waves. Molecular motion is enhanced by the oscillation and implosion of the cavitation bubbles, causing a stirring effect in the dyebath. Because of the solid/liquid interface that occurs when cavitation takes place, the outcome is an asymmetric implosion, yielding microstreaming on the solid surface, which significantly interrupts the diffusion interlayer and promotes bulk transport in the substrate.

The advantages of using ultrasound in dyeing are:

- It saves energy.
- It makes it possible to dye PET fibers at a lower temperature.
- It reduces the pollution load.
- It improves the processing efficiency (with better color depth).
- It causes little damage (wear and tear) to materials.
- The processing cost is low.

Various means are used to generate ultrasonic waves; in general, different configurations of whistles, hooters, and sirens—as well as piezoelectric and magnetostrictive transducers—are used. Optimal transfer of the ultrasound to the ambient air is enabled by the working mechanisms of sirens and whistles. With use of magnetostrictive and piezoelectric transducers of ultrasonic waves, only low-oscillation amplitudes are produced, causing difficulty in transferring gases (Fig. 22). The frequency and intensity of the waves, the temperature, and the vapor pressure of the liquid are factors on which the occurrence of cavitation depends.

Recently, the ultrasonic energy used in textile industry processes has been increased because of its capability to speed up chemical and physical responses through cavitation. Uniform mass transfer (which is the foremost objective of the textile-dyeing process) can be obtained by use of ultrasonic energy and is achieved

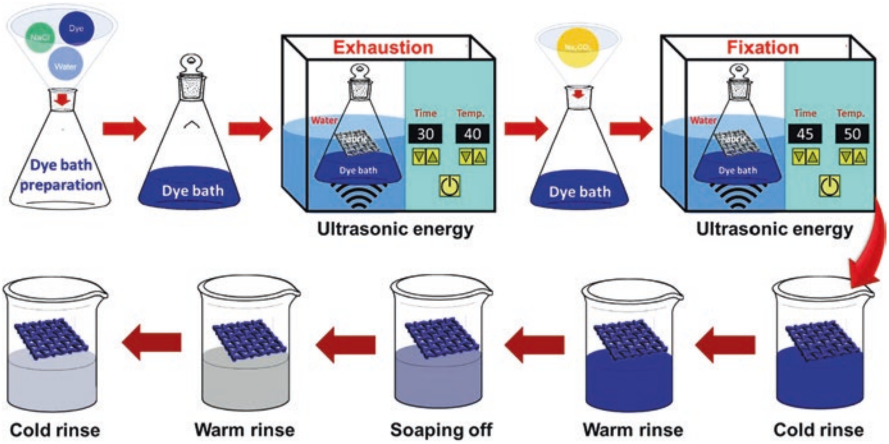


Fig. 23 The ultrasound-assisted exhaust dyeing process. (Reproduced from Babar et al. [98], with kind permission from Elsevier)

through high temperature, an extended processing time, and/or greater consumption of auxiliary chemicals. Additionally, use of ultrasonic energy in textile dyeing is energy saving and eco-friendly, as noted by numerous works describing its success. Figure 23 provides a simple description of ultrasound-assisted textile-dyeing techniques. In the last two decades, environmental awareness has increased, as shown by the research output focusing on eco-friendly technologies. Ultrasound-assisted dyeing is one of them. Its use has been studied extensively, using various fibers such as cotton [99], lyocell [100], cellulose acetate [101], wool [102], nylon [103, 104], and acrylic [105].

3.8.1 The Glass Transition Temperature

Probable dilation of an amorphous region due to the mechanical effects of ultrasound in textile wet processing has been proposed, i.e., the glass transition temperature in synthetic fibers. The effectiveness is decreased in polyester in particular, proving the viability of dyeing at a lower temperature. For penetration into the amorphous regions of synthetic fibers, prior to dyeing, the fibers must be heated above the effective glass transition temperature. When commercial dyeing is considered, plasticizers are frequently added to lower the glass transition temperature. Ultrasound allows fibers to be dyed at a low temperature, rather than requiring lowering of the glass transition temperature, as predicted. In a wet textile process, diffusion and convection in the interyarn and intrayarn pores of the fabric lead the mechanisms of mass transfer (Fig. 23). The major steps in mass transfer in textile materials are:

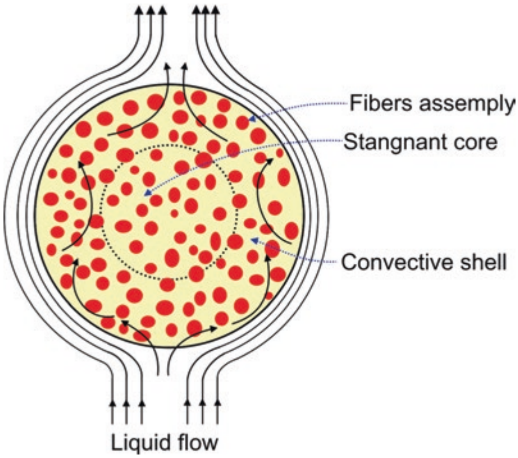


Fig. 24 Liquid flow in the yarn structure

- Mass transfer from intrayarn pores to interyarn pores (Fig. 24)
- Mass transfer from interyarn pores to the liquid boundary layer between the textile and the bulk liquid
- Mass transfer from the liquid boundary layer to the bulk liquid

Jato et al. [104] studied ultrasonic dyeing of nylon nanofibers. In this work, they applied two different disperse dyes. During the dyeing, different conditions were used: different temperatures, different times, and different concentrations. In addition, the dyeing was carried out at an output power of 180 W and at a 38 kHz frequency. The color strength was increased with an increase in the temperature up to 80 °C; thereafter, it reduced with respect to use of an ultrasonic bath. On the other hand, it increased with a conventional batch-dyeing process (Fig. 25). Figure 26 shows time-dependent ultrasonic dyeing; the color strength is increased with an increase in time up to 30 min; thereafter, there is no significant improvement in the ultrasonic dyeing. In the same time, the conventional dyeing method results in 40% less color strength. From Fig. 27 it can be seen that there are differences in K/S values with respect to conventional and ultrasonic methods [106]. In this case, K/S values are higher with the ultrasound-assisted dyeing method.

3.9 Microwave-Assisted Dyeing

In the electromagnetic spectrum, between radio waves and infrared radiation, the wavelengths between 1 m and 1 mm (analogous to a frequency from 300 MHz up to 300 GHz) are occupied by microwave frequencies (Fig. 28). As a form of electric heating, microwave heating is assumed to be generation of heat in conductive materials with low electricity by the action of a high-frequency electric field.

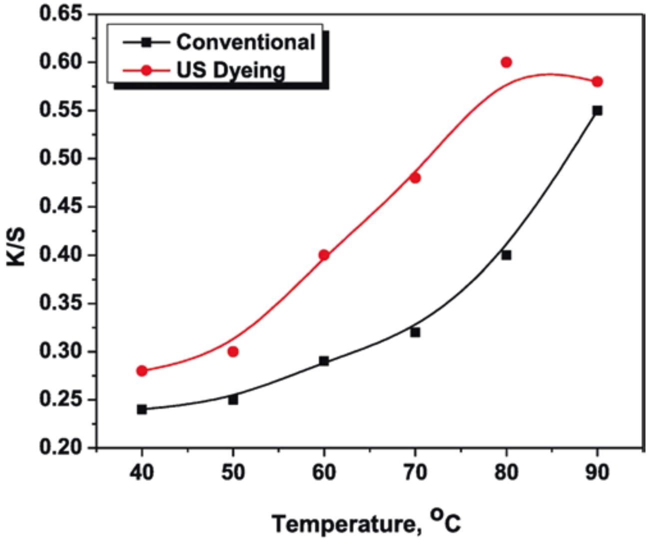


Fig. 25 Effect of dyeing temperature on coloration of nylon 6 nanofibers. (Reproduced from Jatoi et al. [104], with kind permission from Elsevier)

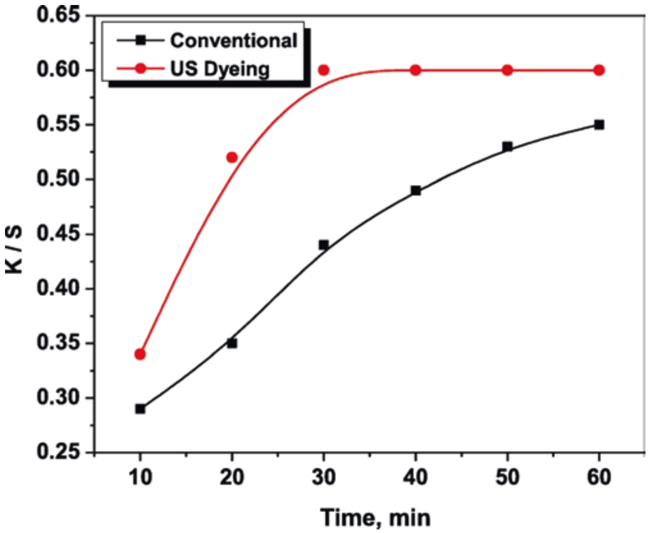
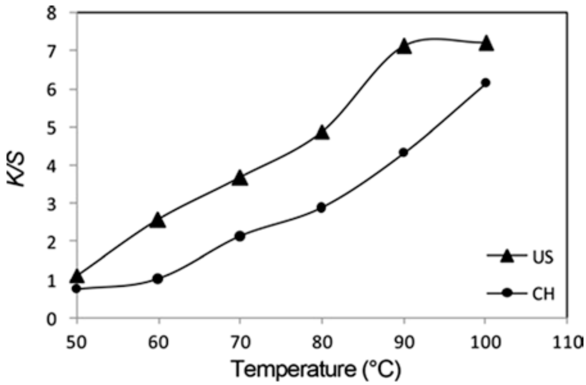


Fig. 26 Effect of dyeing time on coloration of nylon 6 nanofibers. (Reproduced from Jatoi et al. [104], with kind permission from Elsevier)

Because of its similar physical properties, microwave heating must be observed as a form of dielectric heating. In response to high-frequency field polarity changes, dipole molecules experience oscillations with the alternating field influence.

In comparison with chemical bond energy, microwave photon energy is low; thus, the molecular structure of a compound is not directly affected by microwaves

Fig. 27 K/S value versus dyeing temperature used for coloration of polyamide fabric. (Reproduced from Peng et al. [106], with kind permission from Springer)



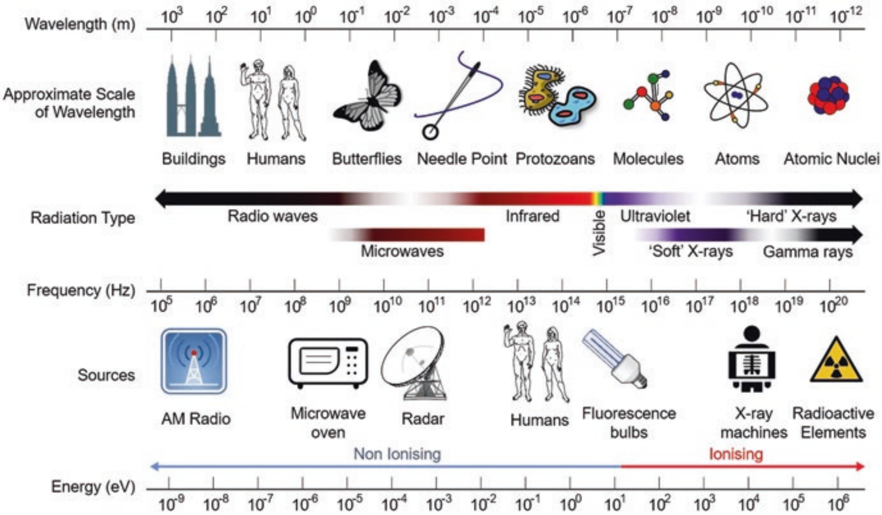


Fig. 28 The electromagnetic spectrum

and its electronic configuration is unaltered. Microwave heating is an alternative to conventional heating, producing fast, effective, and uniform heating due to penetration of material particles by microwave energy. Microwave energy is directly and internally absorbed by materials in volumetric heating and converted into heat, leading to rapid, controlled, selective, and uniform heating. In addition to this, diffusion of dye molecules is enhanced by microwave heating, increasing the rate of dye fixation in polymeric textiles. Dielectric and thermal properties are the properties considered in microwave dyeing. The dielectric property is the intrinsic electric property that causes dyeing through dipolar rotation of the dye and the influence of the microwave field on dipoles. There are two polar components in an aqueous dyeing solution, and the high-frequency microwave field oscillates at 2450 MHz, stimulating the vibrational energy in the molecules of water and dye. This mechanism of

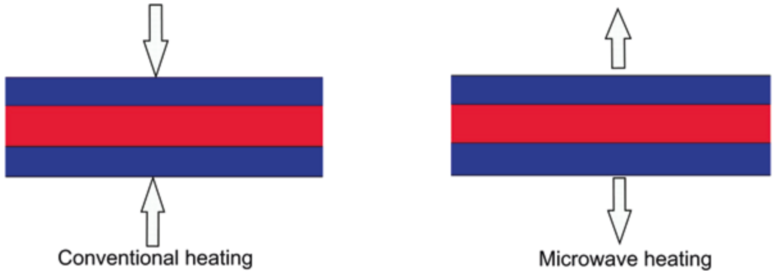


Fig. 29 Microwave (volumetric) heating versus conventional (surface) heating

heating results in ionic conduction, a type of resistance heating. The resultant collision of dye molecules and fiber molecules is subject to acceleration of ions through the dye solution. The penetration of the dye into the fabric and the depth of the penetration are enhanced by the mordant, making this technique both environmentally benign and superior to conventional dyeing techniques. The microwaves accelerate a huge number of chemical processes. Reactions that run for a long time at high temperatures under conventional conditions are mostly achieved more quickly with less energy input in microwave-assisted dyeing, as microwave heating is volumetric heating (which is fast), while conventional heating is surface heating (which is slow) (Fig. 29).

4 Conclusion and Future Scope

In addition to dyes, numerous other chemicals are involved in the process of dyeing. Some of the dyeing solution ends up in the fabric, but the rest is left over in the dyebath. A dyebath containing these chemicals may produce a high BOD, making treatment of this effluent difficult. Hence, it is essential to recover and reuse these chemicals in order to reduce the effluent load. If the use of chemicals cannot be reduced, there is a possibility to recover some of them. An exhausted dyebath contains a huge quantity of remaining auxiliary chemicals. In some circumstances, recovery of sodium hydroxide, synthetic size, or heat is possible. There is a great demand for dyeing and finishing of textile fibers/fabrics using eco-friendly methodology. Thus, it is worthwhile to create innovative production techniques. In this regard, various benefits have been shown with use of plasma technology, laser treatment, and supercritical fluids that are environmentally friendly, enabling the surface properties of inert materials to be modified with little effort. Further, it is anticipated that in the coming years, the environmental problems caused by dyeing and finishing plants in the textile industry will be resolved by use of physical treatment processes; hence, it is necessary to introduce these on a huge scale. Biopreparation with enzymes can be used without degrading cellulose and causing losses in its weight or strength, as can happen when either scouring or cellulosic treatment is used.

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Ozone: An Alternative Oxidant for Textile Applications

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Abstract Ozone is a triatomic form of oxygen (O_3) with an outstanding oxidation potential. Ozone is generated via ozone generators; two main types of ozone generators are corona discharge units and ultraviolet lamps. Either air or oxygen may be used as the feeding gas, but an oxygen generator is required if the feeding gas is air. The ozone concentration in the outlet gas mixture of an ozone generator increases as the purity of oxygen gas inlet increases. The high oxidation potential of ozone gas has encouraged research studies on the utilization of ozone for textile applications. Oxidative agents are used in desizing, bleaching, dyeing, clearing, surface modification, and wastewater treatments for applications in textile sector. The main oxidative agent used in the textile sector is hydrogen peroxide. Use of an activator, generally caustic soda, and high temperatures are required for hydrogen peroxide bleaching. On the other hand, ozone is usually applied at room temperature because of its decreasing solubility at high temperatures, and ozone is active in the whole pH range compensating the requirement of pH adjustment chemicals. Of course, the pH of the aqueous solution affects the reactions of ozone, but ozone is capable of giving oxidation reactions in neutral, acidic, or alkaline solutions. In textile industry, ozone is utilized in various processes such as: denim applications, cotton pretreatments, dyeing and finishing, polyester dyeing and clearing, treatment of various textile fibers (wool, polylactic acid, etc.), and textile wastewater and color removal treatment. In this chapter, potential uses of ozone as an alternative oxidant for textile applications are reviewed in detail. It is important to point out that ozone utilization may result in chemical substitution, waste reduction, and energy conversation in textile processes, leading to more sustainable world for future generations.

Keywords Ozone · Ozonation · Textile · Desizing · Bleaching · Clearing · Wastewater treatment · Surface modification · Wet processing

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1 Introduction

The world population will increase around 35% by 2050. The increasing population and economic growth are believed to create an increase in the consumption of textiles. The increase in textile consumption will possibly increase the use of water and energy, as well as the chemicals and total discharged wastes in the textile industry [1]. The textile sector utilizes huge amounts of electricity, fuel, and water with corresponding greenhouse gas emissions (GHGs). Textile manufacturing, especially wet processes, uses a large quantity of water, and produces a significant volume of contaminated effluents. Saving water and minimizing water pollution have become a key strategy to move textile industry toward more environmentally friendly processes [1–4]. Sustainability is usually divided into three categories: social, economic, and environmental. Compliance with all three categories is essential for the full implementation of sustainability. Ozonation is a sustainable process that saves water and energy. At the same time, ozonation process does not require chemicals or uses less chemicals at low temperatures, does not produce waste, and reuses water [5–7].

This chapter gives detailed information about ozone as an alternative oxidant for textile applications. First, ozone and its advantages are introduced. Then, the principles of ozone production and measurements of ozone are discussed. Finally, different usage and application areas of ozone technology in the textile industry such as in denim applications, cotton pretreatment, dyeing and finishing, polyester dyeing and clearing, treatment of various textile fibers (wool, polylactic acid, etc.), and textile wastewater and color removal treatment are reviewed. This chapter aims to give a detailed perspective on the use of ozone in the textile sector.

2 Ozone

Ozone, composed of three atoms of oxygen, can be utilized to oxidize many organic and inorganic impurities. It is an irritating pale blue gas, is reactive, is heavier than air, and cannot be stored or transported. For this reason, it has to be generated "in situ." The German chemist C. F. Schönbein discovered ozone and named it so based on the Greek word "ozein" (to smell). The first large-scale ozone application was for water purification. It is known that ozone is thermodynamically unstable and spontaneously reverts to oxygen; the structure of ozone molecule [3, 8, 9].

$$3O_2 \leftrightarrow 2O_3 \quad \Delta H_{1\ \mathrm{atm}} \qquad 1\ \mathrm{atm} = 284.5\ \mathrm{kJ.mol^{-1}}$$

Structure of ozone molecule [3, 8, 9]

Table 1 Physical properties of ozone gas [8, 9]

Properties of ozone gas	
Chemical formula	O_3
Molecular weight (g/mol)	47.998
Appearance and odor	Colorless and odorous
CAS number	10028-15-6
Density, gas (0 °C, 101.3 kPa)	2.144 kg/m^3
Water solubility	4.9 ml/l (0 °C)
Melting temperature (101.3 kPa)	−192.5 °C
Boiling temperature (101.3 kPa)	−111.9 °C
Surface tension (−183 °C)	3.84×10^{-2} N/mm
Viscosity (−183 °C)	1.57×10^{-3} Pa.s
Heat capacity (liquid) (−183 to −145 °C)	1884 J/kg.K
Heat capacity (gas) (25 °C)	818 J/kg.K
Evaporation temperature	15.2 kJ/mol
EU hazard class	Oxidizing agent (O)

Ozone is not a stable substance and breaks down into oxygen, with different half-lives basically depending on the temperature. Owing to its relatively short half-life, ozone should be generated onsite and it could not be stored like other chemicals. The physical properties of ozone are shown in Table 1 [8].

Ozone was first suggested as a bleaching agent for wood due to environmental factors. Therefore, studies on the utilization of ozone as a bleaching agent in the manufacture of wood pulps have been intensified. Ozone is a highly competitive bleaching chemical that, in comparison with the equal bleaching power, is typically 1.2–1.5 times less costly than chlorine dioxide from an economic point of view [10]. Ozone has a higher oxidation potential than many known chemicals. The oxidation potentials of the commonly used hydrogen peroxide, ozone, fluorine, and hydroxyl radicals are 1.77 eV, 2.07 eV, 3.06 eV, and 2.80 eV, respectively. Ozone, which has a high oxidation potential, is also an effective disinfectant and plays an important role in the treatment of drinking water. Without leaving residues, ozone is converted into its raw material, oxygen [11].

2.1 Advantages of Ozone

- Ozone is a very strong oxidant and is used as an important disinfectant in the treatment of water and air.
- It does not leave any organic waste after water treatment.
- Ozonation can be carried out in any media and does not involve any other chemicals.
- Ozone eliminates different inorganic, organic, and microbiological problems.

- Ozone eliminates taste and odor problems in water and air.
- It is an environmentally friendly molecule and is not an air pollutant.

3 Principles of Ozone Production

Ozone must be produced in situ because it cannot be stored and transported and is very reactive. There are two basic methods for generating ozone artificially:

1. Corona discharge
2. Ultraviolet radiation

All ozone-generating methods depend on the applied energy. The bonds holding the oxygen atoms in a molecular form break with the energy, which allows them to dissociate and then reform as ozone.

1. Corona Discharge

The corona discharge method is fully related to the electrical discharges which are supplied by an ozone generator. These electrical discharges, known as corona discharges, pass through air gaps. At that time, the oxygen molecules (O_2) are broken down by a high voltage (electrical discharge). The "O" atoms formed bind with O_2 molecules, resulting in the formation of a three-atom oxygen molecule (O_3). This method is commonly used in laboratories and industrial studies.

Corona discharge cell configuration [16]

2. Ultraviolet Radiation

Energy is needed to generate ozone from oxygen. When the oxygen molecule is exposed to light, it decomposes due to the energy of light. This is related to the wavelength of the absorbed light. The decomposed oxygen reacts with other oxygen molecules. For breaking down the oxygen molecule, wavelengths of less than 200 nm are needed. This is because like oxygen, ozone absorbs and damages light. Therefore, the ideal wavelength is 185 nm. These methods are not suitable for water treatment, but it can be used for air treatment [12–16].

4 Measurements of Ozone

Measuring ozone concentration is important for the continuity of process parameters and for the determination of operating conditions, and environmental and cost analyses. The unstable structure of ozone, its rapid solubility in water, and its reaction with wastes make it difficult to be analyzed. Ozone can be analyzed by titrimetry (iodometric), direct and colorimetric spectrometries, amperometry, oxidation-reduction potential (ORP), and chemiluminescent methods [3].

5 Ozone Usage in Industrial Applications

Ozone can be used in two phases: gaseous and aqueous. Especially using ozone in aqueous phase is better and more practical than that in gaseous phase because when ozone gas is used with water (aqueous phase), it ensures the recirculation of water, thereby reducing the usage of water which provides a significant increase in water quality and savings. In addition, the half-life of ozone in the gaseous phase is more than the half-life in the aqueous phase, so it decomposes more slowly [10, 15].

Solubility of ozone is related to pressure, temperature, and ionic strength. The movement of ozone to the solution media is more efficient as being bubbles of ozone gas. The ozone generator contractors, reactors, and injectors assist the ozone gas to form into small bubbles [13]. Ozone decomposition in pure water is very slow at room temperature, but ozone molecules decompose in the presence of catalysts as well as organic contents, hydroxyl ions, trace metals, hydrogen peroxide, heat, and UV light [16].

Ozone is a preferred gas for use in industry due to its many positive properties: versatility of ozone gas; its replacement by traditional applications; savings in operational costs; decrease in working time, energy, and water usage; and increase in reliability. Ozone can generally be used for hygienic purposes, for cleaning, for processing and storing food, in animal husbandry, in agriculture, for disinfection, treatment, and protection processes, and in textile industry [11, 17, 18].

In this chapter, the applications of ozone gas in the textile sector are reviewed. The use of ozone gas in the aqueous phase is very important for textile applications where wet processes (washing, dyeing, rinsing, desizing, scouring, bleaching, etc.) are common. Ozone in aqueous phase as a method of operation is more suitable for wet processing machines. Ozone in gaseous phase necessitates special airproof machinery for reasons of occupational health and safety and comfort.

Many parameters affect the ozone gas concentration and dispersion, such as turbulence, temperature, pressure, and solution composition (pH, ionic strength, and reactive substances). Also, the type of conductor is a parameter that affects the physical mass transfer rate of ozone into water [3].

5.1 Ozone Applications in the Textile Industry

Ozone is a gas used in many textile processes, especially wet processes. Ozone gas utilization in textile industry can be grouped into five main sections:

- Denim applications
- Cotton pretreatments, dyeing, and finishing
- Polyester dyeing and clearing
- Treatment of various textile fibers (wool, polylactic acid, etc.)
- Textile wastewater and color removal treatment

5.1.1 Denim Applications by Ozone

Denim finds its usage as a timeless, ageless, and sexless product in our life. Denim products are different from classic apparel production because cutting and sewing processes are not the final stage of denim jean production. The subsequent different washing types or finishing stages have constituted into a major industry itself. It is chiefly designed to bring a specific, unique, and aesthetic finish to the final garment. In order to give the desired effect on the denim, a number of mechanical and chemical processes are applied to the fabrics. In the production line, washing and drying are mechanical processes, whereas bleaching of denim by sodium hypochlorite is a chemical process. The washing of a denim garment brings with it major added values; however, it also possesses the potential to result in environmental or human health damage. Bleaching denim with sodium hypochlorite causes a huge problem of AOX (adsorbable halogenated organic compounds) [6, 19–22]. Approximately 70 L of water is used for one denim. Annually, denim production is to the tune of 5 billion pieces in the world; 350 million m^3 of water is used in jean production as shown in Table 2. Wastewater formation after denim production and stone washing methods are harmful to the environment and human health [19, 21].

Denim industry was the first one to use ozone in the textile garment manufacturing sector. The use of ozone in denim finishing leads to a reduced environmental impact. Ozone is capable of breaking down the dyestuffs, including indigo, into smaller and colorless fragments. This oxidizing capacity of ozone is utilized for fading denim garments to substitute the use of enzymes, pumice stones, or hypochlorite bleaching processes [19, 20, 22, 23]. Studies have been conducted on the use of ozone gas for bleaching purposes in denim fabrics, and it has been concluded that the bleaching performance of the ozone gas in fabrics at 60% wet pickup is better [20, 23, 24]. Besen and Balcı studied fading of indigo-dyed yarn in hank form before weaving and garment processes. They concluded that different fading effects could be achieved by ozonation of dyed yarns in the hank form [25]. He et al. also studied ozone on three typical denim yarns (cotton, lyocell, and polyethylene terephthalate (PET)) for fading of color. They concluded that PET is not faded by ozone; however, ozone can be used to fade the dyed cotton or other cellulosic yarns [26]. Ozone is successfully used to recover the backstaining of indigo garments. Other oxidizing agents such as potassium permanganate and benzoyl peroxide are available for denim garment processing; however, the most important advantage of ozone is its ecofriendly nature, and it is a good alternative to other techniques. Isatin and anthranilic acid may form during oxidation of indigo and these products may

Table 2 The total water consumption of jean production [19]

Water consumption in jean production	
Average water consumption per jean produced	70 L
Estimated annual production of jeans	5000 million pairs
Total water consumption of jean production	350 million m^3

cause yellowing. When the fading process is applied much more, it needs to be rinsed with water to remove yellowing [3, 19, 27, 28].

Some studies have shown that ultrasound and nano-bubble methods, which when combined with ozone, increase the effectiveness of ozone. Ultrasonic cavitations improve the penetration of ozone into the fabric and then ozone decomposes indigo; therefore, ozone is much more effective when used along with ultrasonic energy [3]. One of the innovative processes that use ozone gas in the denim sector is nano-bubble technology. Ozone gas can be injected into the system instead of air to obtain nano-bubbles. By means of nano-bubble, the efficiency of ozone gas in the liquid surplus will be increased and the washing effects desired to be shown to customers in a shorter, more efficient, and environmentally friendly way will be obtained [19, 29].

One of the chief troubles in the denim production is indigo backstaining. Backstaining decreases the white–blue contrast and results in an evenly distributed bluish color all over the garment comprising local abraded areas, pockets, and labels. Experts have tried different methods of washing to prevent backstaining, such as higher liquor ratios, special rinsing agents such as intermediate rinsing agents, dispersing agents, and soaping [19, 30]. Morali et al. (2016) applied ozonation and ozonation + hydrogen peroxide as pre- and posttreatments to wastewater in a denim production facility. Color, COD, BOD values of samples were tested before and after biological application. High color and COD removal rates were achieved by ozonation. However, as ozone dose and time increased, the color and COD removal values did not increase contrary to expectations [31].

5.1.2 Cotton Pretreatment, Dyeing, and Finishing by Ozone

Cotton is the most preferred fiber in the textile industry due to its being comfortable, healthy, and easily accessible. For this reason, all new technologies are generally applied to cotton products. But cotton needs pretreatment processes (bleaching, scouring, desizing, etc.) before dyeing and finishing process due to its natural structure (oils, wax, mote). The literature contains many ozone studies that have investigated the effects of many parameters such as ozone concentration, application time, and ozone utilization alone or in combination with other technologies (ultrasound, UV, plasma, etc.) [32–47].

The purpose of the study by Perincek et al. (2009) was to explore the effects of ultrasound, ozonation, and ultraviolet, known as new advanced processes, on cotton woven fabric. Cotton fabrics were bleached by the combination of ozone with ultrasound and ultraviolet. At the end of the experiments, ultrasonic treatment followed by ozonation resulted in sufficient whiteness levels and hydrophilicity values of the fabric. According to the results, advanced processes could be utilized in pretreatment of cotton fabrics. At the same time, applications of new processes support savings of thermal energy, water, and chemicals [32]. Eren and Öztürk (2011) studied the ozonation of cotton fabrics. Bleaching results are successful owing to high oxidation potential of ozone, and the whiteness degree is at an acceptable level. The starch size removal and the water absorbency of the greige cotton samples were enhanced by ozonation. Ozonation was not enough for removing the motes [33]. Gashti et al. (2013) did a research on surface oxidation of cellulose by ozone gas and introduced ozone gas before fluoromonomer grafting [34]. Results displayed that the ozone gas pretreatment oxidized the surface of the cellulose fibers by enhancing the reactivity of the substrate toward the fluoromonomer with successful grafting of the fluoromonomer on the cotton fiber fabrics. It was further reported that ozone and fluorocarbon treatment combination on cotton fiber could enhance the contact angle because of higher efficiency of the water-repellent polymer on the surface of the ozone-gas-treated cellulose fibers [34].

Perincek et al. (2013) used ozone alone and in combination with hydrogen peroxide in the bleaching of linen fabrics. In this study, Box–Behnken experimental design model was used. In the bleaching process, first ozone was applied at different time periods and then hydrogen peroxide was used to bleach the fabrics under different conditions. As a result, three optimum prescriptions were obtained about using the combination of hydrogen peroxide and ozone, and it was reported that after bleaching with peroxide for 15 min, significant results were obtained and after application, time and chemical usage were saved [35]. Eren et al. (2014) explored the combination of ozone gas and ultrasonic methods for bleaching cotton fabrics. The ultrasonic method was used both in the homogenizer (UH) and in the ultrasonic bath (UB). Whiteness value increased as ozonation time (90 min) increased only in ozonation processes. There was also an increase in whiteness and a decrease in yellowness in ozone applications with a homogenizer (UH). It was reported that ultrasonic bath had no significant effect on whiteness. None of the processes carried out with ozone had a negative effect on the strength of cotton fabrics such as conventional methods. FTIR results showed no significant effect on surface morphology by different ozonation processes, and cotton fiber surface was smooth after the treatments. COD values of bath water after ozonation were found to be very low compared to hydrogen peroxide. Consequently, the combination of ozonation with the UH process (Ozonation + UH), applied at 30 °C for 30 min, could be utilized effectively for cotton bleaching instead of the conventional hydrogen peroxide bleaching [36].

Benli and Bahtiyari (2015) applied the conventional and ecofriendly (ozone–ultrasound) methods to cotton fabrics. Conventional methods such as desizing, scouring, and bleaching were performed on greige fabrics. Environmentally friendly methods such as ozonation and ultrasound processes also were applied to the fabrics step by step. It was observed that desizing, hydrophilicity, and whiteness values obtained in ozone–ultrasound combination application were very close to those obtained by the conventional method. After pretreatment, the fabrics were dyed with natural dyes (such as pomegranate peel). No chemicals were added during staining. The fastness values of all dyes were as good as expected. As a result, it is concluded that ozone–ultrasound combination can be used before dyeing cotton fabrics with natural dyes and can be used with little modifications in greige fabrics such as linen, jute, and wool [37]. Piccoli et al. (2015) examined the effects of time, pH, and ozone flow rate that impregnated the industrial wetting agent and water-containing solution to greige-knitted cotton fabrics in a closed medium. It was observed that the whiteness value increased and the strength decreased as the ozonation time increased. The best results have been reported with short ozonation time and low ozone concentration. The process utilized nearly 45% less water [38].

Arooj et al. (2015) studied the effects of additives for the optimization of ozone bleaching processes. The raw cotton fabrics were bleached with ozone alone and in combination with peracetic acid, hydrogen peroxide, and surfactants. The whiteness and fabric strengths of the samples with added surfactant gave significant results. It has been reported that bleached fabrics with ozone along with hydrogen peroxide have similar quality after dyeing. The finest outcomes with respect to whiteness and strength of ozone-bleached fabric were achieved with the addition of surfactant (2 g/L) at an ozone dose of 50 g/h, pH 5, and ozone treatment time of 45 min at ambient conditions [39]. Eren et al. (2016) investigated the effect of ozonation on color stripping of reactive-dyed cotton fabrics. Three different ozonation times were examined (15, 30, and 45 min), and the best results were achieved at 45-min ozone treatments. COD values of ozonation process decreased by 94% compared to conventional process [40].

Kan et al. (2016) analyzed the impact of plasma-induced ozone treatment on the color fading of reactive-dyed cotton fabric. According to the results, ozonation time and air ratio affected the color fading. The color fading increased as the ozonation time increased [41]. Perincek (2016) examined the removal of optical bleaches on cotton fabric using ozone. The results indicated that ozonation could be successfully utilized to decolorize optically bleached samples. As the ozonation time increased, the removal of optical bleaching agents increased and there was chemical deformation. Therefore, care must be taken to select the optimum processing time. The use of ozone in the removal of optical bleaches also saves water, energy, time, wastewater, and the use of harmful chemicals. At the same time, this study presented a new patterning method for cotton fabrics. This novel technique results in fashionable products such as Batik or tie-dyed cloths [42]. The cotton fiber was bleached using ozone and ultrasonic method and then dyed with natural dye by Bahtiyari and Benli. There was no need for mordanting before dyeing of fabrics bleached with ozone, and good color and fastness values were obtained. As a result, it was stated that ozone-bleached cotton fabrics are ready for dyeing and use less water and chemicals in the process [43].

Fig. 1 Photos of discharge printed samples by ozone [46]

Yiğit and Eren (2017) applied desizing process with ozone gas to the cotton fabrics. Different ozonation times (15–30 min) were used. Hot and cold afterwashings were applied to the samples in this study. As the ozone application time increased, desizing rate also increased, and mote count decreased. It is evident that ozone application wastes have much lower COD values than standard desizing bath wastes [44]. Eren and Yetişir (2018) investigated the effectiveness of bleaching with ozone gas on cotton fabrics. It was observed that whiteness/yellowness and desizing values of samples treated at ozone bleaching at 30 °C were better than those treated at 80 °C. This situation was interpreted as the decrease of the solubility of ozone gas at high temperatures [45]. Yiğit et al. (2018) investigated ozone application for discharge printing of reactive-dyed cotton. Outcomes revealed that comparable dye discharge (%) at the design patterns could be achieved by ozone treatment. But contour sharpness did not reach the levels of traditional discharge printing. A higher gas flow (10 l/min) rate, longer treatment (10 min) time, and moisturizing of 40% pickup rate led to better outcomes in this respect. A slight strength loss was monitored; nonetheless, the COD load of total process effluent was decreased very markedly. It was clear that discharge printing by ozone may contribute to cleaner production and new pattern method, at least for some patterns. Figure 1 shows discharge printing by ozone utilization on reactive-dyed cotton fabrics [46].

Zhong et al. studied plasma-induced ozone for color-fading process of sulfur-dyed cotton fabric. This study showed that color-fading treatment with the plasma-induced ozone can be utilized to remove the color from the dyed fabric and the process is effective in terms of uniformity and evenness [47].

5.1.3 Polyester Dyeing and Clearing by Ozone

After clearing for polyester dyeing, processes are conventionally carried on with reductive chemicals. Ozone technology is being used for these clearing processes, and thanks to ozone as it does not use any chemicals. So, polyester-clearing processes using ozone technology is an environmental friendly method. Elnagar et al. (2014) investigated the dyeability of polyester and nylon fabrics utilizing UV/ozone radiation. The natural dyes were used. At the end of the study, polyester and nylon fabrics dyeability increased with aid of UV/ozone [48]. Rahmatinejad et al. (2016)

increased the polyester materials' hydrophobicity property by modifying the surfaces by chemical pretreatments, UV/ozone irradiation, and fluorocarbon treatment combinations. The study focused on the application of UV/ozone radiation along with different chemical pretreatments on fabrics and the effects of fluorocarbon finishing results. The results of surface modification of UV/ozone irradiation and fluorocarbon treatment studies were more effective than using only fluorocarbon-treated fabric. With the combination of fluorocarbon treatment and UV/ozone irradiation, more hydrophobic polyester fiber surfaces were obtained [49].

Eren (2006 and 2007) investigated the combination of after-clearing and decolorization by ozonation on disperse dyeing of polyester. The study was carried with three different dyes and processed at 1- and 3-min ozonation periods. Results showed that decolorization and wash fastness tests obtained with 1- and 3-min ozonation periods in the dyebath at room temperature were good. The 3-min ozonation decolorization and COD removal ratios were better compared to 1-min ozonation [50, 51]. Eren et al. (2012) examined the after-clearing of PES disperse dyeing with gaseous phase of ozone. The ozone for the clearing of the dyed substrates was treated by blowing the ozone from the ozone generator on to the wet fabric substrates. The results specified that 3- and 5-min ozonation times were appropriate to obtain comparable wash fastness outcomes with traditional reduction clearing without significant color differences for the substrates dyed with C.I. Disperse Yellow 23 and C.I. Disperse Blue 79 dyes. But the ozonation time had to be enhanced to 15 min for C.I. Disperse Red 82. This novel technique of application possesses the benefit of being readily adoptable for continuous treatment lines and lower water consumption [52].

5.1.4 Ozone Treatment of Various Textile Fibers (Wool, Polylactic Acid, Etc.)

Atav and Yurdakul (2011) investigated the effect of ozone gas on the dyeability of mohair fibers. The optimum conditions of the ozonation process were detected as 60% wet pickup, pH 7, and 30 min. After determining the appropriate conditions for ozone, it has been reported that the mohair fiber could be dyed at 90 °C and 80 °C with 1:2 metal complex and reactive dyestuffs without any reduction in color strength. In addition, an increase in the standard affinity of ozonated samples was observed. It has been reported that energy saving is also provided since dyeing is performed at a lower temperature and time compared to the conventional method [53]. Perincek et al. (2011) explored the effects of ozone and ultrasound method on the dyeability of angora fibers. The effect of ozonation time and moistening on the dyeing properties of the fiber was investigated in this study. Conventional method and ultrasound application after ozonation were compared with respect to color yield. It was stated that the dyeing properties of the fibers and the moisture absorption after ozonation improved as the ozone time increased. Ultrasound application also increased the penetration of dye molecules into the fiber. As a result, it has been reported that ozone and ultrasound application increase the dyeability of Angora rabbit fibers [54].

Devaraju and Selvakumar (2012) used raw silk (Mulberry) and wild silk (Tussah) in order to investigate the effects of ozonation on dyeing. Fabrics were dyed with the same type of acid dyes. It was reported that ozone application reduces dye uptake, because ozone application breaks down the chains that help dye uptake next to silk molecules [55]. Avinc et al. (2012) ozonated the soybean fiber fabrics at different room temperatures. In that study, physical properties and fiber surface integrity and microstructures were examined. In order to compare the results, the whiteness values after hydrogen peroxide application were also observed at high application times (˃300 min). The expected loss of strength (22%) after all bleaching methods was also calculated after ozonation. The results stated that the strength losses obtained after high ozone application time were not very different from those obtained using hydrogen peroxide bleaching. Examination of SEM results showed that no findings were in relation to cracking, pitting, or deterioration damage at the end of the high ozonation period [56]. Lakshmanan (2014) conducted a study on the differentiation of moisture, pH, and process time steps to give a bleaching effect similar to bleaching with hydrogen peroxide using ozone in angora fibers. As a result of ozonation, whiteness and dyeability properties of the fibers were improved compared to those of untreated angora fiber [57].

Balci et al. (2015) investigated the effect of ozone and plasma on the physical properties of the fabric, where ozone and low-frequency oxygen plasma were applied to raw and degummed silk fabrics. Plasma and ozone processes were applied alone and in combination for different periods of time. The color difference values of the raw silk fabric treated with plasma and ozone were not significant, whereas color difference values of degummed silk fabric showed significant change. It was found that the decrease in the whiteness and the increase in the yellowness properties of the silk fabrics were more distinct with the increase in application time [58]. Perincek et al. (2015) investigated the effects of different bleaching processes (ozonation + oxidative + reductive bleaching), which contain ozone bleaching, on soybean fiber. It is stated that bleaching processes combined with ozone gas led to increase in whiteness and hydrophilicity values and provided less fiber deformation [59].

Wang et al. (2016) conducted ozonation at different time periods to improve the surface properties of protective aramid fibers used as reinforcing materials in high-performance composites. It was stated that there was improvement in tensile strength and elongation of aramid fibers and fabrics depending on ozonation time [60]. Rahmatinejad et al. (2015) studied hybrid fluorocarbon coating on wool treated with UV/ozone. During application, wool was modified by UV/ozone treatment to increase hydrophilicity [61]. Shao et al. (2001) studied the influence of UV/ozone exposure and peroxide pad-batch bleaching on the printability of wool and reported that printability performance of treated wool was akin to that of chlorinated wool [62]. Benli and Bahtiyari (2018) studied the effects of ozone treatment on dyeing of casein fibers with natural dye, and they reported limited increase in the whiteness of casein fibers [63]. Atav and Namırtı (2016) studied the influence of ozonation Vprocess on the dyeing properties of polyamide fabrics with walnut rind natural dye and reported an increase in the color yield [64].

5.1.5 Textile Wastewater and Color Removal Treatment by Ozone

There are many studies in the literature on textile wastewater and color removal [16, 64–68]. Eren and Anis (2009) applied ozonation for clearing of polyester dyeing. It has been reported that as a result of ozone, both sufficient fastness is achieved and color removal of the waste solution is carried out [69]. Avsar and Batibay (2010) applied ozone as an alternative to chemical techniques for the treatment of textile wastewater. Kinetic results exhibited that ozonation is more effective on color removal and COD values than chemical application [70]. Somensia et al. (2010) examined the effectiveness of ozonation in the treatment of textile wastewater. The results stated that pre-ozonation of textile wastewater is an important step for decreasing acute ecotoxicity as well as improving the biological solubility of wastewater [71].

In a study by Turhan et al. (2012), synthetic waste solution which contains water-soluble basic dye [methylene blue] was ozonated for decolorization. The COD of the basic dyestuff wastewater was decreased and color removal was monitored under basic conditions [72]. Günes et al. (2012), investigated decolorization of reactive dyeing effluent that have different chromophore group by ozone application. Metal-containing reactive dyes having formazan copper and anthraquinone chromophores were found to be effective in the decolorization processes. pH is an important parameter that contributes to decolorization efficiency [73]. Eren et al. (2013) performed ozonation process instead of reductive washing after dyeing polyester fabrics. High washing fastness levels were obtained after this process. Specifically, the color difference values of the sample painted at a rate of 7% indicate the success of the posttreatment with ozone [74].

Arooj et al. (2014), the same water bath was used repeatedly for greige cotton fabric bleaching by ozone. Although the whiteness effect of ozone was weaker compared to the conventional method, dyeing results in medium and dark ratio were better than conventional process. The ozonation processes were not affected by the pollution caused by the repeated use of bath water, and even after 20 repeated uses of bath water, the whiteness values of the fabrics were reported to be within acceptable limits. The application of the ozone bleaching process and the repeated use of process water save chemical, energy, water, and wastewater treatment costs [75]. Decolourization was investigated in which residual dyeing effluent from textile dyeing process was treated using ozone in the same machine where it was generated by Shaikh et al. (2014). When the process conditions were optimized, it was found that 100% color removal and 90% COD reduction were possible [76]. Shaikh et al. (2014) applied ozonation to clean the wastewater of a soft drink company, and after ozonation, the wastewater was used for dyeing cotton fiber. At the end of ozonation, it was determined that the wastewater could be used in the cotton fiber dyeing process. The method was found to be successful and it was stated to be environmentally friendly [77].

Zhou et al. (2015) studied the recovery of dyeing wastewater by ozonation, activated carbon, and biologically ventilated filter applications. These integrated processes were applied for biologically treated dyeing wastewater collected from a textile factory working with cotton products. The study results found that ozone changes the organic molecular structure, destroys chromophore groups, increases biodegradability, and reduces the genotoxicity of biologically treated dyeing wastewater. It was stated that the quality of reusable water is obtained by integrated processes [78]. It is known that carbon fibers exhibit specific tensile strength, high modulus, and outstanding wear resistance. For this reason, it is widely utilized for the reinforcement of advanced composite materials. Hence, numerous surface treatment techniques, such as wet chemical or electrochemical oxidation, ozone treatment, polymer or metal coating, and plasma treatment, have been performed to enhance the surface functional groups. Ozone is preferred for composite application due to its high oxidation properties [79].

6 Conclusion

Textile is a multifaceted industry so there are many study for investigating. Scientists primarily conduct and insert studies into the literature. After that these studies are commercialized after being evaluated in economic and environmental terms and applicability. Ozone application is one of the most innovative and needed processes. Ozone is applied in textile processes due to its water-, energy-, and time-saving credentials. At the same time, the production of ozone gas by atmospheric oxygen and there isn't need of chemical usage in the ozone processes, are the factors leading to reduction in processing costs. In particular, ozone can be used alone or in combination with other processes such as ultrasound, UV, and plasma. Ozonation can be used in textile companies for washing and treating denim fabrics, bleaching cotton fabrics, after-clearing of polyester, decolorization, and clearing wastewater. Nowadays, scientists use ozone not only in bleaching processes but also in new process types like discharege printing processes. Denim producers are trying to improve the washing performance of denim products by completing ozone application with innovative processes such as nano-bubble. Recently, ozone technology has also been used for surface modifications in composite applications. There is no doubt that ozone will play a more important part in the near future both in the textile industry and in the literature studies. It is expected that scientists will focus more and more on other possible uses of ozone and the possibility of different ozone applications in the textile industry in a wider context. It is clear that many textile-related industries will be affected by the development of ozone gas use. For example, machines and chemicals suitable for working with ozone gas can be produced. With the development of machineries and equipment compatible with ozone gas, the number of studies that will focus on more ecofriendly sustainable textile production will increase.

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Innovative Technologies for Sustainable Textile Coloration, Patterning, and Surface Effects

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Abstract The environmental impact of textile dyeing and finishing is of paramount concern in the textile industry. Enzyme and laser processing technologies present attractive alternatives to conventional textile coloration and surface patterning methods. Both technologies have the capability to reduce the impact of manufacturing on the environment by reducing the consumption of chemicals, water and energy, and the subsequent generation of waste.

Two emerging textile processing technologies, laser processing and enzyme biotechnology, were investigated as a means of applying surface design and color to materials with a focus on improving the efficiency and sustainability of existing textile design and finishing methods.

Through industrial stakeholder engagement and interdisciplinary research involving textile design, fiber and dye chemistry, biotechnology and optical engineering, this design-led project brought together design practice and science with a commercial focus. Each technology was used to modify targeted material properties, finding and exploiting opportunities for the design and finishing of textiles. The work resulted in a catalog of new coloration and design techniques for both technologies making it possible to achieve: selective surface pattern by differential dyeing, combined three-dimensional and color finishing and novel coloration of textile materials.

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The chapter provides a literature review mapping the use of enzyme biotechnology and laser processing technology within textile design and manufacturing to date, identifying current and future opportunities to reduce environmental impacts through their application. The methodological approach, which was interdisciplinary and design-led, will be introduced and the specific design and scientific methods applied will be detailed. Each of the techniques developed will be discussed and examples of the design effects achieved will be presented. And, an indication of the reductions in chemical effluent, efficiencies in resource use, and design-flexibility in comparison with traditional textile coloration and surface patterning techniques will be given.

Keywords Textile coloration · Laser processing · Enzyme processing · Agile manufacturing · Sustainable design · Material finishing · Textile design

1 Introduction

Color, pattern, and surface effects are fundamental elements of textile design and production, and critical to the functional and expressive role they play in material culture. Dyeing, printing, and finishing processes offer extensive opportunities for creativity and innovation within this area, but in the context of globalized mass production, they have become one of the most environmentally damaging facets of the textile industry. Due to the scale of the industry, the environmental and social impacts are significant and have been identified as one of the key challenges to achieve sustainability within the sector. Traditional methods routinely involve harmful chemicals that can have devastating effects on workers' health and the local environment through exposure and water and air pollution. In addition, vast amounts of water and energy are consumed during processing, leaving large water footprints in the developing economies where much industrial activity currently occurs, adding to the decline of water, reducing sources of clean water, and increasing associated costs [77].

In response to this, advances in technology are emerging that facilitate new methods of textile coloration, pattern, and surface effects with promising signs for more environmentally friendly processing [42]. Methods such as plasma processing, supercritical carbon dioxide dyeing, ultrasonic dyeing, and digital printing have begun to be adopted within various industrial contexts. Plasma treatment, for example, aids more efficient dyeing through facilitating increased dyeing rates, dye-bath exhaustion, and improved dye homogeneity on all fiber types [37]. Supercritical carbon dioxide dyeing, adopted for some product ranges by brands such as Nike and Adidas, claims waterless processing without effluent production, resulting in high dye fixation and good leveling on polyester with potential for application to a wider range of substrates [8, 17]. Within the context of circular design and manufacturing, ultrasonic dyeing has been implemented to enable natural dye solutions for natural and regenerated fiber by IndiDye® [33]. Within this process, ultrasonic pressure waves push the dye into the core of the fiber eliminating the need for chemical fixatives, auxiliaries, and wastewater [26]. And, digital printing methods have enabled more bespoke and on-demand modes of textile coloration, pattern, and surface design through platforms such as Spoonflower, which have the potential to minimize surplus stock and preconsumer waste [84].

Alongside these approaches, enzyme and laser processing technologies present attractive alternatives to conventional methods of producing color, pattern, and surface effects and have the capability to minimize the impact of manufacturing on the environment through increasing efficiency and reducing the consumption of chemicals, water, and energy. This presents opportunities for sustainable innovation through the redesign and modification of existing products and systems. Further, both technologies have the potential to catalyze and facilitate new postindustrial systems of production and consumption through opportunities for open and codesign, agile, and responsive manufacturing.

1.1 Overview

This chapter provides a summary of research undertaken to investigate laser processing and enzyme biotechnology as means of applying color, pattern, and surface effects to textiles with a focus on providing more efficient alternatives to traditional techniques. Through industrial stakeholder engagement and interdisciplinary research involving textile design, fiber and dye chemistry, biotechnology, and optical engineering, this textile-led project brought together design practice and science with a commercial focus. Each technology was used to modify targeted material properties, identifying and exploiting opportunities for the design, and finishing of textiles. The work resulted in a catalog of new coloration and design techniques for both technologies.

This chapter provides overviews of the use of laser processing and enzyme biotechnology within textile design and manufacturing to date, identifying current and future opportunities to reduce environmental impacts through their application. First, the methodological approach, which was interdisciplinary and design-led, will be introduced. Each of the techniques developed during the work will be discussed, and examples of the design effects achieved will be presented. Finally, an indication of the reductions in chemical effluent, efficiencies in resource use, and design flexibility in comparison with traditional textile coloration and surface patterning techniques will be given.

1.2 Methodology

The work undertaken employed a textile-led interdisciplinary methodology, drawing on methods associated with design, craft, science and engineering. These areas find a natural meeting point within textile practice, which tacitly draws on knowledge from each [68]. While it has been noted that engineers and designers rarely meet within commercial settings [52], the need for interdisciplinarity within research and innovation has grown in response to the complexity of current societal challenges [19, 25, 53]. Within this context, textile design research methodologies have evolved over recent decades to construct bridges between concepts of beauty and utility, aesthetics and function, which enable the investigation of the imaginative alongside the technical, and more latterly toward the development of "quantified design" [25].

The research outlined in this chapter is aligned with such thinking, employing methods originating in design practice and craft, alongside scientific experiment in a unified approach. This was underpinned by the establishment of a team of researchers with backgrounds in design, textile chemistry and biotechnology and optical engineering. Distinct but aligned periods of creative exploration and scientific experiment were undertaken and synthesized through design practice [51, 52, 70]. This generated both qualitative and quantitative data, which was analyzed to understand: the creative potential of the techniques established; the properties and qualities of resulting textiles as relevant to industry; and the potential savings in chemical, water, and energy use. The aim was to investigate the creative potential of laser and enzyme processing as more sustainable alternatives to traditional methods of achieving textile coloration, pattern, and surface effects. As such, the work progressed to: establish workshop conditions for textile sampling using both laser and enzyme processing; develop new techniques for coloration, patterning, and surface effects; and create textile design collections for analysis, review, and evaluation. The following text provides further detail relating to the methods employed in regard to both the laser and enzyme investigations, respectively.

2 Laser Processing

A laser is a device that emits an intense beam of light composed of electromagnetic waves that are in phase (coherent) and of the same wavelength (monochromatic). Infrared and ultraviolet laser irradiation can be harnessed for photothermal and photochemical properties, respectively. Lasers are used widely in manufacturing for materials processing, including cutting, marking, welding, and drilling, as well as for medical procedures and measurement applications [10]. The use of laser technology for textile processing is less established. However, as research develops and the cost of machinery becomes more affordable for factories and educational institutions, their use has become more widespread [30].

Lasers provide an energy efficient means of material processing and have been shown to have fiber modification capabilities that can enhance and improve dyeability without excessive water or chemicals, therefore offering potential environmental benefits compared to traditional textile dyeing processes. For graphic processing, they enable specificity and control by digital generation of imagery. The effect of laser irradiation on different textile substrates varies depending on the method of application and the material. Laser technology's advantages of digital control for design flexibility and precision capabilities coupled with noncontact processing offer unique benefits not achievable by other means. It is these unique attributes and controllable parameters of the laser that offer potential for novelty and innovation through consideration of new processes and opportunities for textile design.

For the design of textiles, laser processing has been utilized across the fashion, accessory, and home textile market sectors. Couture and high street clothing sectors have embraced laser technology to create fashion-led effects, such as fringing, and as a form of garment embellishment. Offering precision cutwork with heat sealing of fabric edges to prevent fraying, laser cutting technology has become standard equipment in university art and design departments, leading to a growth in creative use within textile design. For example, Hur [32] used the laser to cut individual textile units to build customizable, modular fabrics, while Moriarty's [58] layered laser cut rubber "lace" gave a new aesthetic to the traditional textile process of lace making.

While laser technology excels in providing efficient, noncontact cutting, it can also be harnessed for the purpose of textile surface modification. Lasers have been used to replace chemical and wet processing techniques to recreate conventional textile surface design effects such as devoré and stonewashed denim. Infrared CO_2 laser technology has been adopted successfully for commercial processing of denim in the manufacture of worn or weathered-look jeans. Through precise parameter control, infrared laser irradiation can fade the color of indigo-dyed denim by removing a thin layer of dye from the surface of the cotton, revealing the white undyed fiber underneath [38, 62, 63]. In comparison to traditional stone washing processes, the technique has eliminated the use of chemicals and reduced water use by 85% saving significant wastewater effluent [18]. This has led to the development of garment and textile-specific laser machinery. For example, Jeanologia [34] produced laser processing equipment capable of processing fabric lengths and direct-to-garment (DTG) laser finishing equipment that allows the garment to be processed in three-dimensional form.

Advantages of utilizing infrared laser irradiation as an efficient, dry, and targeted heat source have positive implications for reduction of wastewater and processing time of textile production in comparison to traditional wet finishing methods. These advantages have been beneficial to denim manufacture in creating laser-faded effects on denim [18, 63]. As such, use of CO_2 laser technology has become increasingly commonplace in the textile industry [62]. The use of laser technology on other textile substrates presents numerous further opportunities for sustainability in the field of textile research. This section reviews emerging laser-based techniques for textile coloration and surface patterning by utilizing laser irradiation for fiber modification, dye fixation, or thermal setting.

2.1 Laser Coloration and Surface Patterning: Fiber Modification

Research studies have reported harnessing the photochemical and photothermal energy that laser processing can provide to modify textile material properties. Studies that have examined the effect of laser irradiation on the properties of synthetic fibers and fabrics using ultraviolet (UV) [6, 36, 88] and infrared (IR) [7, 49] irradiation have reported an increase in the dye absorption properties of synthetic polymers, resulting in improved dye performance. Laser-enhanced dye uptake has been identified on PET (polyester) [3, 21, 36], polyamide (nylon) [9, 21], and polypropylene textiles [76]. Enhanced hydrophilic properties of polymer fibers after laser irradiation have been attributed to an increase in the amorphous: crystalline ratio [7, 49] that improves bonds between dyestuffs and polymer due to the creation of more functional groups after laser irradiation [7, 76]. Capacity for enhanced dyeing has also been attributed to morphological changes to polymer fibers [36], with surface roughness providing increased surface area for improved adhesion of dye particles to fiber [5, 6, 21, 76, 87].

Increasing the intensity of laser irradiation increased the color strength of laser pretreated synthetic fabrics after dyeing [40, 49, 76]. Therefore, by controlling the intensity of laser irradiation delivered to the substrate, the uptake of dye on the material could be controlled, allowing varied depth of shade across the textile surface. High-intensity laser irradiation increased the wettability, light, rubbing, and wash fastness of tested fabrics; however, properties such as bending rigidity and tensile strength were negatively affected by an increase in laser intensity [31, 76].

On cotton, unlike synthetic fibers, laser modification was found to reduce the amount of direct dye absorbed, leading to decreased color strength as laser intensity increased [15, 50].

Fewer studies have investigated the effect of laser irradiation on the properties of wool; however, a small number have shown that laser irradiation can reduce felting and shrinkage of woolen textiles [60] and that UV [67, 89] and IR [54] laser irradiation can improve the dyeability of wool. A combination of laser and plasma treatments was shown to increase hydrophilic properties as an all-over treatment on woolen textiles [20]. UV irradiation was found to disrupt the cysteine disulfide bonds on wool fibers and increase surface oxidation leading to a reduced water wetting time [75], suggesting that UV irradiation increased the hydrophilic properties of wool fibers.

The effects of laser irradiation on coloration for textiles have been studied from a design perspective, identifying the potential for surface pattern achieved through tonal dye differentiation after laser pretreatment [1, 3, 9, 51, 67]. Periolattoa et al. [67] suggest potential for design outcomes using stencils to mask UV irradiation on wool, resulting in selective UV exposure on the substrate. Drawing on the digital graphic potential of a CAD controlled laser, Bartlett [9] identified the potential for using an increased dye uptake on synthetic textiles to create imagery, while Akiwowo [3] further developed a laser-based pretreatment for PET textiles by considering improved dye uptake as an alternative patterning method.

Within the study presented Morgan et al. [54] explored CO_2 laser technology, as an effective surface design tool for wool and wool blends by ascertaining the effect of infrared laser irradiation on the surface and dyeing properties of wool substrates, revealing the potential for textile surface design. The laser technique used laser irradiation to modify the surface of woolen textiles, increasing dye affinity. The process removed microscopic scales from the wool fiber surface, resulting in an enhanced dye performance in the laser-treated areas (Fig. 1).

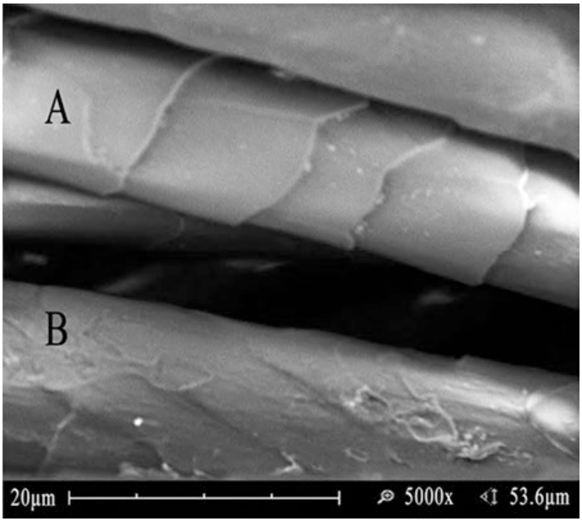


Fig. 1 Effect of selective laser irradiation on wool fibers. Wool fiber A: wool scales intact. Wool fiber B: scales have been removed by laser irradiation [54]

Fig. 2 Laser-enhanced dyed and engraved wool samples [51]

Targeted designs were laser marked on the surface of the cloth making use of differential dye uptake to achieve multitonal surface design on wool. Laser engraving was found to be effective in removal of the felted or brushed surface fibers of milled wool, to reveal the underlying woven structure. Used in parallel to the dyeing procedures, laser pretreatment combined three-dimensional relief surfaces with the multitonal design effects (Fig. 2).

Infrared laser irradiation as a pretreatment to dyeing PET/wool-blended textiles with reactive and disperse dyes facilitated a novel method of generating multicolored textile surface design [51]. Dye exhaustion and color difference values were calculated, revealing laser irradiation to have a positive effect on the uptake of disperse dye. Microscopic analysis of the laser-irradiated fabric showed an increased PET surface area on the blended textile, causing PET properties to dominate the laser irradiated area. When cross-dyed in a mixed dye bath, the disperse dye was the

Fig. 3 Laser patterned PET/wool blend (55/45) design samples dyed with contrasting disperse and reactive dye colors [51]

predominant color on the laser irradiated areas, while untreated areas retained the reactive dye color (Fig. 3).

It was demonstrated that the laser pretreated wool or blended textiles could be dyed at a reduced temperature and time, saving water and energy while combining coloration and patterning in one process. During coloration, the potential for an estimated 54% reduction of energy was displayed compared to immersion dyeing procedures. Textile performance tests showed that high fastness to washing and rubbing was achieved to meet current industry and consumer standards.

2.2 Laser Coloration and Surface Patterning: Dye Fixation

Existing research studies that utilize laser irradiation for textile coloration and patterning predominantly employ the laser as a pretreatment to dyeing textiles to enhance the substrate's affinity for dye [3, 9, 21, 36, 49, 54, 76]. However, mechanical tests have shown that the thermal stress of laser irradiation applied to the substrate is ultimately a damaging action [7, 15]; therefore, achieving a high depth of shade was detrimental to the tensile strength of the material, revealing scope for improved performance of existing laser dye techniques. In addition, laser pretreatment techniques used in the creation of surface designs had limitations; only tonal design effects could be achieved. Textile dyeing is an energy-dependent process; therefore, the photothermal properties of infrared laser irradiation present potential to activate a dye reaction on a textile substrate in a targeted manner suitable for the design and patterning of textiles [51]. Attempts toward a laser dye-fixation approach to surface design of textiles can be recognized in a small number of studies. Some success has been reported in introducing dye at the point of laser irradiation [9, 22, 39, 51].

Kearney and Maki reported a system for fixing reactive dye to cotton by way of an argon-ion laser [39] after screen-printing dye onto fabric in the form of a paste. The study provided a feasible low-heat dye-fixation method; however, at a maximum speed of 0.6 mm/s, the process was slow and the screen-printing stage of the process negated the advantage of noncontact laser processing. Textile dyeing company, Zaitex, and Textile equipment company, Tonello, developed a "Garment Flash Printing" system for adding pattern to cotton textile garments using a laser [11] involving a laser, pigments, and a polymeric binder to add color to cotton fabrics [22]. The process involved the use of a laser to fix the pigment, applied as a resin as an all-over treatment on cotton fabric. Tonello developed the method from a commercial perspective, specifically focusing on application for denim garment finishing.

Bartlett [9] considered the effects of laser irradiating a fabric wet with dye, identifying a slight increase in uptake within the dye bath. In this research, Morgan [51] further explored the potential of a dye reaction that takes place at the point of laser interaction providing technical refinement of a laser dye-fixation technique and exploration of its creative potential. A laser dye-fixation approach to textile coloration led to the development of the "*peri-dyeing*" technique. The prefix *peri* denotes around or adjacent [64]. The peri-dyeing technique considers the laser as a targeted energy source for "on-the-spot" fixation. It involved applying dye locally to the surface of a textile substrate followed by laser irradiation: Therefore, the dye reaction takes place at the point of (or adjacent to) laser interaction with the dye liquor and textile material.

The laser-based peri-dyeing technique [51] allowed intricate, targeted surface design of textile substrates. Photographic quality graphics and multicolored surface design effects were achieved on natural wool and synthetic PET and polyamide fabrics. The noncontact laser apparatus allowed precision detail to be achieved on highly textured fabrics or finished three-dimensional garments, providing an advantage over digital printing methods. The permanence and durability of the coloration process were assessed through material performance testing procedures, including fastness to washing, rubbing, and tensile strength, which met with commercial standards across all conducted tests [56]. Peri-dyeing enabled digital design innovation, direct-to-garment processing, and potential for customization in the manufacture of finished textile goods with sustainability benefits through reduced energy, water, and chemical consumption [57] (Figs. 4, 5, 6, and 7).

2.3 Laser Surface Texturing: Thermal Setting

Adding surface texture and three-dimensional effects to textiles can provide enhanced functional properties, such as insulation, absorption, compression, or strength in addition to adding shape, movement, and design aesthetics. Three-dimensional surface effects can be added during textile construction, stitching, or via wet techniques such as devoré, flocking, felting, and shibori. Lasers have been

Fig. 4 Laser peri-dyed wool textiles [51]

Fig. 5 Laser peri-dyeing on textured and brushed wool fabrics [51]

Fig. 6 Peri-dyed PET textiles: Multicolor and photographic designs [51]

Fig. 7 Direct to garment peri-dyed PET sportswear prototypes [56]

used to create design-led three-dimensional forms, such as laser-assisted origami textiles [47], laser-bonded synthetics [24], and laser-molded textiles by using IR laser irradiation to heat-set predetermined shapes in synthetic textiles [55].

Laser welding has been used to bond seams in garment construction and in fashion. In the case of thermoplastic fiber fabrics, such as PET, lasers can be used to create stitch-less, water-resistant seams. As reported by The Welding Institute (TWI), this technique often requires an additive that is applied to the seam interface and reacts under the laser energy, melting and bonding the two surfaces together [16]. Current uses of this technology include Airbags, medical and protective clothing, and footwear with sealed seams. Goldsworthy [24] explored the design potential of laser welding technology to bond synthetics producing three-dimensional and relief qualities. By harnessing the laser for bonding and lamination of the fabrics to produce multilayered materials, Goldsworthy was able to develop a range of surface finishing methods while keeping the fabric 100% recyclable. Furthering this technique, Paine et al. [65] used laser welding technology to create targeted compressive effect on garments.

Resulting from the study presented, Morgan et al. [55] report on a technique for three-dimensional molding of synthetic textiles using the photothermal properties of infrared laser irradiation. They describe a system to apply and control the three-dimensional effects through controlled tension and targeted laser irradiation. The molding technique was used to design accurate surface architectures, engineered surface effects, and three-dimensional design features on knitted PET and polyamide textiles (Fig. 8). Combining three-dimensional laser molding with laser dyeing processes attained an effect akin to shibori dyeing. However, the laser-based technique provided unique design aesthetics, offering control, with a level of precision and repeatability that cannot be achieved with existing shibori processes or textile production techniques.

The use of laser technology to create three-dimensional textile forms presents efficient processing advantages over traditional methods: Unlike regular textile embossing equipment, for each new design, the dry laser process does not require physical molds or plates to be cast, stitching, or complicated loom set-up, instead,

Fig. 8 Laser-molded PET and polyamide textiles [51]

offering ease of pattern change through digital generation of designs. The use of purely synthetic materials may provide additional sustainability benefits for ease of material recovery, redesign, and recycling at end of primary use.

3 Enzymatic Processing

Enzymes are biocatalysts that catalyze specific chemical reactions within the cells of all living organisms, resulting in the growth and maintenance of the cell. The majority of commercial enzymes are sourced and obtained from a variety of different microorganisms such as bacteria, fungi, and yeast. However, these naturally occurring enzymes are often not found in nature in large quantities and, therefore, require isolating and fermenting for industrial use [61].

Enzymes differ from chemical catalysts in several distinct ways and bring a wide range of processing benefits. Reactions catalyzed by enzymes are generally very fast and highly specific, typically performing one type of reaction effectively. Enzymes are capable of catalyzing reactions under comparatively mild reaction conditions, such as at temperatures below 80 °C, under atmospheric pressure, and at around neutral pH. In contrast, chemical catalysts often require high temperatures, high pressures, and use of extreme pH. Therefore, enzymes can dramatically reduce energy and chemical consumption and production costs. Enzymes are biodegradable which can help reduce the impact of manufacturing on the environment. Enzymes rarely get involved in side-chain reactions, which eliminate the production of by-products making them extremely efficient during processing unlike typical chemical catalysts which are less specific and often produce unwanted by-products which can prove difficult and costly to dispose of. Furthermore, enzymes are not consumed in reactions and remain unchanged, offering the possibility of repeated and continuous reuse, therefore leading to potentially new sustainable industrial processes such as closed loop [2, 35].

Advances in biotechnology have led to the development and manufacture of new commercial enzymes. These enzymes may have improved properties such as stability under certain conditions, higher activity at lower temperatures, and reduced dependency on additional chemicals (cofactors) being present [61, 66].

Consequently, enzymatic approaches have found a wide range of applications in the textile industry [4, 14, 27, 28, 43], ranging from replacing conventional production methods to novel fabric finishing treatments. Enzymatic desizing is one of the earliest examples of enzymes being implemented on an industrial scale. The enzyme amylase is used in the enzymatic desizing process to break down and remove "size" (starch), a protective lubricant which is commonly applied to yarns during the weaving of fabrics. Since its adoption during the early part of the twentieth century, it has proved to be a valuable method replacing conventional processes which required the use of harsh chemicals such as oxidizing agents [29]. Another group of enzymes called cellulases has found acceptance within textile wet processing. Cellulases are used to bio-polish cotton fabrics, and enzymatic removal of surface microfibers enables fabrics to maintain a new look for longer. Cellulases and another enzyme group known as laccases are also used in the production of denim fabrics and garments to produce stonewashed looks and/or alter the color and shade of dyed denim by fading. Stonewashed effects on indigo dyed cotton denim are used to be created by pumice stones, however, the use of pumice stones caused damage to both fibers and machines. Other well established enzyme-based textile processes include bio-scouring and bleach clean-up, both processes are described in more detail in Shen and Smith [80]. Although the value of enzymes in textile processing has long been evident in terms of environmentally friendly, energy and water savings, improved product quality and process integration, and cost reduction, enzymes to date have not been investigated for their creative potential in textile design.

3.1 Protease and Laccase

Research presented within this section demonstrates the ability of two specific enzymes, protease and laccase, as creative tools to achieve, through controlled application, innovative coloration and/or decorative surface pattern on textiles.

Protease (EC.3.4.21.62) belongs to a class of enzymes called hydrolases, which are capable of breaking down large molecules into smaller fragments. To date, there has been considerable interest in the application of protease to achieve a variety of functional finishing effects on wool through modification of the wool cuticle scale by catalyzing the hydrolysis of peptide bonds in wool protein molecules. Studies have investigated the reduction in wool prickle, improved fiber softness, and anti-shrinkage treatments [78, 79]. However, if not carefully controlled, this group of enzymes can cause significant damage to the wool fiber due to the enzyme penetrating into and attacking the wool fiber core [59, 81], resulting in strength and weight loss [12]. Thus, no commercial treatments have been developed so far, mainly because the use of protease can result in unpredictable, difficult to control reactions leading to unacceptable fiber damage. However, surface modification or controlled degradation of wool fibers through enzymatic treatment presents clear opportunities that could be exploited for aesthetic design purposes.

Laccase (EC.1.10.3.2), belonging to a class of enzymes called oxidoreductase, can catalyze redox reactions, which reduce molecular oxygen to water and simultaneously perform one-electron oxidation of various substrates such as diphenols and aromatic amines with or without a mediator [74, 79].

Laccase products such as DeniLite™ (Novozyme) and PrimaGreen® EcoFade LT100 (Dupont Genencor) based on laccase-mediator systems have found much success as enzymatic processes for decolorizing predyed denim, offering alternatives to traditional abrasive stonewashing processes, where dye is removed from fabrics or garments using pumice stones to achieve color fading and/or worn effects.

In contrast, laccases are also capable of oxidizing an extensive range of basic aromatic compounds, transforming them into colored polymeric products via oxidative coupling reactions [46, 74]. The reaction mechanism of laccase catalyzation is one electron oxidation of aromatic compounds to form free radicals while reducing molecular oxygen into water. These free radicals are very reactive and then undertake further reactions themselves or with the initial aromatic compound and polymerize in a nonenzymatic pathway to form colored products. These colored products are capable of being adsorbed onto or reacting with numerous textile fibers enabling coloration [23, 69, 79]. The potential for laccases to be used within the area of textile coloration, specifically for the generation of decorative surface pattern design, remain relatively unexplored.

3.2 Coloration and Surface Patterning by Enzymatic Degradation

In this study, the enzyme protease was employed to selectively modify a wool/polyester blended fabric to impart decorative surface patterning [73]. A series of controlled experiments for studying the interaction between enzyme and substrate (a compound on which an enzyme exerts its catalytic effect) were undertaken to achieve either partial or complete removal of the dyed wool fiber component with a view to reveal undyed polyester yarns which formed part of the fabric blend, resulting in novel fading and differential fabric relief (Table 1). Longer treatment times resulted in greater weight loss and lighter shades being produced, as reflected by *K/S* values. The activity of protease is highly specific, therefore, it caused neither

Table 1 The effect of protease processing at different durations of time on wool degradation from wool/polyester samples dyed using reactive dye Lanasol Blue CE

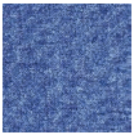
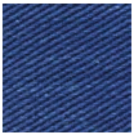
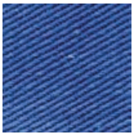
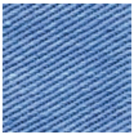
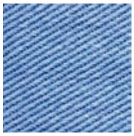
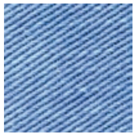
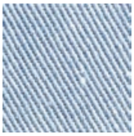
Wool/polyester fabric samples	Duration of enzymatic treatment with protease (h)				
	Untreated	0.5	1	2	4
Predyed at 2% owf					
K/*S* (620 nm)	5.89	3.88	2.93	1.40	0.47
Weight loss (%)	–	10.0	16.5	30.0	40.5

Table 2 The effect on dye decolorization by processing with a laccase-mediator system for different durations of time on cotton (100%) samples ring-dyed with indigo dye (C.I. Vat Blue 1)

Cotton fabric samples	Duration of enzymatic treatment with laccase-mediator system (h)				
	Untreated	0.5	1	2	4
Indigo dyed with 6-dip and 6-nip					
K/*S* (640 nm)	19.67	9.40	5.74	5.94	4.11
Indigo dyed with 1-dip and 1-nip					
K/*S* (640 nm)	6.77	1.92	1.27	0.88	0.61

modification nor damage to the polyester fibers. Investigations concluded that significant subtraction of the dyed wool component from the blend could be achieved if the correct combination of enzyme concentration, agitation, and treatment times were applied.

In a different study, a laccase-mediator system was explored to generate surface pattern design through selectively decolorizing indigo-dyed cotton fabric [70]. A series of controlled experiments were undertaken, which consisted of enzymatic treatments with different processing parameters using 100% cotton fabric ring-dyed with indigo dye (C.I. Vat Blue 1). Experiments were designed to gain a clear understanding of the interaction between the laccase-mediator system and indigo dye and to achieve partial or complete removal of indigo dye from dyed cotton fibers with a view to reveal undyed cotton fibers and yarns which formed the underlying layers of the fabric. Investigations led to the development of an optimized enzymatic process which enabled indigo-dyed cotton fabrics to be processed to achieve various levels of fading by simply altering processing conditions, as shown in Table 2. Longer treatment times resulted in lighter colored shades being produced.

To explore the decorative pattern design potential of protease and laccase-mediator systems, surface-patterning design techniques inspired from traditional Shibori-resist dyeing methods [85] were selected for design trials. Patterns consisting of simple repeats of design elements [86] such as lines or geometric shapes were chosen for exploration to create an all-over repeat pattern across the length of fabric.

Dyed wool/polyester and cotton fabrics comprising different degrees of compression and accessibility were manipulated and prepared using stitching, or folding, pleating, and clamping (as illustrated in Figs. 9, 10, and 11) to achieve surface patterning through enzyme processing. Fabrics were treated in a liquor bath containing the enzymes. In principal, the enzymes would be restricted to selected areas made accessible, therefore, as a result, the enzymes would only be able to degrade or decolorize by fading selected areas of the fabric. This in theory would facilitate the generation of decorative surface patterning through contrast in color and/or texture through the use of localized enzyme treatment.

Results successfully demonstrated a diverse range of highly individual patterns could be generated with the use of varying resist techniques trialed with enzyme processing [70, 73]. The resulting visual aesthetic qualities achieved were heavily governed by the techniques used, which controlled the degree of liquor accessibility and penetration, and consequently the level of wool degradation or decolorization.

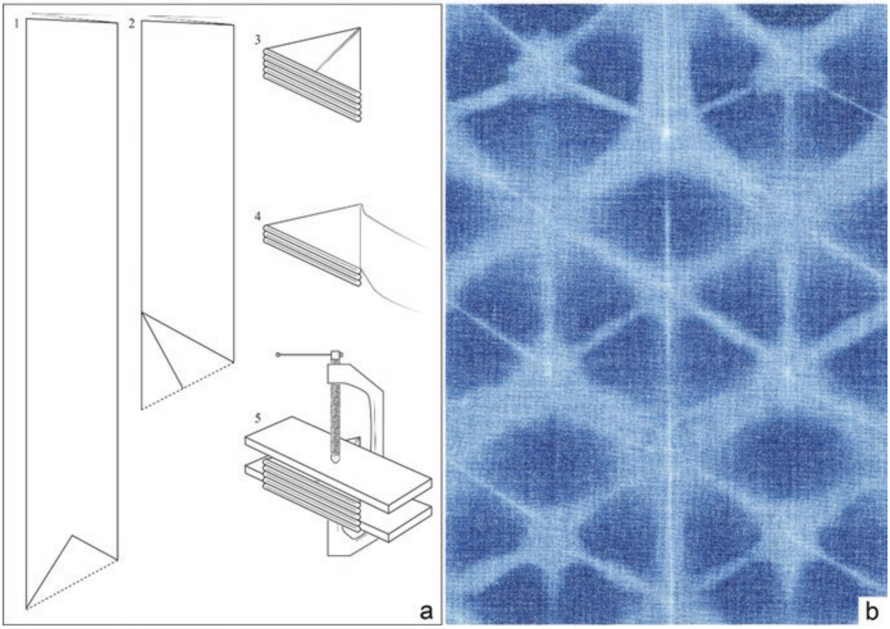


Fig. 9 Illustrated diagram showing Shibori technique using pleat, fold, and clamp-resist method (**a**) to generate a colored pattern design using protease processing on wool/polyester blended fabric (**b**) [73]

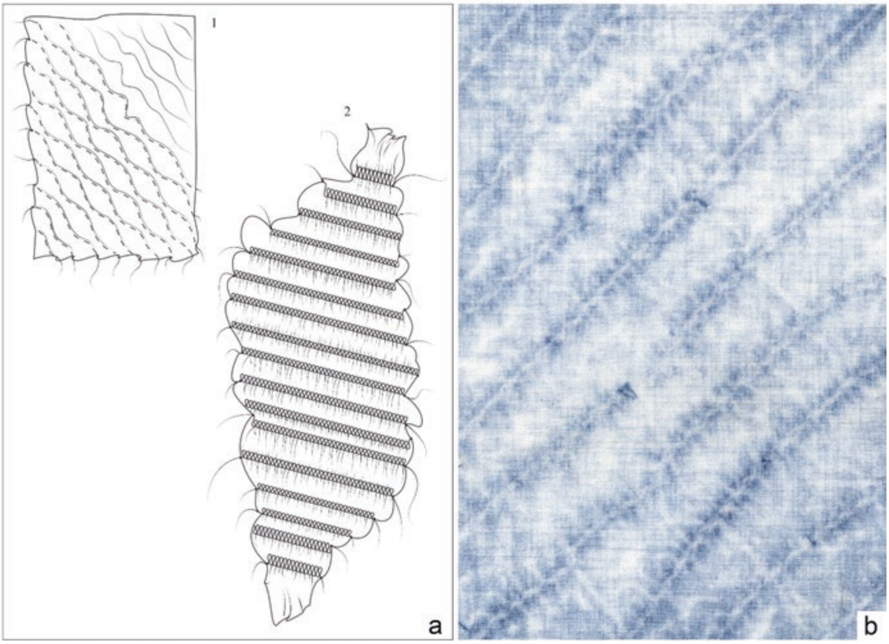


Fig. 10 Illustrated diagram showing Shibori technique using stitch-resist method (**a**) to generate a colored pattern design using protease processing on wool/polyester blended fabric (**b**) [73]

Irregular surface modification resulted in subtle pattern variations and irregularities, and design elements displayed distinctive soft edges. In general, stitch techniques employed (Fig. 10) enabled greater access to the enzyme containing liquor, resulting in lighter and softer colored patterning. In contrast, pleat, fold and clamp techniques allowed a different style of patterning, designs with greater color contrasts and stronger depths of shade resulted from an increased level of pressure and compression applied with the use of a G-clamp, completely restricting enzyme access to some areas of the fabric (Figs. 9 and 11).

3.3 Enzymatic Surface Modification for Subsequent Coloration and Surface Patterning

Certain chemicals such as the cationic surfactant cetyltrimethylammonium bromide (CTAB) present on wool fiber can decrease the activity of protease [82, 83]. Therefore, the application of CTAB as a pre-treatment was explored as a chemical resist method to selectively inhibit the activity of protease towards wool fibers to impart decorative patterning. Preliminary studies found that a pre-treatment with CTAB followed by enzyme processing was capable of altering wool fiber characteristics enabling differential coloration (dye uptake) and felting properties during subsequent dyeing and post-processing (Table 3). Fibers treated

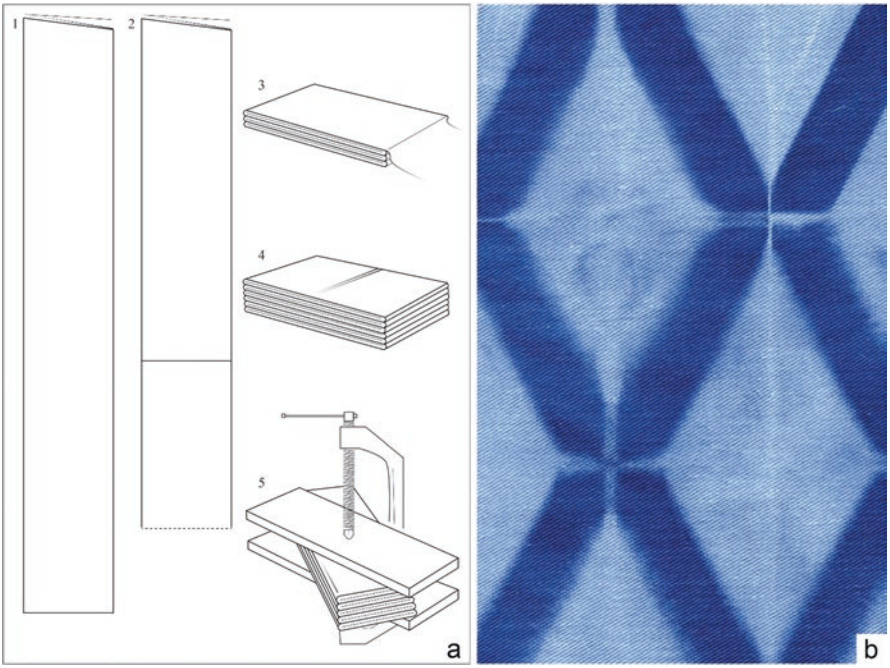
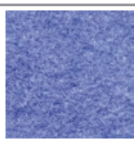
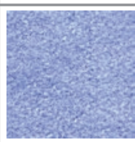
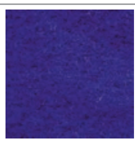
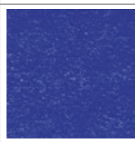


Fig. 11 Illustrated diagram showing Shibori technique using pleat, fold, and clamp-resist method (**a**) to generate a colored pattern design using laccase-mediator system on 100% cotton fabric (**b**) [70]

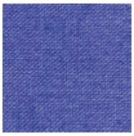
Table 3 The effect on dye uptake of CTAB pre-treated 100% wool fabrics followed by protease treatment and post-competitive dyeing using acid dye

C.I. Acid Blue 140	CTAB followed by protease treatment	Protease treatment
Competitively dyed at 0.5% owf		
Competitively dyed at 5% owf		

with CTAB and protease altered the dye uptake and anti-shrinkage properties. These contrasting properties present opportunities that could be exploited for textile design, however, further work would need to be undertaken to explore its creative potential.

Another enzyme pre-treatment method explored the application of protease within a printing paste to selectively modify wool fiber cuticle scales to generate

Table 4 The effect on dye uptake of protease pre-treated 100% wool fabrics followed by competitive low temperature dyeing using acid dye

Dye	Non-protease treated sample	Protease pre-treated sample
C.I. Acid Blue 140		
C.I. Acid Blue 45		

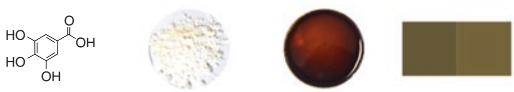
surface pattern. The enzyme was restricted to the surface of the fiber using textile screen printing methods. Protease applied within an Indulca (a polysaccharide product of gum guar) printing paste led to wool fiber modification through the disruption and removal of wool cuticle scales resulting in greater fiber hydrophilicity, leading to easier dye diffusion especially when dyed at lower temperatures (Table 4). The effects of differential dye uptake in terms of shade depth were explored to produce surface patterning, however, further study is required to produce well-defined surface pattern with this method [70].

3.4 Coloration and Surface Patterning by Enzymatic Polymerization

In this study, the potential for laccase to be used within the area of textile coloration, specifically for the generation of decorative surface pattern design, was investigated. A selection of natural phenolic compounds and non-phenolic compounds consisting of naphthalene and benzene derivatives (Table 5) were carefully selected as laccase substrates to synthesize dyes in-situ on either nylon 6,6 or wool fabrics.

Laccase catalysis of the selected aromatic compounds resulted in a variety of colors being produced in aqueous solutions and on both wool and nylon fibers after enzymatic treatment [70]. Each aromatic compound was catalyzed by laccase to form characteristic color shades, predominately ranging from yellows, oranges, and browns as seen in Table 5. It is believed that the coloration created on both fiber types was a result of colored dimeric, oligomeric, and polymeric products formed by laccase oxidation of aromatic substrates, which are capable of reacting non-enzymatically in a nucleophilic manner forming covalent bonds with amino groups found on the surface of nylon and wool fibers [69], to result in reasonably good color fastness to wash. In general, wool fabric samples were darker in comparison to nylon samples which were lighter and/or brighter. The differences in coloration observed between nylon and wool were due to differences in dyeability characteris-

Table 5 Chemical structures of aromatic compounds selected for study and their corresponding laccase-catalyzed colored solutions and coloration of nylon and wool fabrics [71]

Group	Aromatic compound	Chemical structure and form	Coloured product	Coloration on nylon and wool
1	1,2-Dihydroxybenzene			
	1,4-Dihydroxybenzene			
2	2,7-Dihydroxynaphthalene			
3	Catechin			
4	Ferulic acid			
	Gallic acid			
	Syringic acid			
5	2,5-Diaminobenzenesulfonic acid			
	3-Amino-4-hydroxybenzenesulfonic acid			

tics arising from different types and quantities of functional groups present in each fiber (especially amounts of primary amine groups) and aromatic compound structures affecting the various types of molecular interactions occurring between fiber and laccase-synthesized products, in addition to different levels of affinity, rate of uptake, and final saturation values [72].

Prajapati et al. [72] found that a diverse color palette could be produced with the use of three different aromatic compounds as laccase substrates: 1,4-dihydroxybenzene, 2,7-dihydroxynapthalene, and 2,5-diaminobenzenesulphonic acid.

Table 6 Color range achieved on wool and nylon when treated with 2,7-dihydroxynapthalene in the presence of laccase using different pH and buffer systems

pH	Wool				Nylon			
	AC	CI	PH	BI	AC	CI	PH	BI
3			–	–			–	–
4				–				–
5				–				–
6				–				–
7				–				–
8	–			–	–			–
9	–	–			–	–		
10	–	–	–		–	–	–	
11	–	–	–		–	–	–	

Source: Prajapati, C
AC acetate buffer, *CI* citrate buffer, *PH* phosphate buffer, *BI* bicarbonate/carbonate buffer

Various reaction processing parameters such as buffer systems and pH values, laccase and aromatic compound concentrations, and reaction times were investigated to establish the range of achievable colors, all in the absence of additional chemical auxiliaries. Previously, unreported colors such as blues, greens, and pinks were achieved. The use of varied buffer systems, pH values, and aromatic compound concentrations proved most beneficial for extending the ranges of possible hues. For example, the use of the compound 2,7-dihydroxynapthalene in the presence of laccase resulted in a variety of hues, ranging from yellow, green, and blue across both fiber types simply through pH control (Table 6).

To determine the coloration and design potential by laccase catalyzation of the selected aromatic compounds, fabrics were specially constructed using a combination of undyed nylon, wool, and polyester yarns. Basic plain, twill, satin, and sateen structures in addition to simple jacquard weaves were used to generate a selection of woven fabric designs. Weaves were then dyed using the one-step laccase-catalyzed coloration process. As shown in Fig. 12, the use of different fiber types and weave structures enabled simple color variations to be produced. Shadow, reserve, and contrasting effects are achievable with the newly developed laccase-catalyzed dyeing process.

Fig. 12 Examples of one-step laccase-catalyzed coloration on nylon, wool, wool/polyester, and specially constructed woven jacquard designs, using different dye bath conditions. (Source: Prajapati, C)

4 Summary and Conclusions

An overview of the alternative techniques for producing color, pattern, and surface effects on a range of textiles using laser and enzyme processing are shown in Table 7.

This chapter shows how two different novel approaches, the biological and the digital, can disrupt conventional textile processing each offering potential sustainability benefits within the context of current textile design and manufacture and within emergent and future postindustrial systems of production and consumption.

4.1 Key Sustainability Benefits of Laser Processing for Textile Design

The laser-based coloration and design techniques offer innovation with potential sustainability and economic benefits for the field of textiles via eco-efficient manufacture. For example, laser-enhanced dyeing offers potential reductions in energy and wastewater effluent through reduced dyeing temperatures and improved dye performance. Low-temperature processing reduces overall dyeing time and temperature from standard practice, displaying potential for an estimated 54% reduction of energy during dye production in the case of the laser pretreated and dyed wool [54]. The ability to reduce energy used in dyeing by over half would offer exceptional savings with both economic and environmental benefits. Some loss in tensile strength was apparent after laser irradiation, and despite enhancing the affinity for dye, the process did not altogether omit immersion dyeing procedures. These issues were addressed via the laser peri-dyeing technique [51], which added additional water, energy, and chemical saving benefits, further reducing the water and dye required for coloration of wool and synthetic substrates by elimination of dye baths used in conventional exhaust dyeing procedures, while retaining permanence and durability. Laser molding [55] described a dry and efficient process that does not require additional materials, such as thread for stitching. Therefore, using the

Table 7 Overview of alternative techniques for textile coloration, patterning, and surface effects

Selective surface pattern by differential dyeing	Laser coloration and surface patterning: fiber modification Enzymatic surface modification for subsequent coloration and surface patterning
Combined three-dimensional and color finishing	Laser surface texturing: thermal setting Laser coloration and surface patterning: fiber modification Coloration and surface patterning by enzymatic degradation
Novel coloration of textile materials	Laser coloration and surface patterning: dye fixation Coloration and surface patterning by enzymatic polymerization

technique for surface design effects could eliminate the need for additional wet finishing or embellishment for decorative and functional textiles.

Combining the functionality of the laser to perform multiple production tasks at once, such as pattern cutting or laser engraving milled wool as well as the laser dyeing techniques, would allow additional environmentally sustainable benefits to the process compared to outsourcing each individual stage of the production process in addition to storage and transport between phases. Combining techniques in one stage has potential to offer fast response in today's fast changing market, with easily changed CAD files allowing smaller product runs than financially permitted by exposing individual screens for screen printing or die cutters for product pattern cutting. Therefore, as well offering sustainability through reduced temperatures and improved dye performance, laser technology could offer additional advantages through a potential change in production systems.

The flexibility and immediacy of digital processing benefit short-run production, textile sampling, and garment prototyping compared to conventional textile processing techniques that are aimed to be cost-effective for bulk manufacture. Processing limitations of laser techniques may include restrictions in size of the laser bed area, or processing speed for bulk and large volume manufacture. Similar to digital textile printing, turn-around times may be slower than that of rotary or screen-printing methods when volumes increase. However, garment and textile-specific multihead laser machinery capable of direct-to-garment (DTG) finishing and processing of continuous fabric lengths have already been commercialized for the denim industry [34], showing that application-specific laser machinery can be engineered to overcome size and speed constraints for emerging laser textile processing techniques.

The laser-based design techniques discussed in this chapter are capable of digital design generation and targeted, direct-to-garment processing on textile or garment "blanks," postconstruction. Further research involving partners from four sectors of the textile industry [56] identified commercial viability and the opportunity for these digital laser processes to move the design stage further down the production cycle to allow for late-stage decisions and design flexibility, providing a responsive approach to design and distributed manufacture. Providing the textile industry with responsive or agile manufacturing opportunities such as these may offer reduced lead times and smaller minimum orders to reduce surplus stock and minimize or eliminate the creation of excess waste of textile goods; in addition, they may facilitate bespoke or customized production opportunities.

4.2 Key Sustainability Benefits of Enzymatic Processing for Textile Design

Studies discussed in Sect. 3.2 demonstrated the ability of protease and laccase as creative design tools for coloration and surface patterning by enzymatic degradation. With both studies, effects similar to those achieved with conventional surface design processes such as devoré ("burnt out") and discharge printing were achieved. Both patterning styles have remained popular and significant since first introduced because the effects obtained from these processes are often different and aesthetically superior to direct screen-printing styles [48] and digital textile printing. Although both processes are simple and inexpensive methods for producing patterned fabrics through the application of a chemical paste, the processing pastes require the use of either strong alkalis such as sodium hydroxide or reducing agents, in addition to chemical auxiliaries [73]. The heavy use of these compounds can be toxic and hazardous to handle and generate effluents that are difficult to treat and damaging toward the environment [41, 45].

In contrast, surface patterning through enzymatic hydrolysis with protease or decolorization with laccase-mediator system offers simpler, cleaner, and safer alternative processing methods, which principally eliminate or reduce the use of conventional reducing and/or oxidizing agents, chemical auxiliaries, and elevated temperatures for processing. The precise reaction specificity of enzymatic processes facilitates specific and targeted textile finishing without causing undesirable effects such as deteriorating fabric qualities and causing damage to other components. In addition, both enzymatic processes offer new unique design aesthetics which enable the production of individual non- identical, but corresponding surface design patterns with subtle variations, irregularities, and unique characteristics which would be difficult to reproduce and replicate by the means of conventional textile processes. Currently, there is considerable interest within the textile industry to create fabrics with artisan aesthetics, and these qualities are understood to be positive in the current industry where consumers regularly seek individual and unique pieces.

Conventional dyeing processes generally involve the use of different chemicals and dyeing auxiliaries in addition to high temperatures to assist the dyeing process. The coloration of wool and nylon can be achieved with the use of several dye classes, the most important of which are acid, mordant, and premetallized dyes, all of which are applied under acidic conditions with the use of high temperatures, generally at the boil [13, 44]. Coloration and surface patterning by enzymatic polymerization discussed in Sect. 3.4 present advantages over conventional dyeing methods, principally the elimination of premanufactured dyes and chemical auxiliaries, and dyeing at ambient temperatures, therefore reducing energy use, the complexity of the dyeing process, and downstream processing, leading to possible economic and environmental advantages. Although the study shows that a good range of colors is achievable by this method, it is not known yet whether a full gamut of color shades can be achievable. The enzymatic dyeing process offers opportunities for multiple colors and shading to be achieved through simple alterations in processing conditions, which is currently not possible with conventional dyes and methods. The results also demonstrate the ability of laccase as a novel creative tool, which permits effective surface patterning through controlled application for shadow and contrast colored effects.

The opportunities discussed could provide the textile industry with realistic and viable options to use enzyme-based coloration and surface patterning processes, however, further study is required to examine whether the enzymatic processes have the potential to be scaled up to a viable industrial process which can be reproducible and meet commercial standards.

Note This work was undertaken through the *LEBIOTEX* project (Laser Enhanced Biotechnology for Textile Design) – a collaborative research venture between De Montfort University and Loughborough University in the UK. The project was led by Professor Jinsong Shen (De Montfort University) and Dr. Faith Kane (now at Massey University, NZ) with consultation from Professor John Tyrer (Loughborough University, UK) and Dr. Edward Smith (De Montfort University, UK), and research work undertaken by Dr. Laura Morgan (now at University of the West of England) and Dr. Chetna Prajapati (now at Loughborough University). The initial project ran from 2012 to 2015 and explored new opportunities for sustainable textile coloration and surface design using enzyme and laser technologies. The project was funded by the Arts and Humanities Research Council (AH/J002666/1) and was supported by industrial project partners Camira Fabrics, Speedo, and Teresa Green Design.

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Sustainable Finishing Process Using Natural Ingredients

M. Gobalakrishnan, D. Saravanan, and Subrata Das

Abstract Textile finishing is an important process for improving the value of the textile products, and many finishing processes involve hazard chemicals and auxiliaries. With growing awareness on environmental problems, both manufacturers and consumers expect sustainable solutions in the entire supply chain, wherever possible. Needless to state that the textile manufacturers are also seeking sustainable finishing solutions and processes using natural and safe ingredients for providing value addition. Advanced finishing processes like encapsulation methods and plasma treatments improve the sustainability by increasing the affinity and durability of the processes. In this chapter, sustainable preparatory processes, finishing practices for flame-retardant finish based on bio-based flame retardants, antimicrobial finish, bio-finish and UV protection finish have been discussed.

Keywords Natural ingredients · Plasma treatment · Flame retardant · Silk degumming · Bio-polishing · Antimicrobial finish · UV protection · Sustainable processes

1 Introduction

Finishing is an important process in textile manufacturing to meet customers' expectations and provide value-added products in the market. Various chemical finishing processes, such as softening, stiffening, water and oil repellent, mildew proof, moth proof, back filling, crease resistant, durable press finish, wash and wear

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or wrinkle recovery finish, degumming of silk, bio-polishing, flame retardant, anti-microbial, UV repellent and anti-static, and mechanical finishing processes, such as sanforizing, calendaring, raising and singeing, are given to textile materials to enhance the aesthetic and functional properties of the fabrics. During twentieth century, most of the developmental works were aimed at enhancing the comfort properties of the fabrics and garments along with various functional finishes by improving 'use' value, enhancing 'esteem' value and imparting 'gimmick' values. Nowadays, due to increasing awareness on the global warming and carbon footprint, the use of the sustainable finishing processes with natural ingredients is increasing in every stage of fabric and garment processing. Accordingly, various stages of manufacturing processes undergo continuous changes to ensure environment-safe, customer-safe products with minimum or no damage to the environment.

2 Roadmap of This Chapter

In this chapter, the following sustainable finishing processes are discussed.

- Bioprocessing using enzymes
- Degumming of silk
- Plasma treatments for dyeing and finishing of textile materials
- Antimicrobial finish using natural herbals
- UV repellent finish
- Flame-retardant finish – natural green-based finish for cotton

3 Bioprocessing of Textile Materials

Enzymes are process and environment-friendly safe biocatalysts that can aid both preparation and finishing of textile materials like cotton, wool and silk. The use of enzymes in the various preparatory processes has been reviewed in the past by many researchers [1–3]. Thermophilic alpha amylase enzymes are capable of desizing starch based on size formulation to an adequate degree in a short duration (1 minute) in a steamer [4]. Low-molecular-weight tamarind kernel powder-sized fabrics can be desized by cellulase steeping and cellulase padding methods [5]. Earlier malt-based enzymes were used in desizing and discontinued at later stages due to inconsistency in power and unstable nature at higher temperatures. With bacterial amylases, the desizing process can be accelerated considerably because of the higher working temperatures of the enzymes and higher stability in the presence of substrates. Bacterial amylases exhibit higher thermal stability and activity to achieve the most effective size removal. An attempt has been made to study [6] the complementary effect of the different enzymes, amylase and temperature stable lipase on the desizing and thereby facilitating the effectiveness in scouring operation.

It is suspected that amorphous pectins may also have an influence on non-absorbent characteristics of cotton since 85% of the carboxyl groups in the pectins are methylated. Pectin is a linear polymer having a molecular weight above 30,000 and up to 100,000, formed by a linear alpha (α: 4) linkage of D galacturonic acid residues statistically interspaced with rhamnose units. The insoluble Ca, Mg or Fe salts of pectin can be converted into soluble form by exchange of polyvalent cations with monovalent cations such as NH_4 and Na [7–9]. Pectinase, a multicomponent enzyme that differs in substrate preference, reaction mechanism and action pattern, is highly effective in depolymerizing vegetable pectins having varying degrees of esterification. The typical individual components of pectinases include pectin lyases, polygalacturonases and pectate lyases, which directly act on the glycosidic bonds within the pectic polymer chains, while pectin esterase hydrolyses the esters to create more sites for polygalacturonases and pectate lyases. Pectinase treatment results in the complete or partial removal of the cuticle or breakdown of the continuity of the cuticle [8, 10]. Comparisons have been made on the properties of alkaline pectinase and alkali-treated fibres [11], and combined effects of pectinases and proteases have also been discussed in the past [12]. Synergistic effects are obtained with combined treatment using pectinase and cellulase in enhancing properties like absorbency and wicking [11]. Influence of various yarn structures on the efficacy of enzymatic treatment [13] and effect of enzymatic treatment on different fibres and the handle values have been studied extensively [14]. Alkaline pectinase treatment does not degrade cellulose and so results in less weight loss in the process [15]. Bio-scouring using acid pectinases has also been reported in the literature [16], and the surface of pectinase-scoured fabrics appears clear compared to alkali-scoured samples, demonstrating the difference in their mechanism and fabric-safe treatments. A treatment that combines protease and lipase with pectinase enzymes could be expected to reduce the extractable impurities and residual pectin further with improved absorbency.

4 Degumming of Silk

Sericin in the silk forms a cementing layer on the surface of the twin filaments facilitating good adhesion to keep the filament intact. The gum present in the silk filament is chemically a non-filamentous protein because of which raw silk possesses neither lustre nor the softness that is commonly associated with silk. Besides fibroin and sericin, raw silk also contains other natural impurities, which include small amount of silk wax (0.4–0.8%), inorganic matter (0.7%), carbohydrates (1.2–1.6%) and coloured pigment (0.2%). The nature of pigment varies with the type of silk [17]. Colour and pigments in the domesticated silk appear prior to cocoon formation (yellow and green pigments) or 1 or 2 days after the cocoon formation (brown pigments), which is mainly decided by dietary nature of the worms. Degumming is defined as a process involving 'the removal of sericin (silk gum) from silk yarns or fabrics, or from silk waste prior to spinning at controlled conditions intended to have little or no effect on the underlying fibroin' [18–23]. Fibroin is water insoluble while sericin is soluble at elevated temperatures but swells in the presence of many chemicals [24]. The removal of sericin in degumming is a combination of various effects such as dispersion, solubilization and hydrolysis of different peptide linkages.

In 1918, Kanegurachi Cotton Co. used an enzyme obtained from a vegetable oil filter cake or from an animal body tissue known as proteolytic enzyme for degumming raw silk. Enzymes are used as the alternatives for alkalis, acids or soaps to preserve the physical properties, to uniform removal of sericin and to reduce the pollution levels [25]. The hydrophilic nature of sericin accounts for relative ease with which it can be solubilized during degumming and digested by proteolytic enzymes. Enzymatic hydrolysis of sericin proteins can be achieved using various types of enzymes, namely trypsin, chymotrypsin, pepsin, bacterial proteinases, papain, carboxypeptidase A & B, degummases and leucine aminopeptidase. Papain has been recommended for degumming of silk, and it preferentially hydrolyses the peptide bonds formed by the carboxyl groups of lysine and arginine, supplemented by soap treatment. Degumming of silk with papain requires the pre-treatment with hot water to swell the sericin. Papain is sulphydryl enzyme and is active at 70–90 °C and pH of 5–7.5, whereas the bacterial enzyme alcalase is active at 60 °C and pH of 9 [26]. Because of wide specificity, papain removes most of the protein substrates extensively compared to trypsin. It also hydrolyses derivatives of glutamine, histidine, glutamic acid, leucine, glycine and tyrosine [27]. In the case of highly twisted yarns, proteases fail to remove the sericin completely, which can be enhanced by mechanical agitation, ultrasonication [22, 28, 29]. A combination of lipase and protease has also been tried for degumming [29, 30] in which lipase is capable of hydrolysing waxes into fatty acids and alcohols and provides positive effects on wettability.

5 Plasma Treatment

Water-free processing, solvent-assisted processing and low-wet pickup processes have been tried to reduce the pollution load created in the wet processing with varied levels of success. Plasma treatments can be carried out on thin films, natural fibres, man-made fibres and fabrics produced from various fibres and blends. Plasma treatment offers eco-friendly, water-free processes in many cases, to the existing range of various wet processing methods. Plasma is considered as the fourth state of matter, after solid, liquid and water, and it contains ionized gas comprising ions, electrons, atoms and molecules [31, 32]. Plasma was identified by Sir William Crookes as early as in 1879; however, 'plasma' was applied to ionized gas only in 1929 by Irving Langmuir [33].

In the gaseous substance, if the collisions between particles of matter, caused by very high temperatures, increase then the initial gaseous state comprising neutral molecules or atoms develops into an ionized state with an equal density of positive-

Table 1 Types and characteristics of plasma [33]

Type of plasma	Requirements	Characteristics
Glow discharge	Formed by applying direct current (DC), microwave (50 Hz), RF (40 kHz, 13.56 MHz) over a pair or series of electrodes	Produced at low pressure Offers highest possible uniformity and flexibility
Vacuum glow discharge	Microwave (GHz) power supply	Produced at low pressure Offers highest possible uniformity and flexibility
OAUGDP[a]	RF frequency	Uniform active species, high average concentration
Corona discharge	Formed at atmospheric pressure Using low frequency or pulsed high voltage over an electrode pair	Corona consists of small lightning-type discharge Non-homogeneous, high local energy levels
Dielectric barrier discharge, filamentary	Formed by applying a pulsed voltage over an electrode pair with one covered by a dielectric material	Lightning-type discharges are created Provides uniform treatment

[a]*OAUGDP* One Atmospheric Unit Glow Discharge Plasma

and negative-charged particles. Presence of free electrons makes plasma electrically conducting, responding to the electric and magnetic fields and can also be an efficient sources of radiation. The plasma modifies the surface of the fabric by the bombardment with high-energy electrons and ions. The combinations of the gases are used to achieve better process performance and flexibility in the processing methods [33]. Various types of plasmas used in the alteration of the properties of textile materials are listed in Table 1.

The classification systems of plasmas dwell on temperature, pressure, type of current used and type of gas used [31–35]. The two broad categories, on the basis of temperature, of plasmas include hot plasmas and cold plasmas. Table 2 shows some of the typical applications of the plasma technology and the related effects obtained in the substrates [33–35].

5.1 Plasma Processing for Dyeing and Finishing

Surface modification of textile materials to create a reactive surface suitable for dyeing and finishing treatments has been attempted by many researchers [36–40]. The exhaustion levels of raw cotton fabric pre-treated with corona show the similar values as that of bleached fabrics. Formation of carboxylic acid groups within the cuticle layer was suggested and also an increase in surface acidity. However, such increase in exhaustion is impaired with the addition of ionic or non-ionic wetting agents. Corona-treated fabrics tend to be darker in colour than the untreated samples with deviations in chroma and hue mainly due to differences in the initial undyed

Table 2 Plasma applications and their effects on substrates [33]

Process	Nature of process	Effects obtained
Alteration of surface energy	Alters chemical nature of surface by active species, embedding or removing of charges	Wettability, wickability, printability, dyeability, washability, functional applications
Alteration of cohesive properties	Increases surface-to-surface contact cohesion, increases 3D cross-linkages among fibres	Cross-linking of polymers, washability, handle modification
Alteration of adhesive properties	Adhesion, surface energy is increased by active species plasma. Adhesion results from combination of mechanical, chemical, electrostatic, permeation, diffusive, surface roughness, micro-profile contributions	Painting of surfaces without volatile organic chemicals (VOC), composite structures, medical applications
Alteration of electrical characteristics	Increases surface conductivity, embeds or imparts electrostatic charges and deposits on the surface	Antistatic finish, charging and discharging action in photocopying, filtration, breathing masks, charge embedding in non-wovens
Alteration of surface finish	Results in microscopic physical damage, removal of adsorbed monolayers, inducing chemical reactions	Adhesion of liquids/adhesives, etching, scratch resistance, altering optical characteristics
Altering bulk properties	Changes occur due to change in surface energy and/or cohesive properties in microscopic scale	Modification of tensile and compressive strength, elasticity, density, hand
Removal of microorganism	Environmental stresses, physical/chemical disruptions	Sterilization, disinfection, cleaning and antisepsis

substrates. However, no significant difference was observed in the fastness values. In printing, the corona helps to improve the binding among fibre-binder-pigment system, which is responsible for increase in wet/dry rubbing fastness [33, 37].

Hydrophilization has been carried out on cotton using radio frequency plasma at 20 kHz with power of 0.64 W/cm^2 and pressure of 0.6–8 mbar to reach the saturation of hydrophilization [41]. Hydrophilization increases with penetration depth and velocity of penetrating front. The effect of plasma treatment on fabrics made of various fibres and the relevant results are detailed in Table 3.

In the case of water repellency fluorine content, the ratios of F/C, F/O control the effect obtained in the process, which appears to be higher for C_3 F_6. The effective plasma time appeared to be 10–15 minutes. Surface resistivity of the samples after plasma treatment reduces due to the presence of polar groups on surface of cotton fibres and the formation of voids and cracks, which also influences electrical conductivity. An attempt has been made to compare the repellency effects obtained by the conventional repellent-finished fabrics and the fabrics treated with CF_4, C_3F_6 plasma, where plasma-treated fabrics showed better repellency and zone inhibition against microbes [33, 40].

Table 3 Effect of plasma finishing on various fabrics

Fibre	Process	Gas	Effect	Results
Cotton	Hydrophilicity and wettability (RF plasma)	Air–O_2	Weight loss, increase in C=O, COOH contents, increase in vertical wicking	Strong etching
		Air–O_2		Generates greater changes in fibres
	Hydrophobicity (RF plasma)	CF_4, C_3F_6	Lower results for CF_4 than C_3F_6	C_3F_6 polymerizes by plasma and plasma-inducing methods. CF_4 yields plasma polymerization, atomic fluorine only
Linen	Wicking (RF plasma)	O_2–Ar	Weight loss, etching effects, wicking rate decreases under all conditions	No significant effects on prolonged exposure but causes degradation
Flax	Topographical study (RF plasma)	Ar, O_2	Etching of surface and revelation of fibrillar structure	O_2 plasma shows faster rate, bigger micropores, shrinkage
Wool	Hydrophilicity (RF plasma)	Water vapour	Removal of fatty layer, generation of hydrophilic groups	Epicuticle is removed
	Shrink resistance (glow discharge)	O_2	Felting decreases, becomes shrink resistance, alkaline solubility increases and dyes faster	Micropores and cleft created. Subsequent enzyme treatment enhances handle and dyeability
BOPP[a]	Increased surface energy and wettability (RF plasma)	O_2	Formation of new groups like –OH, –C=O. Surface energy increased from 24 to 71 mJ/m^2	Creation of surface roughness, loss of hydrogen, appearance changes due to low reflectance
Nylon	Water repellency (RF plasma)	CF_4	Absorption of F atoms on surface	Air resistance and glossiness improves

[a]*BOPP* biaxially oriented polypropylene film

Grafting of flame-retardant monomers has been successfully carried out on the cotton fabrics to obtain durable effects than that is possible with conventional surface deposits [33, 42]. Acrylate monomers containing phosphorous diethyl acryloyl-oxy-ethyl phosphate, diethyl-e-methacryloyl-oxy-ethyl phosphate, diethyl acryloyl-oxy-methyl phosphate and dimethyl –acryloyl-oxy-methyl-phosphorate have been successfully grafted with air plasma. Phosphoramidates result in the limiting oxygen index values up to 29.5. Development of self-cleaning cotton textiles through RF plasma, MW plasma and UV radiation to introduce functional groups to anchor TiO_2 on textile surface shows the formation of TiO_2 crystallites with 5–7 nm size immediately from the precursor [33, 38].

Plasma treatment offers effect which is often decaying in nature, that is, ageing or durability effect. The effects produced by plasma decrease over a period of time, unless special measures are taken in the selection of gases [33].

6 Anti-microbial Finish

Textile materials, next to the human body, provide an ideal living environment for bacteria, yeast and fungi. Bacteria such as *S. epidermidis, S. aureus* and *Corynebacterium* sp. are found in the human skin and *Staphylococcus*, *coryneforms*, micrococcus bacteria have been isolated from head, arms and legs of the human body. Human body consists of two types of sweat glands, namely eccrine glands, which are distributed over the surface of the body whose secretion is inhibited by atropine, and apocrine glands, which develop from the hair follicle and are found mainly in axillae. Contamination of the skin in the form of faeces and urine and other body effluents, burns and diaper rash on the skins of infants promote the microbial growth. Over 75% of foot infections were attributed to the dermophytic fungi, *Trichophyton interdigitale* and *Trichophyton rubrum*, which multiply in socks [43] while using. Laundering methods are not efficient in removing these athlete's foot fungi from the socks, which indicates the possibility of the cross infection.

The speedy growth in the textile industry has created many opportunities for variety of innovative finishes to address the discomfort that might arise due to the growth of microbes, in terms of dope addition, topical treatment like coating and lamination. In today's world, naturally renewable resources are increasingly required as a result of human efforts to protect the environment. The definition of various terms and the agents related to antimicrobial and antimicrobial finishes is extensively dealt by many authors like antimicrobial agent, bacteriostat, bactericide, disinfectant, sanitizer and detergent sanitizer. The broad classification of various agents includes antibacterial agents – substances effective against bacteria, antimycotic agents – substances effective against pathogenic fungi, and antivirus agents – substances effective against viruses. The USFDA definition of antimicrobial agents applies only to products for topical application to living tissues.

Antimicrobial fabrics have its large acceptance as surgical clothes, undergarments, baby clothing, etc. Antimicrobial finishing treatment is now extended to the traditional clothing and home textiles. The antimicrobial agents kill or inhibit the growth of pathogens and control their effect. The natural fibres like cotton get easily attacked by the microbes, because of the presence of carbohydrates in the fibres. Antimicrobial-finished fabrics have wide variety of applications in sports clothing, footwear, medical textiles, furniture, automotive textiles, intimate apparels, etc. The presence of microorganisms in the fabrics causes unpleasant odour and staining and also causes health problems. Microbial infections cause inflammation, allergy and skin diseases and, therefore, the garments which are worn next to the skin require antimicrobial finish.

Currently, many synthetic antimicrobial agents are banned according to the United States and European standards, and there is an increasing demand for eco-friendly antimicrobial textiles based on natural antimicrobial agents such as chitosan, which do not cause any harm to the wearer on long-term usage of such materials. Different plants such as papaya, aloe vera, neem, banana and hemp extracts can be used for the purpose of imparting antimicrobial finish to the fabrics. Many plants contain the compounds such as tannin, flavonoids and terpenoids which are responsible for antimicrobial activity on application. They have the potential to exhibit both bacteriocide (which kills the micro-organism) and bacteriostatic (which inhibit the growth of micro-organism) effects. There are various natural antimicrobial agents available, but limited studies have been carried out for their antimicrobial activity on to the textile materials.

1. *Papaya (Seed and Leaf)*

    The papaya seeds and leaves are collected and dried in shade for 15 days and ground to powder form using a mortar. Five grams of powder is mixed in 100 mL of distilled water or solvent extracted using 70% methanol. The solvent extract is kept in the water bath for 1 hour at 40 °C. The extract is then filtered using filter paper to reduce the volume to 10%, and the filtrate is ready for the applications [44].
2. *Aloe Vera*

    Aloe vera gel is collected and dried in the air-dry machine at temperature 50 °C for 3 hours, and the dried gel is soaked with methanol for 1 week and filtrated using filter paper. Bleached cotton fabric is dipped in the extract for 5 minutes and it is padded. The treated fabric was dried at 80 °C for 3 minutes and cured at 110 °C for 2 minutes [45, 46].
3. *Neem*

    The methanolic extract is carried out using the neem leaf powder and it left for 48 hours. Then, the methanol was evaporated using rotary evaporated. The extract can be applied on to the fabrics using dip and padding techniques [47].
4. *Banana (Leaf and Peel)*

    Banana peels are cut into small pieces and boiled in a 1-L solution of 0.1% NaOH. The solution is filtered using filter paper, and the extract is collected. The banana peel extraction is used in the dyeing bath at 80 °C for 90 minutes under continuous stirring. After the treatment, the fabrics are washed with water and air-dried [48].
5. *Mango*

    Leaves of mango tree are collected and washed thoroughly with water, dried under direct sunlight and ground to fine powders. The extraction is carried out using aqueous method at 98 °C for 60 minutes. The extract is filtered using filter paper, and the application of extract can be carried out at 80 °C for 60 minutes using the material-to-liquor ratio of 1:50 to obtain antimicrobial properties [49].
6. *Pomegranate*

    Pomegranate rinds are collected, dried for 3 days and ground to fine powders. Ethanolic extraction of pomegranate rind powder is carried out, and the extracts are collected and dried using rotary vacuum evaporator. The application of extracts on fabrics is carried out for 30 minutes at 80 °C using material-to-liquor ratio of 1:30 [50–52].
7. *Combinations of Various Sources*

    (i) *Pomegranate + Onion*

Peels of onion and pomegranate are collected, shadow dried and crushed for extraction. Ten gram of the powder is soaked in 100 mL of distilled water in a round bottom flask for overnight. The extraction is carried out using soxhlet extractor and concentrated using the rotary evaporator at 50 °C [50].

(ii) *Neem + Aloe Vera*

Aloe vera gel was extracted by removing the outer layers of leaves and smashed for 90 minutes and then filtered. Neem leaves are collected and dried and ground to fine powders. Then, the methanolic extraction is carried out, and the extracts are collected to treat the fabrics at 80 °C for 30 minutes [47].

(iii) *Tulsi + Turmeric + Neem*

One gram of powder of each plant is taken and added to the distilled water. One percent of chloroform is added to each in the distilled bath and allowed to dissolve for 24 hours. The solution is then filtered using filter paper, and filtrate is applied to the fabric by pad-dry-cure method using the material-to-liquor ratio of 1:20 [53].

Although the plant sources are non-toxic and eco-friendly, there is difficulty in achieving the wash durability after the application. The other challenges faced in the application of antimicrobial finish are the availability of plant in bulk, their extraction and their purification methods. The function of the finish also varies depending on the maturity level of the plant, their geographical location, fabric applied, etc. The disposable materials like surgical cloth and bandage which are not washed may be treated with direct application method like pad-dry-cure method, while encapsulation, resin treatment can be used for better durability in the case of applications where the final products are washed multiple times. An effective study was regulated to evaluate the plant extracts both qualitatively (AATCC-147) and quantitatively (AATCC-100) for their antimicrobial activity. Although the plant extracts have shown antimicrobial activity, the vital issue is the wash durability. The durability of antimicrobial fithe plant extracts have shown antimicrobial activity, the vital issue is the wash durability. The durability of

7 UV Protection Finish

Ultraviolet rays in the solar spectrum constitute very low fraction but highly influence all the living organisms on the earth and their metabolism. An appropriate amount of sun bath promotes circulation of blood, invigorates metabolism and improves resistance to various pathogens. Penetration of UVR in top layer of the skin leads to damage in the lower layer. This produces premature ageing of skin with other effects, which may include roughening, blotches, sagging and wrinkles. The most common type of skin cancer is squamous cell and basal cell cancer, which is usually removed by excision or topical treatments. The solar energy in this UV

Table 4 Characteristics of solar spectrum

Wavelength region (nm)	Classification	Radiation intensity (W/m^2)	Radiation intensity (%)	Mean photon energy KJ/mol
280–320	UV B	5	0.5	400
320–360	UV A	27	2.4	350
360–400		36	3.2	315
400–600	Visible region	325	51.8 (up to 700 nm)	240
600–800		255		170
800–1400	IR radiations	329	42.1	110
1400–3000		143		55

region comprises about 5–6% of the total radiation incident on the earth, and the quantum energy of UV radiation is of the order magnitude of the organic molecules bond energies [54–56]. Table 4 shows the solar radiations and the mean photon energy of the radiations [57–60].

In solar spectrum, the fraction up to about 175 nm is absorbed above the stratosphere and the radiation up to 280 nm is intercepted in the ozone layer of the stratosphere. Stratospheric ozone has minimal effect on UVA, but greatly attenuates UVB transmissions. UVC radiation in the range of 100–280 nm is hazardous to the skin and eyes, and the most harmful UVR is UV-B peaking in the range of 310–300 nm [61–68]. The relationship between skin cancer incidence and UV dose is well correlated, and many researches have been carried out to assess the impact of the UV rays on various living organisms especially humans.

The human skin is the body's largest organ and acts simultaneously as an interface and a barrier against with the environment, and UV light is completely absorbed by the epidermis and corium. UVA rays cause transformation of melanin precursors-rapid pigmentation in few hours, which is not long lasting. These radiations penetrate into the skin, causing ageing, leading to loss of elasticity and folds. UV-B rays, the shorter wavelength, can penetrate only a few millimetre into the skin, but cause relatively stable pigmentation, which accumulates in the outer skin (epidermis). The liberation of active oxygen molecules by UV-B rays causes damage to the skin (skin burn). Though UVB is a relatively small fraction of total UV radiation (~10% total), it appears to be the major cause for erythema, sun tanning, photo carcinogenesis and photo ageing, which penetrates less deeply into the epidermis than UVA radiation. Overdose of UVA results in skin ageing acceleration, photodermatosis (acne), while over dose of UVB results in acute chronic reactions and damages like skin reddening (erythema) or sun burn, eye damages (conjunctivitis and opacification of the cornea). Higher dose of UVB causes DNA damage at the molecular level of the fundamental building blocks, single-strand breaks and the shape of the DNA changes, which cannot be read by the protein building enzymes as a result, distorted proteins can be made or cells can die.

UV rays falling on textiles are partly reflected, absorbed and partly transmitted through the interstices between warp and weft yarns and also through the fibres [2], and optical porosity of a fabric limits the potential of a fabric to provide protection against UVR. At low ultraviolet protection values, fabrics provide less protection than expected from the test results. Many commercial products and processes have been developed to produce fabrics with high level of UPF using various dope additions and topical applications for almost all types of fabrics produced from cellulosic fibres, wool, silk and synthetic fibres [62, 63, 66, 69, 70]. Most of the commercial products have the compatibility with the dyes and other finishing agents applied to the textile materials, and application of these agents can be carried out using simple padding, exhaust method, pad-thermofix and pad-dry-cure methods [57, 71–74].

Extracts of natural products like green tea, black tea, curcumin, silymarin, soy, *Pongamia pinnata,* grapes, nuts, carrot, tomato and papaya have been reported to exhibit UV protection properties [75–78]. Extracts obtained from the seeds of *Vitis vinifera*, *Silybum marianum*, *Pongamia glabra*, *Glycine max* and their effectiveness of UV protection have been reviewed recently. Leaf extracts of *Mentha piperita*, *Azadirachta indica*, *Ocimum sanctum* and *Aloe vera* exhibit marginal protection against UV rays in the range 290–320 nm [77]. However, there is a long way to go before these products are commercialized for textile applications.

8 Flame-Retardant Finish

Among the various functional finishing processes, flame retardant plays a vital role for saving the life of the human beings [79]. Synthetic fibres are widely used in flame-retardant finishes, but the synthetic fibres exhibit poor biodegradability. Various natural fibres like cotton, jute, flax, hemp and sisal are used as renewable materials for flame-retardant fabrics and, moreover, these fibres are partially or fully recyclable. Natural fibre composites have replaced the carbon, glass and other man-made fibres in the applications on flame-retardant materials, and substantial work has been done on flame retardancy on cotton fabric to increase its efficiency. Inorganic salts, urea, diammonium phosphate, boric acid and borax are widely used flame retardants for cotton and other cellulosic fibres as non-durable finishing agents [80–82]. The susceptive nature of the antimony- and halogen-containing flame retardant has been questioned for its use [83] as flame-retardant agents. For the past 50 years, phosphorous- and nitrogen-based flame retardants reported high effectiveness due to their synergistic effect [83]. However, when these compounds are applied in acetic conditions on cotton fabric, the tensile and tear strengths are reduced and the fabric becomes stiffer.

The first patent on flame retardant of canvas and linen materials can be traced back to the year 1735, where borax was used as the flame retardant [84]. Still, borax is used as flame retardant for non-durable finishes on cotton and cellulosic materials. The period 1950–1980 was called golden period of flame retardants as most of the durable flame retardants were developed during that period, while during the period 1980–2000, very little new research has been carried out. In this period, researchers mainly concentrated on refining the earlier chemistry and optimizing the efficiency of various products. Since 2000, a wide range of cost-effective, environmentally friendly, sustainable flame retardants were developed. Bromine containing flame retardants producing the high char flame retardants. The combustion of cellulose involves two distinct phenomena, flaming and glowing. The direct oxidation of cellulose is normally a slow process described in glowing, whereas in flaming, a complex process consist of solid and gas phases. In endothermic process, heat is evolved during the starting stage and initiate the burning of cotton fabrics. Early-stage, coating theory was adopted in flame retardants and it was believed that the film acts as a barrier for the oxygen to enter into the fabric/fibres for flame propagation.

Pyrolytic degradation of cellulose occurs both at lower temperatures of 200–280 °C and at higher temperatures of 280–340 °C. Gradual degradation, which includes hydrolysis, depolymerization, oxidation and dehydration, occurs at lower temperatures. The degree of polymerization decreases during pyrolysis and reaches the value 200, while rapid volatilization of moisture takes place at higher temperatures at above 280 °C leaving a charred residue. Cellulose of cotton can react with oxygen present in the air to form pyrocellulose or oxycellulose in addition to weight loss due to desorption of moisture [85]. On further heating, the pyrocellulose or oxycellulose decomposes into water, carbon monoxide and carbon dioxide and the flame propagates.

The two main flame retardants that are dominating finishing of cotton, and its blends are Tetrakis hydroxyl methyl phosphonium chloride (THPC) and N-methylol dimethyl phosphonopropionamide derivatives. The World Health Organisation has reported that formaldehyde are carcinogenic in nature, and if you burn halogen-based flame retardant at lower temperature, it releases dioxins. So the use of formaldehyde- and halogen-based flame retardants is limited. Zongyue Yang reported the use of formaldehyde- and halogen-free flame retardants for cotton with two-step process [86]. In his process, cotton is first treated with cross-linking agents, normally a small unit of polymers or oligomers with two or three reactive groups, and then the application of the active phosphorus-based multifunctioned flame retardants. The flame retardant based on phosphorus can react with oligomers or polymers previously applied on cotton fabric with insoluble network, thereby producing a durable flame-retardant finish with no sign of formaldehyde and halogen. This finish gives better flame retardancy and degradation starts only at 240 °C that results in the char yield of 36.5 weight % at 500 °C [86].

9 Sustainable Natural Green Flame Retardants for Cotton

Flame retardants based on biomacromolecules like nucleic acid and proteins produce environmentally safe and sustainable flame retardants for cotton materials. When the intumescent material of a complex double helix of deoxyribonucleic acid (DNA) is subjected to a low heat, it produces a multi-structured carbonaceous shield, normally called char [87–89], over the surface and forms a physical barrier for the transport of oxygen, heat and fuel between the polymer and flame. This intumescent compound (DNA) has three components: acid source, normally a polyphosphate or ammonium phosphate, that releases phosphoric acid when decomposed with heat; a carbon source (saccharides and polysaccharides, cyclodextrins, pentaerythritol, etc); and a blowing agent, normally melamine and guanidine, etc. On heating, it releases excessive amount of non-combustible gases like carbon dioxide, ammonia and water vapour [90]. Alongi, based on the LOI and calorimetry tests, confirmed that the DNA-based flame retardant supports the good flame retardancy [90]. Alongi developed the another sustainable green flame retardant based on hydrophobins or casein that is free from formaldehyde and halogen for cotton materials. This method is the alternative for green flame retardant described in his paper in 2014. It shows good flame-retardant activity on cotton fabrics by changing the resistance of heat flow [91].

10 Conclusion

The uniformity of dyed materials lies in the efficiency of fabric preparatory processes. The natural and added impurities have to be removed thoroughly from the fabrics to achieve uniform absorbency throughout the fabrics. Many factors exert significant influences upon the path of technological developments in the wet processing, and some of the factors include comparable quality with existing process with/without value addition, chemical compatibility to provide multi-functional process, cost reduction by minimizing the use of energy and water, increased levels of process control, monitoring and automation, eco-friendly application methods, etc. Dyeing and finishing of fabrics and garments, on outside, appear to be highly attractive, but both the processes demand great deal of care in preparation and also during the processes. Value-added rejections arising out of these processes slow down the commercial acceptance of both the processes. Developments that take place in other branches of engineering and technology are also effectively utilized in various processes of textile processing to meet such requirements.

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Cellulose Textile Colouring with Clay Particles – An Enviro Safe Process

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Abstract Today, eco-friendly products are in great demand. In the current scenario, there is a necessity for an innovative natural dye to replace the harmful chemical dyes and for reducing the toxic dye effluents. Clay is a natural coloured material which is available in abundance and is used primarily for agriculture and in pottery industry. An attempt has been taken in the work to impart colour to cellulosic textiles using clay-based natural dyes. Different types of soils were sourced and red soil was found to be suitable due to its easy availability. Being a new process development, the first phase involved selection of suitable mordant and fixing agent for the dyeing process. In order to choose suitable fixing agent and mordant, the dyeing process was carried out with various fixing agents like citric acid and poly vinyl alcohol and mordents such as soy milk, myrobalan, stannous chloride and ferrous sulphate. The dyeing performance was analysed by assessing the depth of shade using spectrophotometer. Citric acid and stannous chloride were found to give better results when compared to the other fixing agents and mordents. Further to assess the influence of temperature, time and pH on the dye uptake and fastness characteristics, three levels of temperature, time and pH were selected: 30 °C, 60 °C and 90 °C; 60 min, 90 min and 120 min; and 2, 3 and 4 respectively. The experimental design was developed using Box-Behnken design and 15 samples were developed. The colour strength (K/S), fastness characteristics to washing, rubbing, light and perspiration (acid & alkali) were analysed. The result proved that the clay based dye possesses good fastness properties. The processing conditions were optimised with the help of contour plots.

Keywords Clay · Effluents · Fastness properties · Fixing agent · Mordants
Natural dye · Soil

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1 Introduction

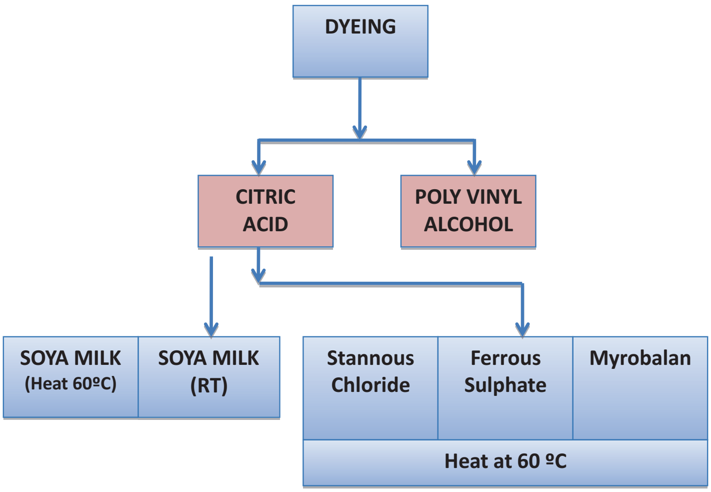
Currently, in the twenty-first century, the market for natural dyes in the fashion industry is experiencing resurgence. The extensively and commercially used synthetic dyes result in imparting strong colours but are carcinogenic in nature [1]. Almost all the countries in the world started banning hazardous synthetic dyes. Natural dyes are dyes or colorants derived from plants, invertebrates and minerals. The types of natural dyes currently in use by the global apparel industry include the pigments extracted from turmeric, marigold flower, tea, pomegranate, myrobalan, madder roots, indigofera plant, etc. Certain problems with the use of natural dyes in textile dyeing are colour yield, complexity of dyeing process, reproducibility results, limited shades, blending problems and inadequate fastness properties [2]. These issues can be overcome with the use of chemicals called mordants. Mordants are metal salts which develop an affinity between the fabric and the dye [3]. Mordants form a link between the fibre and the dye, which allows certain dyes with no or little affinity for the fibre to be fixed [4]. The chemicals that are commonly used by researchers for natural dyeing are ferrous sulphate, citric acid, stannous chloride, poly vinyl alcohol, alum, chrome alum, soy milk, potassium dichromate and copper sulphate.

Deo and Desai [5] conducted an experiment by dyeing cotton and jute fabrics with an aqueous extract of tea, containing tannins as the main colorant species. The dyeing was carried out with and without metal salts as mordants, using three different dyeing methods: pre-mordanting, meta-mordanting and post-mordanting. The resulting wash and light fastnesses of the dyed fabrics were good to excellent. The colour of the fabrics was investigated on computer colour matching system in terms of *K/S*, and CIELAB colour-difference values. Deep shades ($K/S = 3.9$) were obtained for jute in acidic media, while cotton fabrics got the medium depths ($K/S = 2.0$) under identical conditions of dyeing.

Kulkarni, Gokhale, Bodake and Pathade [6] experimented the natural dyeing of cotton using pomegranate peel extract. Use of natural dyes has increased several folds in the past few years due to the eco-friendly approach of the people. The research was concerned with the purification of natural dyestuff extracted from an abundantly occurring plant ‘Punica granatum’. The main colouring agent in the pomegranate peel is granatonine which is present in the alkaloid form N-methyl granatonine. Solvent extraction method was used for the extraction of the dye. The pomegranate peel dye was used for dyeing of scoured cotton cloth using two mordants-copper sulphate and ferrous sulphate in the ratios 1:1, 1:3 and 3:1. Dyeing along with mordanting techniques which included pre-mordanting, simultaneous mordanting and post mordanting was carried out. Study about fastness tests of dyed clothes was undertaken. Large range of shades was obtained with varying mordant ratios and combinations. The production cost of the pomegranate peel dye was also presented.

Sachan and Kapoor [7] optimised the extraction and dyeing conditions for traditional turmeric dye when applied on cotton, silk, and wool fabric using suitable mordant and fixing agent. They concluded that maximum yield was obtained while using solvent extraction method and purest dye was obtained through spray dyeing. The natural dyed fabrics are specifically tested for their fastness characteristics such as light fastness, dry rub fastness, wet rub fastness, wash fastness and perspiration fastness.

Clay is a generic term for an aggregate of hydrous silicate particles less than 2 µm (micrometres) in diameter. Clay consists of a variety of phyllosilicate minerals rich in silicon and aluminium oxides and hydroxides which include variable amounts of structural water. There are three main groups of clays: kaolinite-serpentine, illite, and smectite. The data on dyeing of textiles with clay are not available to a larger extent. According to Srinivasan [8], clay adsorption capacities are usually dependent on the net charges, large pore sizes and surface area. Generally, clays have exchangeable ions that play a crucial role in the environment by being natural pollutant scavengers by way of both cations and anions take-up through adsorption and ion exchange. Ions that are usually found on surfaces of the clay include H^+, K^+, Na+,Ca^{2+}, Mg^{2+}, NH^{4+} and Cl^-, SO_4^{2-}, PO_4^{3-} and NO^{3-}. Cation exchanges readily without affecting the clay mineral's structure. But this generalisation is not always the case because different physico-chemical variables like pH, temperature, pulp density, and point to zero charge also affect significantly the sorption capacity of clays [9, 10]. An attempt has been taken in this research work to impart colour to cellulosic textiles using clay-based natural dyes. Not only does clay dyeing result in beautiful colours, but the process itself is eco-friendly and sustainable. Clay dyeing avoids the use of synthetic dyes, thus eliminating the negative environmental impact of chemically manufacturing it. Many shades can be obtained by mixing and blending different clays together. This chapter discusses the suitable fixing agents and mordants required for colouring cellulose textiles using clay pigments and optimising the process conditions for obtaining good fastness properties. The process flow to fix mordant and fixing agent is as shown below.



2 The Dyeing Process

The grey cellulosic plain weave fabric is desized, scoured and bleached before pre-mordanting and dyed using clay-based natural pigment.

Different chemicals were used to find the suitable mordants and fixing agents for the dye process. Eight different samples using different suitable combinations of mordant and fixing agent were prepared and are illustrated in Table 1.

Depending upon the weight of the fabric, the required MLR of 1:50 is taken. It is allowed to boil till 90 °C and then the bleached cellulosic fabric sample is added; 5% of the mordant (soy milk/ stannous chloride/ ferrous sulphate/myrobalan) is added to the solution. It is heated for 1 h. The fabric sample is then rinsed and dried.

The fabric is soaked in soy milk for 45 min so that the soy milk spreads evenly on the surface of the fabric. The red soil and soy milk are mixed in the ratio of 1:8, respectively. The fabric is added to this solution; 5% of the fixing agent – citric acid – is added. It is then heated to 60 °C for 1 ½ h and kept at room temperature for 2 h. The dyed fabric is cured in a curing chamber. The fabric is then rinsed thoroughly and dried.

The eight samples were assessed for colour strength (K/S) using spectrophotometer, and the mordant and fixing agent used for the sample with highest colour strength value is selected (Fig. 1).

2.1 Process Optimisation

To assess the influence of temperature, time and pH on the dye uptake, an experimental design was developed using the selected fixing agent and mordant.

A Box-Behnken statistical design with 3 factors, 3 levels, with 15 runs was selected for the optimisation study. The experimental design consists of a set of points lying at the midpoint of each edge and the replicated centre point of the multidimensional cube. The independent variables and the experimental runs are listed in Tables 2 and 3, respectively (Fig. 2).

Table 1 Sample identification

Sample no	Dye	Fixing agent	Mordant	Temperature
1	Red soil	Citric acid	Soy milk	60°
2	Red soil	Citric acid	Soy milk	Room temperature
3	Red soil	Citric acid	Stannous chloride	60°
4	Red soil	Citric acid	Ferrous sulphate	60°
5	Red soil	Citric acid	Myrobalan	60°
6	Red soil	Poly vinyl alcohol	Stannous chloride	60°
7	Red soil	Poly vinyl alcohol	Ferrous sulphate	60°
8	Red soil	Poly vinyl alcohol	Myrobalan	60°

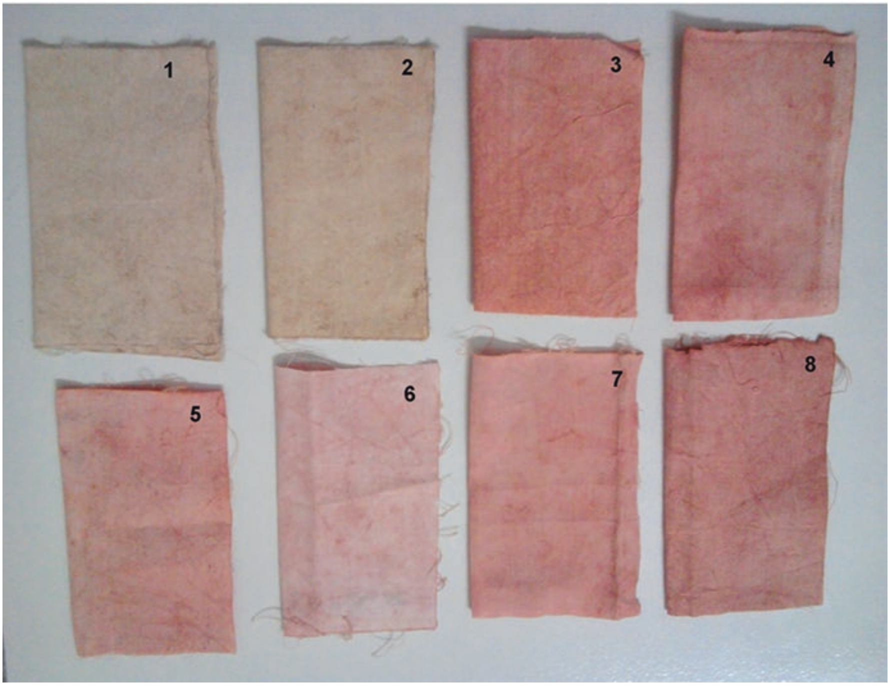


Fig. 1 Samples developed for choosing fixing agent and mordant

This pre-mordanting process is common for all the 15 samples. Depending upon the weight of the fabric, the required amount of water is measured and poured. It is allowed to boil till 90 °C and the bleached cellulosic fabric is added. Then, 5% of stannous chloride is added to the solution and boiled for 1 h and stirred frequently. The fabric is then rinsed and dried. The dyeing conditions used are as follows:

- MLR – 1:50
- Dye concentration – 20%
- Mordant – 5% stannous chloride
- Fixing agent – citric acid (concentration depends upon pH)

The concentrations of citric acid used for different pH values are as follows:

- pH 2 – 6% citric acid
- pH 3 – 4% citric acid
- pH 4 – 2% citric acid

The samples are dyed based on the experimental design on the above conditions.

Table 2 Variables and their levels in Box-Behnken design

Independent variables		Low	Medium	High
		−1	0	1
X1	Temperature	30 ° C	60 ° C	90 ° C
X2	Time	60 min	90 min	120 min
X3	pH	2	3	4

Table 3 Box-Behnken experimental design

Experiment no.	Temperature	Time	pH
1	60 ° C	60 min	2
2	60 ° C	60 min	4
3	60 ° C	120 min	2
4	60 ° C	120 min	4
5	30 ° C	90 min	2
6	30 ° C	90 min	4
7	90 ° C	90 min	2
8	90 ° C	90 min	4
9	30 ° C	60 min	3
10	30 ° C	120 min	3
11	90 ° C	60 min	3
12	90 ° C	120 min	3
13	60 ° C	90 min	3
14	60 ° C	90 min	3
15	60 ° C	90 min	3

2.2 Testing

The following tests are performed for the dyed samples (Table 4):

Effluent test was also done to ensure sustainable environment using the standard ISO 9050.

3 Results and Discussions

3.1 Selection of Fixing Agent and Mordant by Evaluating Colour Strength

The reflectance and colour strength (K/S) of the 8 samples are tabulated below (Table 5):

From Fig. 3, it is seen that sample 3 has higher colour strength of 0.305. The fixing agent and the mordant use for dyeing sample 3 were citric acid and stannous chloride, respectively. It was decided to use citric acid and stannous chloride for further experimental processes.

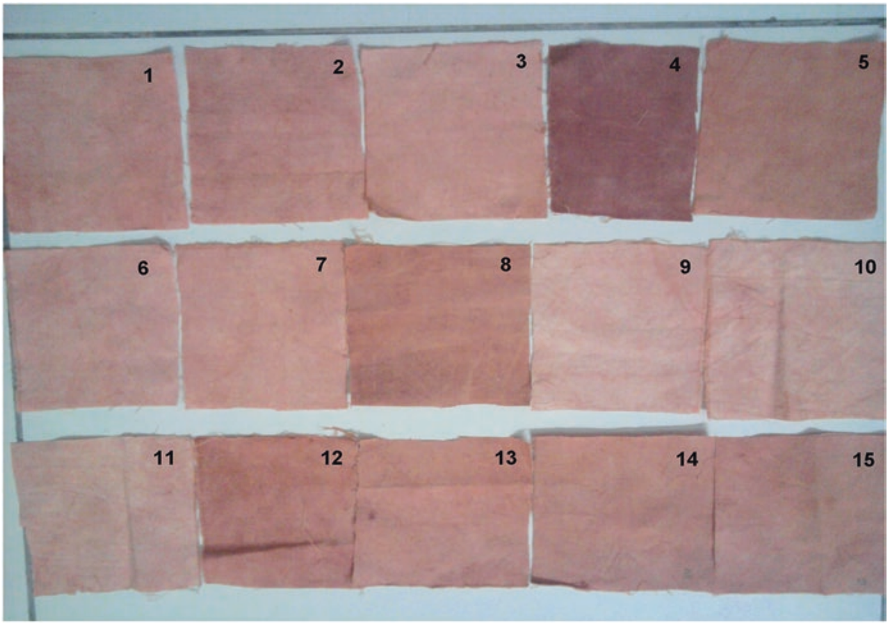


Fig. 2 Clay-dyed samples developed for process optimisation

Table 4 Tests performed

S. no	Tests	Standard
1	Wash fastness	ISO 105 C06
2	Rubbing fastness	ISO 105 X12
3	Light fastness	AATCC 16E
4	Perspiration fastness (alkali & acid)	ISO 105 E-04

3.2 Fastness Assessment

The samples were tested for their fastness characteristics such as wash fastness, rubbing fastness, light fastness and perspiration fastness (acid and alkali). The results of these tests are tabulated below (Table 6).

3.2.1 Wash Fastness Testing

The interactive effects of the dyeing parameters time, temperature and pH on the wash fastness characteristics of the dyed samples are presented in Fig. 4a–c.

Figure 4a–c represents the effect of time, temperature and pH on the wash fastness characteristics of the clay-dyed samples. It is observed from the interaction that as temperature and pH increase, the wash fastness decreases. Increase in temperature

Table 5 Colour strength

Sample no.	Reflectance	Colour strength (K/S)
1	57.613	0.156
2	56.162	0.171
3	49.487	0.305
4	55.565	0.111
5	52.858	0.210
6	62.691	0.098
7	52.594	0.229
8	51.346	0.231

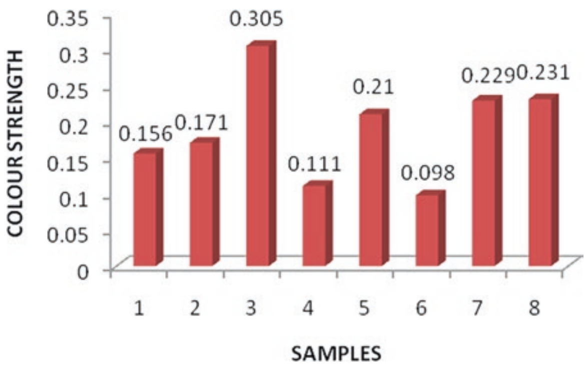


Fig. 3 Colour strength of the dyed samples

and pH resulted in absorption of more dye molecules resulting in deep shade of the dye and during wash, the dye molecule easily come out of the fabric, resulting in poor fastness.

Increasing the time made the dye particles to interact with fabric much better, resulting in good fastness to wash.

The regression equation depicting the effect of time, temperature and pH on wash fastness is as follows:

$$W = +3.0 + (0.15 * A) + (0.25 * B) + (0.2 * C) - (0.52 * A * B) + (0.25 * A * C) + (2.76\text{E} - 015 * B * C) - (0.25 * A^2) + (0.75 * B^2) + (0.12 * C^2)$$

Where

W = Wash fastness
A = Temperature
B = Time
C = pH

Table 6 Fastness test results

Sample no.	Grade				
	Wash	Rub	Light	Perspiration (alkali)	Perspiration (acid)
1	2	4/5	4	4/5	4/5
2	3	4/5	4	4/5	3/4
3	3	4/5	4	4/5	3
4	5	4/5	4	4/5	3/4
5	4	3/4	3/4	3/4	3
6	2	4/5	4	4	3/4
7	2	3/4	4	3/4	4
8	2	4/5	3	3/4	3/4
9	1	4/5	3/4	4	3
10	1	4/5	4	4/5	4/5
11	2	4/5	4	4/5	4
12	4	4	4	4	3
13	2	4	4	3/4	2
14	2	4	4	3/4	2
15	2	4	4	3/4	2

3.2.2 Rubbing Fastness

The interactive effects of the dyeing parameters time, temperature and pH on the rubbing fastness characteristics of the dyed samples are presented in Fig. 5a–c.

The interactive effects show higher rubbing fastness value at a higher temperature and time. From the above figure, it can be seen that the rubbing fastness increases initially with the increase in time and pH, while it tapers down with further rise in the conditions after which it increases again. It is also observed that as the both temperature and pH increase, rubbing fastness increases gradually.

The regression equation which gives the relation between the rubbing fastness and the independent variables is given below:

$$R = +4.0 + (0.125 * A) + (0.125 * B) + (0.0 * C) - (0.25 * A * B) \\ -0.5 * A * C) + (2.77556\mathrm{E}-017 * B * C) - (0.125 * A^2) \\ +(0.375 * B^2) + (0.125 * C^2)$$

Where

R = Rubbing fastness
A = Temperature
B = Time
C = pH

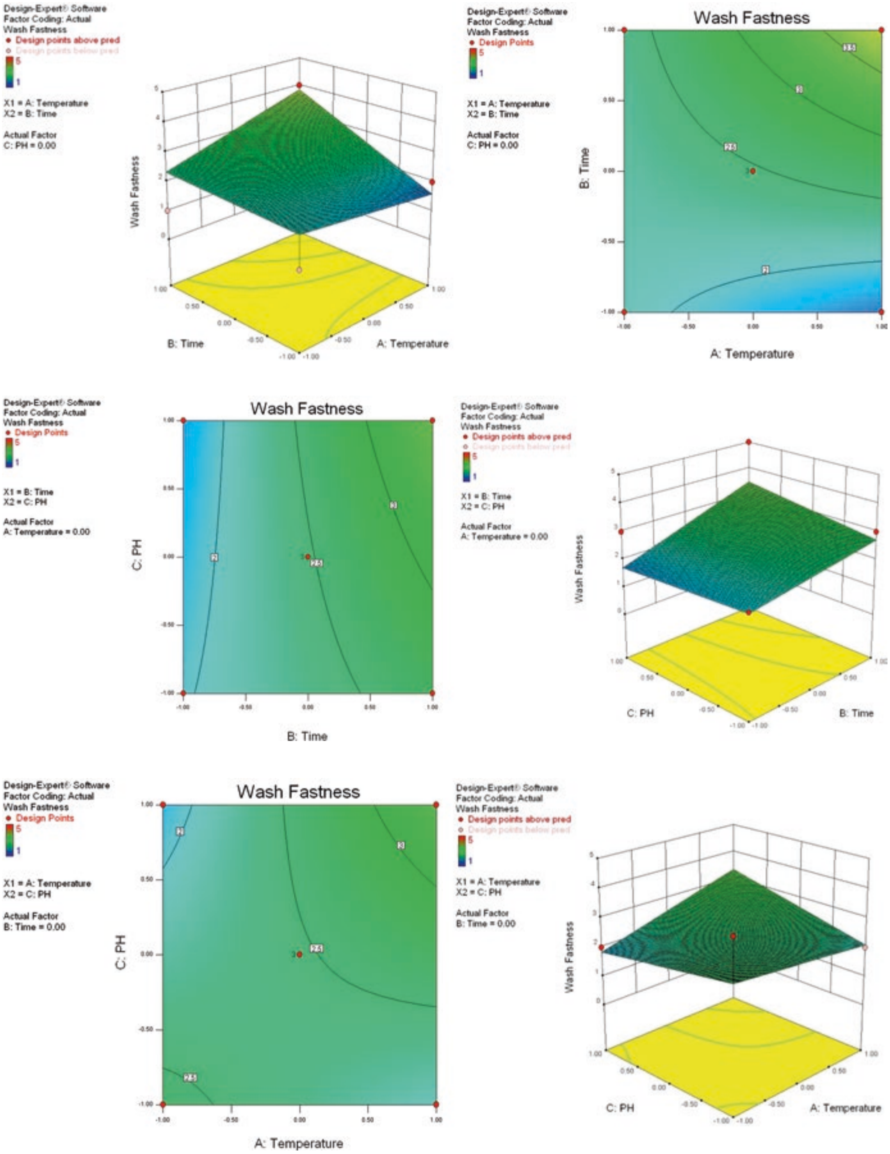


Fig. 4 (**a**) Interaction – temperature and time on wash fastness. (**b**) Interaction – time and pH on wash fastness. (**c**) Interaction – temperature and pH on wash fastness

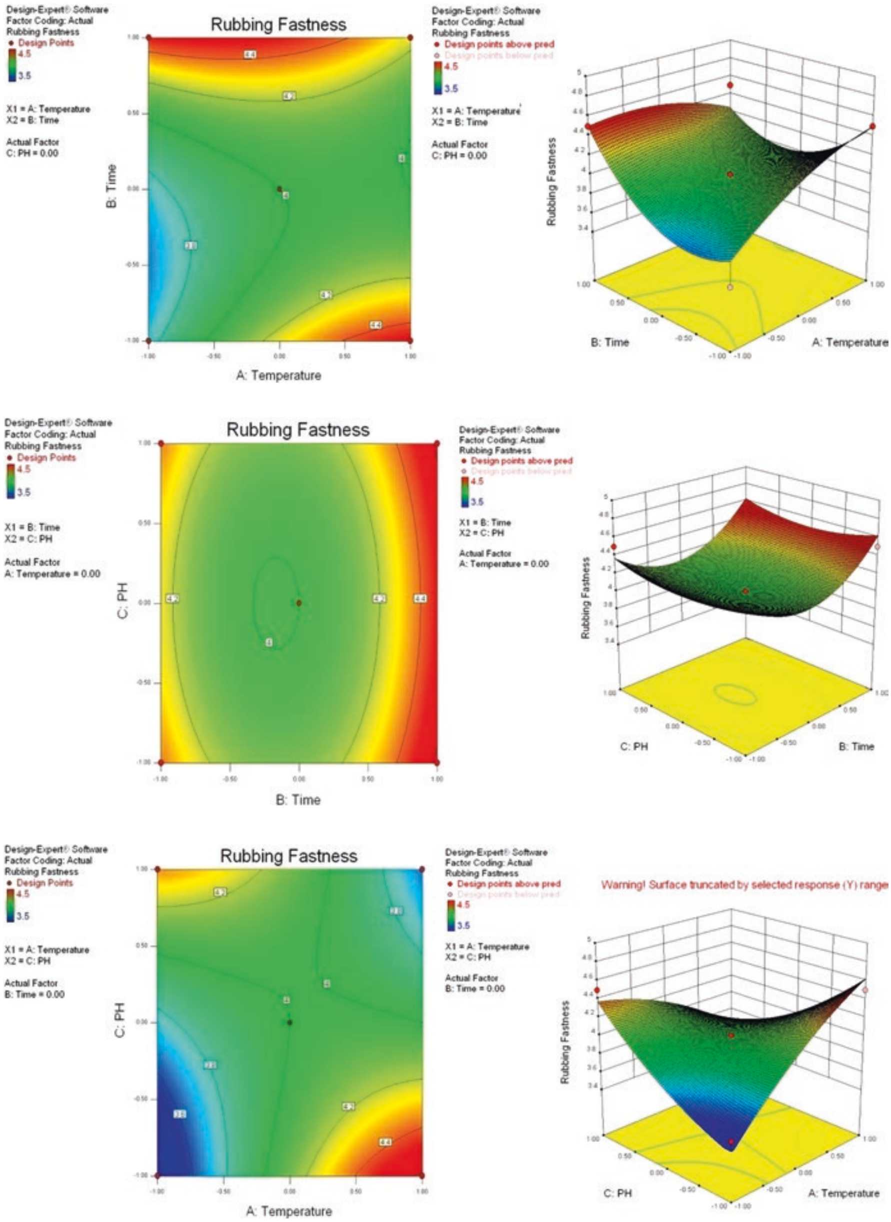


Fig. 5 (**a**) Interaction – temperature and time on rubbing fastness. (**b**) Interaction – time and pH on rubbing fastness. (**c**) Interaction – temperature and pH on rubbing fastness

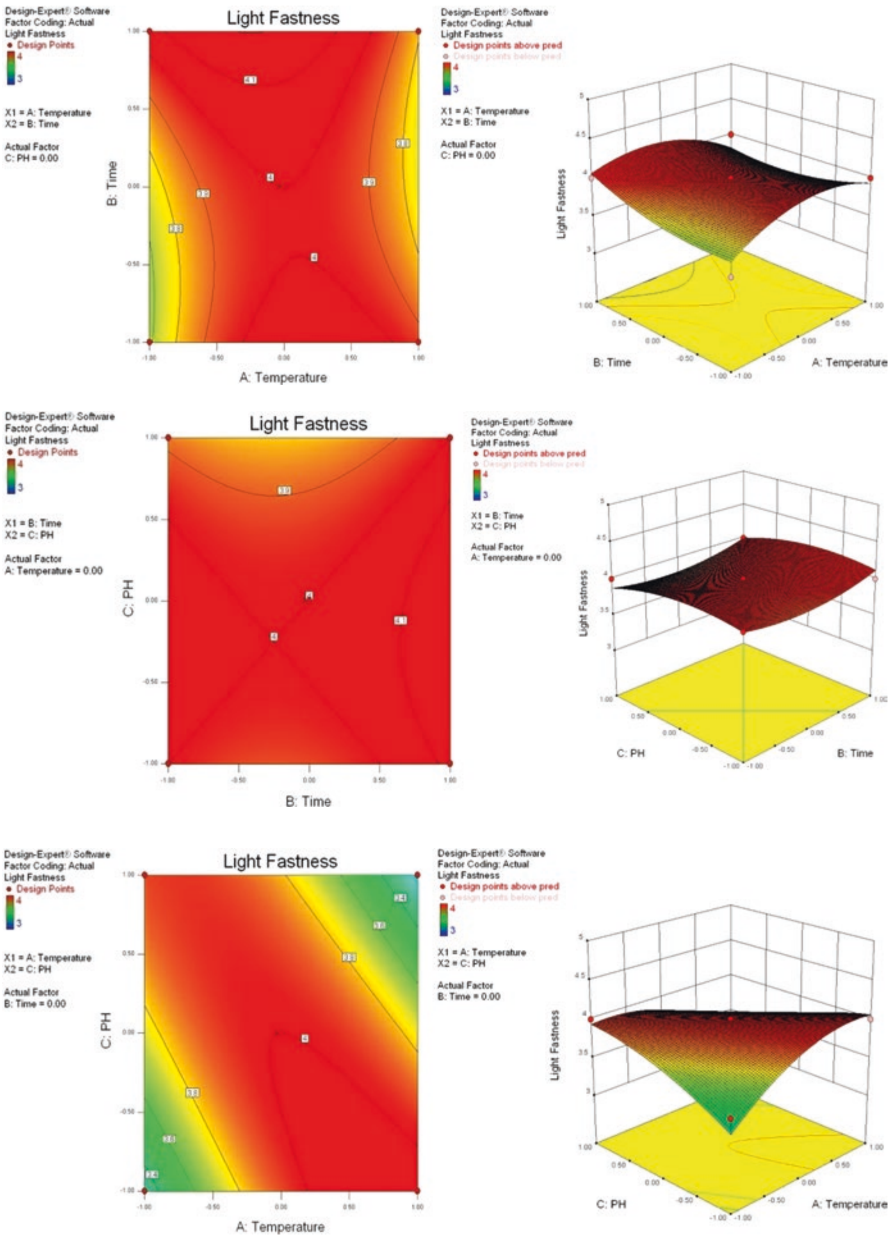


Fig. 6 (**a**) Interaction – temperature and time on light fastness. (**b**) Interaction – time and pH on light fastness. (**c**) Interaction – temperature and pH on light fastness

3.2.3 Light Fastness

The interactive effects of the dyeing parameters time, temperature and pH on the light fastness characteristics of the dyed samples are presented in Fig. 6a–c.

It can be inferred that as temperature and time increase, the light fastness also increases. A similar type of trend is also observed with increase in pH of the process conditions. When solution has high pH, the adsorption capacity and removal of cationic dyes will increase because positive charges on the dye ensure that they are attracted by anionic adsorbent, so there are electrostatic attractions between positive charges of dye and negative surface of adsorbent [11–13].

The regression equation which gives the relation between the light fastness and the independent variables is as follows:

$$\begin{aligned}\text{Light Fastness} = {} & +4.0+(5.20093E-016*A)+(0.0625*B) \\ & -(0.0625*C)-(0.125*A*B)-(0.375*A*C) \\ & -(1.21431E-017*B*C)-(0.25*A^2) \\ & +(0.125*\mathrm{B}^2)-(0.125*C^2)\end{aligned}$$

Where

L = Light fastness
A = Temperature
B = Time
C = pH

3.2.4 Perspiration Fastness

(a) Perspiration – acid

From Fig. 7a–c, it can be seen that the perspiration fastness increases initially with the increase in temperature and time, while it tapers down with further rise in the conditions, after which it increases again. A similar type of trend also appeared in interaction between pH and temperature.

The regression equation which gives the relation between the perspiration fastness and the independent variables is as follows:

$$\begin{aligned}P1 = {} & +2.0+(0.0625*A)-(0.125*B)-(0.0625*C) \\ & -(0.625*A*B)-(0.25*A*C)+(0.375*B*C) \\ & +(0.75*A^2)+(0.875*B^2)+(0.75*C^2)\end{aligned}$$

Where

$P1$ = Perspiration fastness (acid)
A = Temperature
B = Time
C = pH

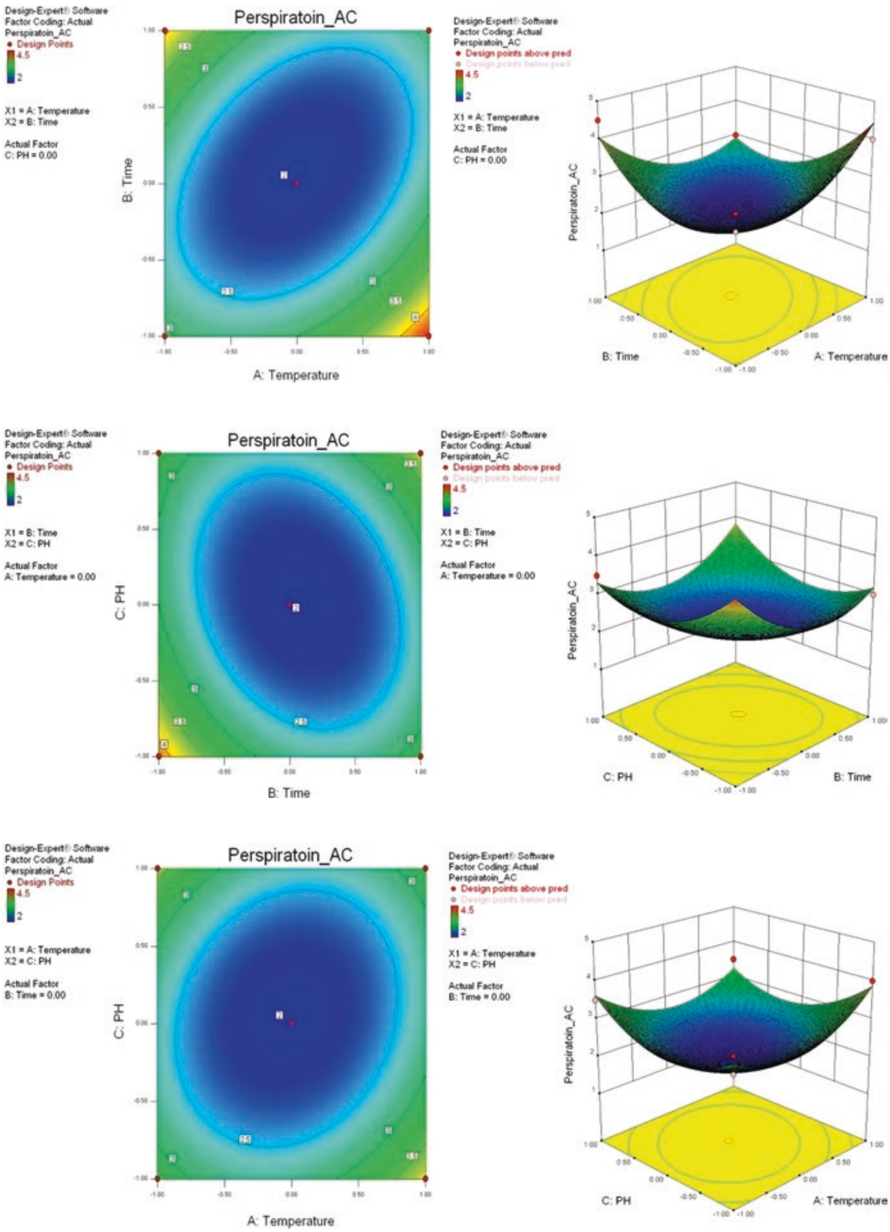


Fig. 7 (**a**) Interaction – temperature and time on perspiration fastness (acid). (**b**) Interaction – time and pH on perspiration fastness (acid). (**c**) Interaction – temperature and pH on perspiration fastness – (acid)

(b) Perspiration – alkali

From Fig. 8a–c, it is understood that as temperature increases, the perspiration fastness also increases. Whereas, when time increases, the perspiration fastness decreases and then increases after a certain point. It can also be seen that the perspiration fastness increases initially with the increase in time and pH, while it tapers down with further rise in the conditions, after which it increases again.

The regression equation which gives the relation between the perspiration fastness and the independent variables is as follows:

$$\begin{aligned} P2 = {} & +3.5-(0.0625*A)-(3.92523\text{E}-017*B) \\ & +(0.0625*C)-(0.25*A*B)-(0.125*A*C) \\ & +(0.0*B*C)-(0.0625*A^2)+(0.8125*B^2)+(0.1875*C^2) \end{aligned}$$

Where

$P2$ = Perspiration fastness (alkali)
A = Temperature
B = Time
C = pH

3.3 Optimum Parameter

To determine the optimum process conditions for maximum wash, rubbing, light and perspiration fastness properties, the point prediction tool of the Design-Expert software was used. Finally, the optimum values of temperature 60° C, time 110 min and pH 4 were considered as optimum. The experiment was conducted with the optimised parameter and the colour fastness properties are listed in Table 7. It is seen that the actual values are in line with the predicted values which confirm the validity of the model used. The fastness is assessed by comparing any staining of specified adjacent fabrics during the test with a set of standard 'grey scales'. The grading is given on a scale of 1–5, where 1 is very poor and 5 is excellent.

4 Fabric Production and Garmenting

In order to develop the samples into product, with the optimised parameters, production of fabric was carried out in the dyeing machine (Fig. 9) with a capacity of 150 kg at M/s. Sunline Textile Processors, Tirupur. Design of an A-line frock was developed and patterns were created for the measurement taken from a kid dress form dummy of size 8. A-line frock was constructed and is shown in Fig. 10.

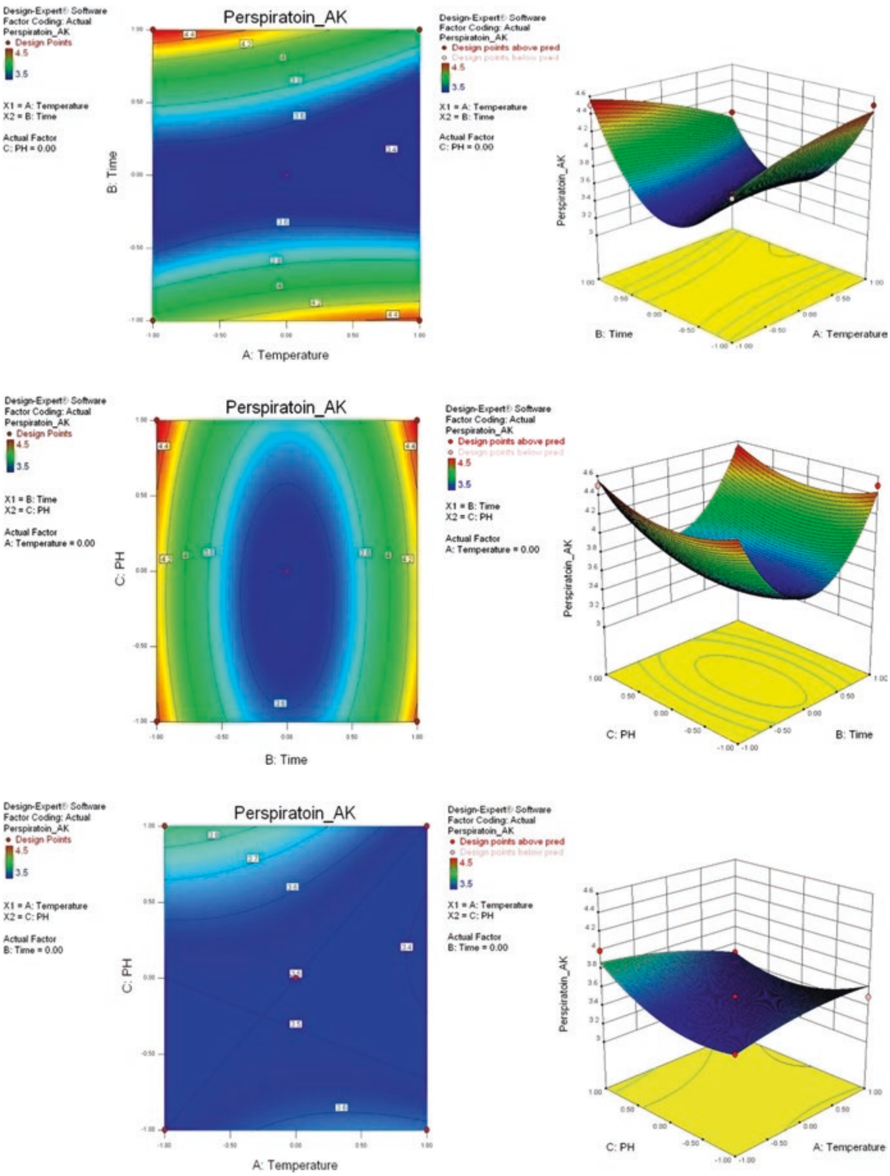


Fig. 8 (**a**) Interaction – temperature and time on perspiration fastness (alkali). (**b**) Interaction – time and pH on perspiration fastness (alkali). (**c**) Interaction – temperature and pH on perspiration fastness (alkali)

Table 7 Colour fastness properties with optimum process conditions

	Wash fastness	Rubbing fastness	Light fastness	Perspiration – acid	Perspiration – alkali
Predicted	5	4/5	4	4/5	3/4
Actual	5	4/5	3/4	4/5	4

Fig. 9 Production of clay-dyed fabric

Fig. 10 A -line frock made out of clay-dyed fabric

5 Conclusions

Based on the higher K/S value, the fixing agent and mordant have been selected as citric acid and stannous chloride, respectively, for dyeing cellulosic material with clay. The processing conditions such as temperature, time and pH are optimised with Design Expert software using Box-Behnken experimental design. It is concluded that that clay, a natural material, can be effectively used as a dyeing medium for imparting colour to cotton textile material. Choosing the process conditions effectively could result in better performance of the dyed fabric fastness characteristics. As the clay is from natural sources, these dyes are not harmful to the environment and are biodegradable; further disposing them does not cause pollution as chemical dyes. Ensuring the use of non-toxic alternatives will help in developing a sustainable textile dyeing process.

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Sustainability in Dyeing and Finishing

P. Senthil Kumar and G. Janet Joshiba

Abstract The dyeing and finishing sector includes processes such as coloration, processing, and functionalization unit in the textile industry which is usually high-cost, energy, and harmful chemical-demanding process. Certain characteristics such as colour, shade, pattern, quality, and type of processing are important in enhancing the fabric properties in the dyeing and finishing sectors. In the current scenario, these wet chemical processing units spend a large quantity of water, dyes, chemicals and accessories during their processing step. Furthermore, this sector produces an immense quantity of industrial effluent which is directed towards the nearby aquatic streams resulting in the destruction of ecosystem and drinking water deficiency. Due to the harmful effects of textile effluent such as water pollution, global warming, weather change, energy demand and water deficit, several attempts were made by researchers to implement sustainability in dyeing and the finishing process. Researchers have investigated the natural dyes obtained from the plants such as turmeric, tulsi, lemon and lavender to reduce the harmful effects of the synthetic dyes. Several materials such as plant extract, biopolymers, biomolecules, proteins, agricultural derivatives and lignocellulosic compounds are used in the finishing process to enhance the strength, stability, wear resistance, water resistance, flame resistance and UV protection. This chapter elaborates the various strategies followed in sustainable dyeing and the finishing process in the textile industry.

Keywords Dyeing · Finishing · Sustainable · UV protection · Strength

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1 Introduction

Textile is one of the integral and fundamental parts of human life, which also plays a significant role in satisfying human needs. They endow in providing clothes and attires utilized by humans and also it destines their lifestyle. Initially, the clothes or textiles are assumed only to cover the human body and provide protection from the external environment, but later various sorts of textiles came into existence which have been utilized in everyday activities of human life. The textiles are the materials which are woven and processed from yarn and fibres derived from both natural and man-made sources. Textile industries occupy an important place in society when compared with other industries. In this industry, the primal matters such as the cotton and wool are processed into textile materials through various processes such as spinning, weaving, dyeing and finishing. *Schematic representation of various types of textile is depicted in* Fig. 1. Britain is the first country to introduce the spinning and weaving processes in the textile industries. In recent times, implementation of various technological advancements and scientific technologies in the production of cotton, silk and wool has played a major role in the development of textile industries [1]. In the current scenario, the net worth of the textile industry including production, manufacturing and sales of textiles and fabrics was estimated to be three trillion US dollars. Textile industry incorporates a wide and assorted scope of items with an even more extensive scope of utilizations. That assorted variety is one of numerous components that make the material business one of the most fundamental to the monetary prosperity of individuals everywhere throughout the world (Study.com). The production and manufacturing of textiles and garments with good quality, feasibility and efficient techniques have become a challenge in the textile industry. Some of the parameters such as colour, shade, quality, texture, surface characteristics, and customer satisfaction, mechanical and chemical characteristics play a major role in the development of the textile industry (Textile world).

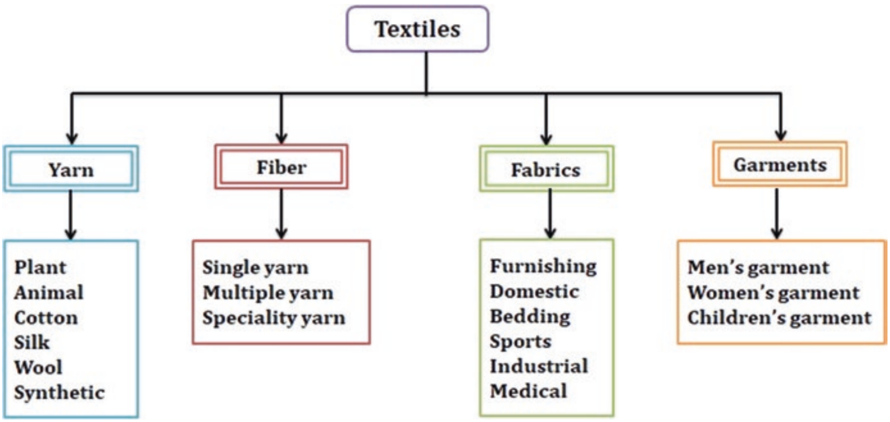

Fig. 1 Types of textiles. (Source: Sewguide.com)

In the textile industries, the processing steps such as dyeing and functionalization are considered to be one of the most significant processes in enhancing the quality of the textiles and garments. This dyeing and finishing process consumes a large amount of water and gushes out a huge amount of textile effluent containing harmful contaminants, which are highly hazardous to living organisms. The discharge of untreated textile effluent containing dyes, heavy metals, salts, acids, and chemicals into the nearby marine resources results in contamination of the ecosystem. Textile effluents show a strong negative impact on the wellness of the living organisms by causing serious environmental consequences such as climatic change, global warming, ozone depletion, water pollution and carbon footprint. Owing to the several deleterious health effects and environmental consequences caused by the textile wastewater pollution, several stringent legislations have been framed and more innovative strategies have been encouraged to lessen the extent of harmful consequences. Interest for natural fibres, natural dyes, enzyme bio-polishing, antimicrobial finishing, flame-retardant finishing, etc., has increased recently to create a safe environment for the future generation. Implementing sustainability in every sector of the textile industry helps in discovering new eco-friendly textile products, which can be degraded biologically and which help in developing a sustainable environment for all the living beings [6]. Sustainability is the present day's growing theme regularly utilized in the field of farming, fibre, design, material, sustenance and financial aspects. In broader terms, sustainability is defined as the process that can address the present issues of the society, without adjusting the natural assets for the future generation. The sustainability policies also focus on reducing the capital cost required for production without comprising on the quality and quantity of any product [6]. This chapter elaborates the dyeing and finishing sector of the textile industries and it also explains the sustainability strategies that are followed in the dyeing and finishing sector of the textile industry.

2 Evolution of Textile Industry

The textile industry is a progressively developing business sector in countries such as China, India, the United States and the European Union. In the global textile market, China is one of the major producers and exporters of raw textiles and garments. Furthermore, the United States remains as the leading producer and exporter of raw cotton and it also plays an important role as the leading importer of raw textiles and garments. In recent times, countries such as Sri Lanka, Pakistan, Samoa and several other South American countries have experienced tremendous growth in import and export of textiles and garments (Study.com). According to reports, by the year 2018, the export rate of China has increased by 3% and it is assumed that the export rate will increase higher in the future years. Countries such as Italy, France and Portugal also play a vital role in the textile sector and the net worth is estimated to be more than 160 billion USD. India occupies the third place in the leading textile producing countries and the net worth of the textile business in India is estimated to be 150 billion USD (Medium corporation). Over 40% of the world's production of garments and materials is in two leading countries such as China and India, which are anticipated to turn into the biggest GDP by 2050. As per the reports, by the year 2030, the demand for fresh nourishment and vitality will bounce by 50% and the demand for fresh water will increase by 30% as the populace will be 8.3 billion. In recent times, elevating capital expenditures clearly shows the progressive development of textile industries. In 2014, around 2 billion dollars are utilized in the textile and clothing sector, simultaneously, the investments for the textile business has elevated from 960 million to 1.8 million dollars during the interval of 2009 to 2014 (The textile association). The material and attire industry has been developing relatively with the adjustments in the realm of pieces of clothing. The leading producers of cotton were India, China and United States, with a production of 6200, 6000 and 4500 thousand metric tons, respectively (Medium corporation). Between the years 2011 and 2015, the global growth rate of textile industry was 4.4%; by the year 2020, it is believed that the textile production rate will increase by a rate of 26.2% and it is expected that the network will reach 846.2 billion US dollars. This demonstrates the uncontrolled development of textile industry over the world; expansion in utilization of textile items will prompt the expansion underway of material items [1].

3 Overall Process Involved in the Textile Industry

Fibre production is the preliminary step in the textile manufacturing process and it is derived from both natural and man-made sources. The natural fibres originate from the plant and animal sources, and the plant crops such as cotton, hemp, linen and bamboo are the main sources of natural fibres. Cotton is by a wide margin the most regularly utilized plant fibre and the cultivation of cotton requires intensive resources, high contributions of water, pesticides, bug sprays and manures, leaving an enormous lethal impression where developed, if not developed naturally or under explicit practical conditions (Fig. 2).

Wool is the major type of fibre derived from animals and they are subjected to processes such as dipping, scouring and washing in order to remove unwanted impurities, fat and waxy substances. The chemicals such as pyrethroids and organophosphates are used in processing the wool. After the fibre is produced, it is subjected to a spinning process to produce yarn using ring spinning equipment. The produced yarn is converted into grey fabric using methods such as knitting and weaving, and the unwoven fabric is treated using binders, solvents and adhesives. The yarn, fibres and fabric are pretreated to prepare those materials for dyeing and the finishing process. The pretreatment process such as washing, desizing, scouring, bleaching, mercerizing and carbonizing are performed to process the fabric. The preprocessed fabric is subjected to dyeing and finishing process. In the dyeing sector, the fabrics are coloured using dyes and pigments which are of natural or synthetic origin. In the finishing sector, some of the special characteristics such as flame

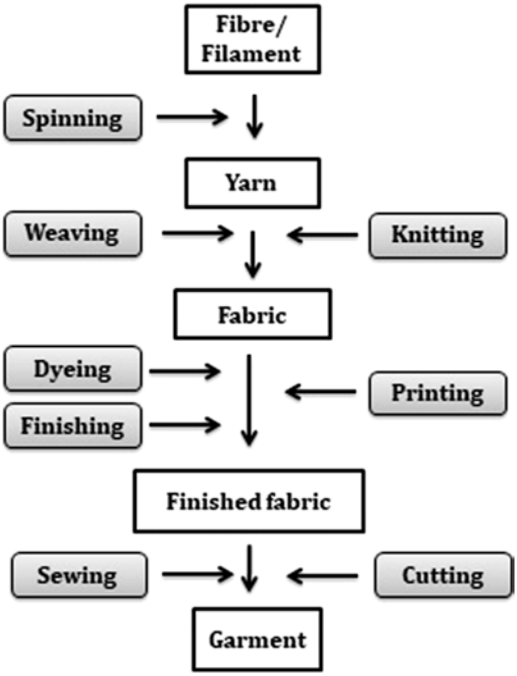

Fig. 2 Flow chart of the textile production process

retardancy, water resistance, antibacterial activity, UV resistance, anti-pilling, anti-static property, crease resistance and wrinkle resistance are incorporated into the fabric. The finished fabric is converted into finished products such as jeans, sweaters, shirt, pants and carpets. In the final step of manufacturing, the garments are made using processes such as cutting and sewing. Based on the necessity of the customer, the fabrics are converted into clothes and garments, in addition printing and designing are done to enhance the quality of the garments (Textile guide).

4 Dyeing and the Finishing Sector

The dyeing and finishing sector of textile is a foundation in the assembling of a material or texture. Dyeing is an important sector through which colour or pigments are applied to the cloth or fabric. From ancient times, colours have been an attracting factor of any cloth or fabric utilized by humans. Colour is also known as pigments and it is strongly shaded in the fabric with the help of a mordant, a chemical which strongly holds the pigments or colour to the fabric even after washing or usage. Basically, natural and synthetic dyes are utilized in the dyeing process of fabrics. The natural dyes are derived from the natural sources such as plants, insects and minerals, whereas the synthetic dyes are derived from various chemical elements (Textile school). There are various natural or synthetic dyes available in the market and it is applied through the dyeing methods such as the following (Fig. 3):

- Natural dyeing
- Synthetic dyeing
- Industrial dyeing
- Dip dyeing
- Tie dyeing
- Resist dyeing
- Batik
- Shibori
- Tritik

Textile finishing is the processing of fabric through various mechanical and chemical finishing methods which enhances the quality of the fabric according to customer needs. It is one of the preparatory techniques used prior to various processes such as dyeing, sizing and manufacturing. The finishing process aids in providing the functional properties such as flame resistance, water resistance and wrinkle resistance to the fibre, fabric or cloth which enhances the quality of the clothes and its longevity. The textile finishing is achieved through three various finishing methods such as mechanical finishing, chemical finishing and enzymatic finishing (Textile learner). Traditionally, the textile finishing is done only to change

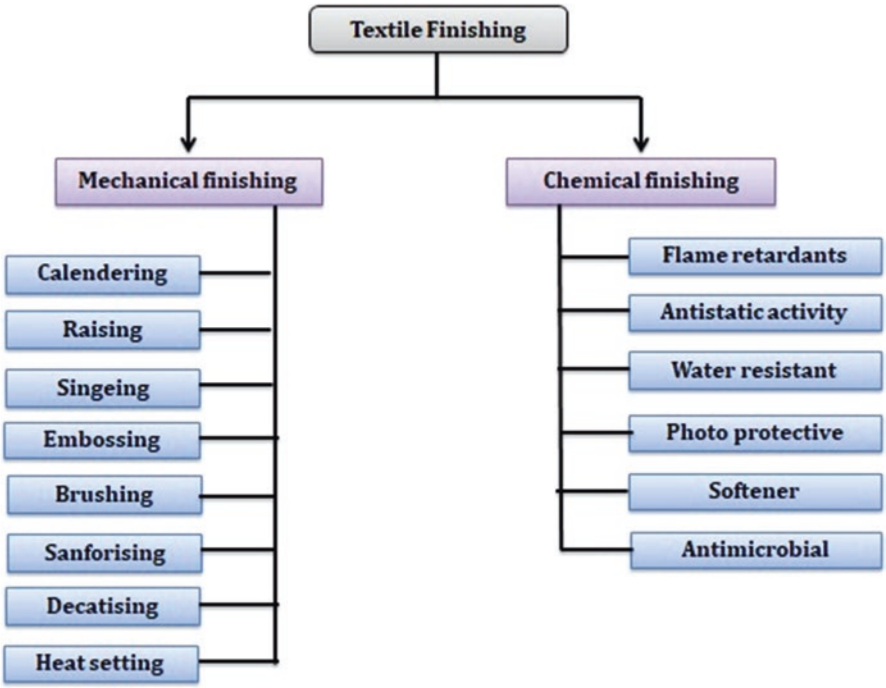

Fig. 3 Various types of finishing process done in textile industries. (Source: Clothing industry)

the texture and folding of the fabric by incorporating stiffening, shearing and softening in garments and clothing. In recent times, the functional finishing of textiles have elevated progressively and is used in a wide range of applications [17].

5 Sustainability in Dyeing and Finishing Process

Dyes have occupied one of the most important irreplaceable compounds of the society and it is of both natural and synthetic origin. The synthetic dyes consist of toxic chemical compounds which are non-biodegradable and highly toxic which alters the characteristics of the environment. Owing to the health effects and other environmental deleterious effects, the removal and treatment of synthetic dyes from the environment is made mandatory. The implementation of the sustainable principle in the dyeing sector helps in reducing the harmful effects of the dyes and other chemicals released after dyeing the fabric. In order to combat the harmful effects of dyes, the synthetic chemicals can be replaced by the natural dyes which are safe and eco-friendly to the ecosystem. Gong et al. have investigated the changes in the pigmentation of the leaves of *Cinnamomum Camphora* and its application in the UV protection and dyeing of silk and wool textiles. The results showed that the extracted pigments of the Cinnamomum plants showed a strong and good dyeing ability in silk and wool fabrics [10]. In the textile industry, the fibres such as cotton, wool, silk, viscose and linen are the most preferred fibres which are used in various applications. Out of all the fibre varieties, cotton is the most used material and because of its super hydrophobic finish, it is utilized in the preparation of various water-resistant and stain-resistant garments. From the customer's point of view, there is a necessity for fabrics with unique features such as microbe resistance, UV protection, water resistance, flame resistance, shrink resistance, crease resistance and stain resistance. In order to satisfy all the requirements of the customers, several innovations have been made in the textile finishing sector to enhance the quality of the garment. In recent times, several materials such as N- Halamine siloxanes, polyhexamethylene biguanide, triclosan and biopolymers are successfully employed in the fabrication of garments with antimicrobial characteristics. Many new nanoparticles such as titanium dioxide, silver and zinc oxide are used effectively in enhancing the finishing properties of the textiles. The improper binding of chemical and other auxiliaries used in the finishing process into the marine sources results in contamination of water, air and soil. In order to lessen the toxic textile contaminants from the environment, various wastewater treatment techniques such as adsorption, ion exchange, membrane separation, coagulation, advanced oxidation process and biological degradation are implemented in the textile industries. Despite the treatment procedure of these wastewaters, utilizing traditional techniques has demonstrated to be extraordinarily inadequate, troublesome and exceptionally costly. This deprivation in wastewater treatment in managing the textile effluents leads to formulation of new sustainable principles in the finishing sector [11].

6 Various Strategies of Sustainability in the Dyeing and Finishing Process

The headway of innovation and expansion worldwide is a challenge in the textile market and has led researchers and technologists to search for or create novel completions of materials with high esteem and diversification. The quick development in materials has opened new windows for the researchers to appear and investigate into new research fields, which incorporate fire-retardant materials, geo-materials, insect-resistant materials, aromatic materials, medical textiles and nano-textile materials. All around, researchers are currently committing extraordinary regard for these intriguing fields of material research and broad research works and numerous licenses have been accounted for various regions of textile finishing and dyeing [11].

7 Solvent Dyeing

Dyeing is one of the most important processes in the textile industry which consumes a large amount of water; further, the effluent released from the dyeing unit is composed of toxic chemicals, dyes, pigments, salts, acids, and organic compounds. The release of textile effluent containing all these hazardous substances into water resources results in the modification of physical and chemical nature of water, and also it makes the water unfit for drinking and other domestic purposes. In order to overcome all the negative effects of dye-polluted wastewater, more than wastewater treatment, textile production and manufacturing with sustainable approaches are mandatory. Solvent dyeing is considered to be one of the outstanding and sustainable techniques which can reduce the severity of the dyes and pigments. In this technique, dyes are dissolved using solvents instead of water resulting in enhanced adsorption of dyes onto fabrics. Supercritical carbon dioxide serves as one of the significant solvents used in efficient dye adsorption of various textile fibres along with dispersing dyes. The solvent dyeing method using supercritical carbon dioxide is highly effective in dissolving the dyes because of its peculiar characteristics such as low viscosity and high density, also it serves as an efficient medium for dyeing the fibres [13].

8 Zero Discharge Dyeing

The wastewater released from the dyeing unit and its treatment always remains as one of the biggest problems in the textile industry. Upgrading water utilization incorporates the reuse of water along with salts and dyes leftover by treating them with some chemical processes. Zero discharge dyeing is one of the effective methods to stabilize water deficiency and water pollution by effective utilization of the spent textile wastewater composed of dyes, acids and salts released from various sectors of the textile industry. This method reduces the risk of textile effluents getting discharged into environmental resources. For reusing the textile effluent, the wastewater released from the dyeing unit is subjected to jigger and is processed for the next batch dyeing. This method is highly profitable and effective, also it consumes less energy and water and satisfies all the conditions of a sustainable industrial process [13].

9 Sustainable Flame Retardants

Amidst the various finishing properties of textile, the flame retardants are one of the most important and essential functional finishing systems required for the wellness of human beings, and these materials have a huge demand in the international market. The development and implementation of polymers in the field of transports, clothing, furnishing and military have increased the probability for flame retardants in the environment. According to the reports of de Boer and Van der Veen, around 465,000 tons of flame retardants were utilized in Europe till the year 2006. Several compounds such as diammonium phosphate, urea, melamine-formaldehyde, THPC, antimony-halogen, phosphorus and nitrogen found in the traditional flame retardants are found to be toxic and have deleterious effects on the environment and living beings. The techniques such as layer deposition, sol–gel process, plasma technology and nanomaterials are found to be less water-consuming functional finishing technique. In order to combat all the negative effects of synthetic chemicals utilized in finishing process, search for sustainable and eco-friendly raw materials derived from biological sources are taking place. In the current scenario, the utilization of caseins, nucleic acid, DNA, proteins and hydrophobins is considered as one of the great alternatives for the traditional finishing materials. These materials help in the production of flame retardants with enhanced thermal stability [14].

10 Irradiation Technologies

As the dyeing and finishing process consumes a large volume of water for processing and also generates a huge volume of water as harmful textile effluent, researchers are in search of alternatives to produce textiles in a sustainable way. Irradiation technologies are considered as one of the biggest substitutes to textile wet processing steps. This technique is eco-friendly, uses no chemicals, consumes less energy, is simple to use, is feasible and is efficient. Alteration of the fibre surface for enhanced uptake of dyes and finishing enzymes using ultrasound, gamma, ultraviolet and plasma radiation is grasping the attention of textile industries for managing sustainable dyeing and finishing [11].

11 Plasma Technology

Plasma technology is the techniques used by the textile industry to enhance some of the properties such as strength, hydrophobicity/hydrophilicity, antistatic properties, adhesion properties, functionalized fibre, dyeing and printing ability of the fabrics. Generally, the most widely used plasma treatments are helium/oxygen or helium/air and its efficacy varies according to the application it is used. Especially in the textile finishing sector, this plasma technique is utilized in applications such as the following:

- Plasma technology helps in imparting antibacterial and fungal properties to the fabric using silver nanomaterial for the medical purposes.
- It is used in enhancing the hydrophobic activity of the fabric for fabricating water-repellent fabrics.
- It improves and enhances the final finishes of the fabric by implementing the surface grafting techniques.
- It enhances the adhesion behaviour of the fabrics to obtain strong and effective printing and dyeing ability of the fabrics.

These technologies reduce the consumption of energy and other resources during the textile finishing process and it is one of the most innovative and sustainable technologies found in the textile industry [14].

12 Sustainable UV Technology

UV exposure at low concentrations helps in killing the pathogens and other disease-causing microbes, which is why it is used in the sterilization process. When humans are exposed to higher concentration of UV radiation it causes wrinkles, skin damage, blisters, ageing, etc. in the skin layer. This is the reason why UV protective clothing has gained attention of the researchers and also it has become a necessity for customers. In order to overcome the harmful effects of the hazardous UV radiation, UV protective finishing is implemented in the textiles. For the synthesis of UV protective clothing in a sustainable way, several natural sources extracted from mulberry, grapes, chitosan, tulsi, aloe vera, honey, almonds, etc., are utilized in UV-resistant fabrics to enhance sun protection and to improve resistance against harmful UV rays [14, 16].

13 Implementation of Nanotechnology

Nanotechnology is one of the widely used technologies in the textile dyeing and finishing sector. This technology uses textile fibres on a nanoscale with a diameter range of about 1–100 nm. The implementation of nanotechnology in the textile fibres has shown a positive impact on the enhancement of the surface area of the separate fibres which is highly helpful in upgrading the breathing ability of the textile fibres. This technique is used in a wide range of applications:

- To enhance the oil and water-repellent characteristics of the fabric
- To improve scratch-resistant garments and fabrics
- To increase the electrical conductivity property of the individual fibres
- To incorporate flame retardancy to the finished fabric
- To help increase the strength and durability of the clothes and garments

The development and implementation of nanotechnology in the textile science can reduce the usage of harmful and toxic chemicals which damage the environment and it is more helpful in the production of textiles in an eco-friendly way [12]. Vankar and Shukla have synthesized silver nanoparticles from the plant extracts of lemon leaves. In this work, the plant extract is used as the encapsulating agent of the synthesized silver nanoparticles. The results of this study concluded that the prepared silver nanoparticles showed good antimicrobial and antifungal activity. In addition, implementation of these prepared silver nanoparticles onto the textile fabrics will enhance the antimicrobial activity and provides protection against harmful microorganisms [15]. Nanocapsules enriched with antibacterial activity promote wound healing properties and microbial resistance on the textile fabrics. These textiles play a vital role in maintaining hygiene and resistance against disease-causing microorganisms. In the fabrication of medicinal textiles, the raw materials possessing anti-inflammatory and antioxidant properties are chosen as the coating materials [17].

14 Energy Production

Apart from conserving some part of energy utilized in the textile production process, it is also essential to frame techniques to generate energy from the textile waste released from the various sectors of the industry. Microbial fuel cell (MFC) is an outstanding technique which can be used effectively for the treatment of textile wastewater. Generally, the MFC is used in converting the domestic wastes, textile effluents and sludge to produce electricity for the betterment of human beings. The organic compounds present in the textile effluents serve as the driving force in the working of the microbial fuel cell. The MFC has increased much consideration due to its capacity to produce energy from natural or inorganic mixes through microorganisms. These cells utilize the toxic textile effluent for eco-friendly production of electricity and it also plays a major role in reducing the negative ill effects of the textile effluent. Implementation of microbial fuel cells in the textile industry remains as one of the sustainable methods of producing energy and also eliminates the toxic content of the textile effluent [1].

15 Conclusion and Future Perspectives

The dyeing and finishing sector of the textile industries is one of the notable sectors in which a large volume of water and energy is consumed; it also generates contaminants such as dyes, pigments, acids, salts and heavy metals which pollute the environment. Traditional dyeing and finishing methods influence the environment in a negative way and the necessity for sustainable approaches is increasing every day. Some of the sustainable approaches such as irradiation technology, plasma technology and nanotechnology are implemented in the textile industry for the betterment of the environment. Further exploration and research in nanotechnology improve the efficiency of the finishing properties. Also, production of energy from the toxic waste released from the textile effluent is one of the best ways to manage the textile effluent released from the dyeing and finishing unit.

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Sustainable Textile Processing with Zero Water Utilization Using Super Critical Carbon Dioxide Technology

Hüseyin Aksel Eren, İdil Yiğit, Semiha Eren, and Ozan Avinc

Abstract Water is a valuable resource for life because of its multifunctional properties. Thus, scarcity of water and augmented environmental awareness are worldwide concerns that result in a sharp escalation in prices for drinking and removal of wastewater. It is widely accepted that the textile sector is one of the highest water consumers. Traditional textile dyeing utilizes huge amounts of fresh water and the used water is disposed as effluent comprising dyes and various chemicals. Water is generally utilized as a solvent in many pretreatment and finishing textile processes in the sector, such as washing, scouring, bleaching dyeing, and finishing. Therefore, the researchers and innovative textile machinery companies have been trying to develop new technologies to dye the textile material with less water usage and even without utilizing any water (waterless dyeing technology). The elimination of the water processing and related chemicals would be an important advancement for the textile dyeing sector. The recent prominent process uses carbon dioxide (CO_2) for dyeing textile substrates. It is a totally waterless dyeing process utilizing recycled carbon dioxide in certain temperature and pressure conditions. In this chapter, supercritical carbon dioxide ($scCO_2$) technology usage in textile scouring, surface modification, desizing, bleaching, dyeing, and finishing processes is reviewed in detail, leading to waterless sustainable textile wet processing. Moreover, the recent commercial and technological developments regarding supercritical carbon dioxide ($scCO_2$) technology are also given.

Keywords Super critical carbon dioxide · Sustainable dyeing · Waterless dyeing · Surface modification · Sustainable textile · Sustainable wet processing

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1 Introduction

Humankind must be very careful when consuming water which is one of the limited resources and which is an indispensable source of life. The textile industry is one of the highest water-consuming sectors. For instance, approximately 100–150 liters of clean water is required for the finishing processes of only 1 kg of textile substrates. Right at this point, the supercritical carbon dioxide ($scCO_2$) technology is here to help us in reducing clean water consumption. In this chapter, supercritical carbon dioxide ($scCO_2$) technology usage in textile scouring, surface modification, desizing, bleaching, dyeing, and finishing processes is reviewed in detail, leading to waterless sustainable textile wet processing. Moreover, the recent commercial and technological developments regarding supercritical carbon dioxide ($scCO_2$) technology are also given. In the below introductory part, brief information regarding the importance of water, the status of water in the world, and the usage of water in the textile industry is given.

1.1 The Importance of Water

Two hydrogen atoms and one oxygen atom (H_2O) constitute water. Water is crucial for our life and it is the most outstanding substance and the most studied material on the Earth because of its excellent property such as being solvent [1]. The fact that it is very difficult to find substitutes for its use in various processes increases the importance of water even more. Water has the potential to be the most debated topic of today and most probably this trend will increase in the near future due to its vital, economic, and strategic importance [2]. Solvents have been integrated into many different industries over the decades. Currently, the most producing and processing sectors such as automotive, electronics, pulp and paper, chemical, mining, food, and textile depend on the widespread utilization of different solvents. As it is known, water is a universal solvent of polar molecules and the most common solvent utilized by living creatures and industrial manufacturing processes, of which the textile sector is one of the leading consumers of fresh water resources [3].

1.2 The Status of Water in the World

Fresh and clean water is a valuable resource that is progressively in high demand. Its increasing usage throughout the world is a dangerous threat [4]. About 70% of our world is surrounded by water, but unfortunately, only 3% of water sources is clean water. A huge amount of this fresh water is in the form of frozen glaciers which is unavailable for human use [5]. It is estimated that the need for fresh water will enhance by 40% with the increased population until 2030, and billions of people around the world will have difficulty finding even the water they need for their daily needs until 2050 [6]. According to the data, the population will enhance by around 35% by 2050. This expected population and economic growth in the developing countries will cause noteworthy rises in the textile manufacture and consumption. For these reasons, significant increases in energy usage, water usage, and possible environmentally harmful emissions are expected in the textile industry and other sectors [7].

1.3 The Usage of Water in the Textile Industry

Next to agriculture, the textile sector is the greatest water consumer. The textile industry includes wet processing and finishing processes, which consume a huge amount of water. These processes are applied for better appearance and functionality of textile materials. However, the use of much water and chemicals for these processes and the resulting wastewater creates environmental hazards. It is widely known that nearly all dyes, specialty chemicals, and finishing chemicals are applied to textile materials in the aqueous media. Water is the best solvent for textile industry as it is for many other industrial applications. Furthermore, most of the aqueous textile finishing processes are followed by a washing combination to eliminate all excessive dyes and chemicals utilized in this stage before carrying on further processing stages. The wastewater contains process chemicals during the textile finishing process, which leads to environmental hazards and sometimes it may be directly released to our ecosystem. It is not only a possible risk for human health but also a risk for the health of the entire ecosystem [8]. Nearly 100–150 liters of clean water is used for finishing 1 kg of textiles [9, 10]. Considering that this consumption will have an end, innovative approaches are being worked out to protect the environment and existing energy resources. It is necessary to continue the existing processes with more ecological methods by giving importance to sustainable works and research studies (Fig. 1).

This chapter gives detailed information regarding the sustainable textile processing with zero water utilization using super critical carbon dioxide technology. First of all, the sustainability, supercritical fluids, and supercritical carbon dioxide are introduced. Thereafter, different application areas of $scCO_2$ technology in the textile industry such as in pretreatment applications, dyeing processes, and finishing processes are reviewed. Finally, the recent commercial developments about $scCO_2$ usage in the textile industry are also covered.

2 Sustainability

The first meaning of the sustainability is the capability to be maintained at a certain rate or level and the second one is the avoidance of the depletion of natural resources to maintain ecological equilibrium [12]. The terminology of sustainability has gained prevalent utilization since 1987, when the Brundtland Report from the World Commission on Environment and Development of the United Nations described the sustainable development as development that “meets the needs of the present gen-

Fig. 1 Principles of sustainability

eration without compromising the ability of future generations to meet their own needs" (p. 45). For instance, when one makes a search on amazon.com for the term "sustainability," one will find out that more than 10,000 book titles contain this word. This information alone shows how important the sustainability approach is. What is more, a search of scientific journal papers on Google Scholar results in significantly much more hits, which indicates that many thousands of papers possess the term "sustainability" in their titles [13]. Sustainability is a multidimensional issue that can be grouped into three important pillars: economy, environment, and society (Fig. 1) [11].

Life-cycle assessment, water footprint measurements, carbon emission management, eco design, and clean production are utilized by many different research studies to measure how sustainable the textile processes are [14]. Ensuring the sustainability in the textile industry will make very important contributions to the sustainability of the world. For this reason, many different cleaner and more ecofriendly production systems such as ozone treatment, supercritical fluids, and enzyme applications are generally preferred due to their sustainable credentials. In the rest of this chapter, textile processes applied in supercritical fluid environment are covered.

3 What Is Supercritical Fluid?

Systems containing gases under high pressure and temperature are called supercritical fluids (SCF). When these systems exceed the critical point values (especially temperature and pressure), liquid can be transformed into a supercritical fluid and organic molecules of low-to-medium polarity dissolve. The supercritical fluid is neither gas nor liquid, but possesses both characteristics. The density of a supercritical fluid is approximately 200–400 times higher than the density of the gaseous state, whereas the density of the liquid state is nearly the same. The density of a supercritical fluid is easily changed by relatively small modifications in pressure and temperature. These fluids display double advantageous characteristics of possessing high density as well as high compressibility and consequently high selectivity of separation. Furthermore, it presents very attractive extraction properties due to its satisfactory diffusivity, viscosity, surface tension, and other physical characteristics. The viscosity of a supercritical fluid is rather low; it might enhance with temperature. The surface tension of a supercritical fluid is essentially non-extant. Table 1 exhibits an order of greatness assessment of physical characteristics typical for gas, liquid, and supercritical fluid states [15–18].

Typical characteristics of supercritical fluids (or species dissolved within) are checked against those of gases and liquids in Table 2.

Supercritical fluids can be utilized in many different application types; mass-transfer processes, phase-transition processes, reactive systems, and finally, materials-related processes and nanostructured materials.

3.1 Mass-Transfer Processes

Industrial applications of supercritical fluids cover mass transfer processes in separation processes such as extraction from solids, pharmaceutical fractionation and purifications, cork treatment, spent rubber tires, drying, cleaning, degreasing, impregnation, dyeing, and tanning of leather [18, 19].

Table 1 Critical points of some substances [15]

Critical points of some substances				
Compound	Boiling point (°C) (1 atm)	Temperature (°C)	Pressure (atm)	Density (g/cm^3)
CO_2	−78.5	31.3	72.9	0.448
NH_3	−33.4	132.3	11.3	0.24
H_2O	100	374.4	226.8	0.334
N_2O	−88.5	36.5	71.1	0.457
Ethanol	78.4	243.4	63	0.276
Ethane	−88	32.4	48.3	0.203
n-Propane	−44.5	96.8	42	0.220
Trichlorofluoromethane	23.7	196.6	41.7	0.554
Chlorotrifluoromethane	−81.4	28.8	39.0	0.58
Diethylether	34.6	193.6	36.3	0.267

Table 2 Comparison of density, viscosity, and diffusivity for typical liquid, gas, and supercritical fluid phase [15, 17]

Typical properties of supercritical systems				
	Unit	Gas	Liquid	Supercritical fluid phase
Density	$kg\ m^{-3}$	1	1000	100–1000
Viscosity	cp	0.01	0.5–1.0	0.05–0.1
Diffusivity	$mm^2\ s^{-1}$	1–10	0.001	0.01–0.1

3.2 Phase-Transition Processes

Phase transition processes are one of the methods of producing pharmaceutical, food, and encapsulating for particle production or formulation in the industry by supercritical fluids. Phase-transition processes with supercritical fluids target to form more beneficial formulations than traditional methods based on dissolving agents such as acetone, methylene chloride, and dimethyl sulfoxide.

3.3 Reactive Systems

Reactions in supercritical fluids or with supercritical fluids have attracted attention for nearly 25 years. However, few reactions have been known for commercial production scales. Supercritical fluids could be utilized as reaction medium or reactive component, and catalysts can be dissolved by supercritical fluids differently from typical reaction media. Reactions can be catalyzed by enzymes in supercritical fluids. On the one hand, sub- and supercritical CO_2 can block biological reactions and be utilized for sterilization. Supercritical fluids are also suitable for recycling polymer applications. In addition to hydrogenation, hydrothermal biomass gasification and oxidation in supercritical water are some usage areas for supercritical carbon dioxide applications.

3.4 Materials-Related Processes

Polymers, emulsions, micro-emulsions, colloids, and nanostructured materials are used as materials-related processes of supercritical fluids [18].

Due to their unique properties, we can clarify the application areas of supercritical fluids with the following examples:

- Foods: purification, separation, extraction
- Medicines and health foods: pharmaceutical fractionation and purification, and lipid removal from bones
- Cosmetics: the extraction of aromas for perfume production
- Cleaning: textiles, electronic parts, complex mechanical device, and fiber optic roads
- Environmental: waste cleaning up of hazardous, redress
- Petroleum: propane de-asphalting, dissolved oil splitting

Nicotine removal, enzyme reactions, production of micro particles in the polymer and monomer processing and chromatographical measurements are also other usage areas of supercritical fluids [15, 17, 18]. Although the supercritical fluid technique has the potential to improve environmental safety and health impact, it also facilitates innovative processing techniques and materials manufacture [20].

3.5 Supercritical Carbon Dioxide

The most popular supercritical fluid utilized in the industry is supercritical carbon dioxide (scCO_2) because of its prominent and good properties such as inexpensiveness, nontoxicity, nonflammability, and environmentally friendly and chemically inert nature under many conditions [17, 20–24]. The critical point of carbon dioxide is 31.1 °C and 73.8 bar for being supercritical fluid [17, 20–23].

Supercritical carbon dioxide could be considered as an expanded liquid or a large quantity of compressed gas, and provides suitable reaction conditions since it is diffusive like gases and solvent like liquids. Another positive feature of the scCO_2 is the easy removal of the fluid by removing the pressure. Supercritical carbon dioxide could be used in many different applications such as separation, extraction, impregnation, dyeing, tanning of leather, and cleaning. This technology is the best for different textile applications as the critical temperature and critical pressure values are low and the operation is relatively easier [21]. Environmentally benign carbon dioxide presents noteworthy potential in its supercritical fluid phase instead of the existing reliance on a range of hazardous, relatively costly, and environmentally damaging organic solvents. Therefore, it is expected that its ecofriendly nature will result in their use on an extensive global basis. Applications of supercritical carbon dioxide are sustainable alternatives to totally eliminate or greatly lessen the necessity of numerous conventional organic solvents. Examples of supercritical carbon dioxide usage areas can be given such as chemical extraction and purification, synthetic chemical reactions including polymerization and inorganic catalytic processes, biochemical reactions involving enzymes, particle size engineering, textile finishing, and advanced material production [19].

4 The Application Areas of scCO_2

Reduction or elimination of the usage of water or chemicals in textile processing is a very important step forward for both producer and world sustainability. At this point, supercritical carbon dioxide (scCO_2) technology appears to be a suitable process option to achieve these sustainable goals. Indeed, scCO_2 technology is able to create much greener and more sustainable eco-friendly textile processing methods. Apart from dyeing processes, supercritical carbon dioxide (scCO_2) technology also can be used for extraction and pretreatment purposes such as scouring, desizing and bleaching, surface modification, dyeing and finishing treatments, such as washing and clearing [19, 25, 26].

In the past, the usage of supercritical carbon dioxide technology in textile industry was very limited with the dry cleaning area. Nowadays, conscious utilizers are more oriented toward products which utilize environmentalist approaches and sustainable energy resources. Hence, many different research studies have been performed on supercritical carbon dioxide utilization in more and more different textile fields. Therefore, $scCO_2$ applications have been commenced to be performed in preliminary pretreatment, dyeing, and finishing processes, and lots of current research studies have concentrated on these fields. Lately, not only dyeing processes but also pretreatment processes such as scouring, surface modification, desizing, and bleaching applications have gained favor in $scCO_2$ technology, leading to huge fresh water saving, and cleaner and a greener way of manufacturing an enormous amount of contribution for world sustainability.

In conventional textile production, almost all textile materials need pretreatment processes such as scouring and bleaching prior to dyeing or printing processes. Consequently, clean water is required not only for the coloration processes but also for pretreatment processes to prepare the fabrics for further dyeing and/or printing stages. Hence, a huge amount of clean water is required and utilized for pretreatment steps prior to coloration. Traditional pretreatment processes such as scouring, hydrophilizing, desizing, bleaching, dyeing and post-dyeing treatments such as washing, clearing, and finishing use vast amount of clean water leading to great amount of effluent load formation [25]. The utilization of $scCO_2$ technology for the aforementioned textile processes is explained below.

4.1 Pretreatment Applications by Utilizing $scCO_2$

Scouring is the pretreatment process that is used before dyeing or printing. The water consumption of pretreatment processes is really high as other textile wet processes. It was stated that scouring process of polyester fibers before dyeing can be carried out in supercritical carbon dioxide. C. Wang et al. studied the scouring probability of polyester fibers by using supercritical carbon dioxide as a medium and the applied pressure was between 96 and 350 bar at temperatures ranging from 313 to 393 K. The oil removal efficiency from polyester fibers was approximately +99% owing to the successful scouring process in $scCO_2$ medium [28]. It was claimed in a US patent that fiber elongation and strength properties of fibers scoured in $scCO_2$ media were better than those of fibers scoured via conventional scouring method. Moreover, it was also stated that cleaning in $scCO_2$ media decreased the polymer damage [27].

In another study, the scouring and bleaching feasibility for flax rove at different temperatures in $scCO_2$ media were investigated. Natural flax rove was used, and system pressure of 28 Mpa and different temperatures (70–80–10–120 °C) were selected and applied for 90 min. The outcomes displayed that many mild grooves and stripes appeared on the flax fiber surface after $scCO_2$ treatment. Thermal characteristics of flax rove were improved with a rise in temperature. Consequently, the outcomes supported that it is technically achievable to use supercritical carbon dioxide media to conduct the scouring and bleaching processes for flax roves [29].

An ecofriendly bio-pretreatment (desizing and scouring) process of raw (greige) cotton fabric by mixed enzymes in $scCO_2$ medium for biodegradation and/or removal of various impurities from the substrate with one bath method was examined. System temperature at 50 °C and pressure at 13 Mpa for 60 min. Were selected for processing conditions. A small amount of ethanol, water, and several enzymes, such as sodium bis-sulfosuccinate, were included in the vessel. This novel method was successfully constructed for desizing and scouring of greige cotton fabrics. The results displayed more noteworthy effects both on fabric weight loss and on capillary rise due to the parameters such as system temperature, mixed enzymes, and addition of water. Therefore, the supercritical bio-treatment process led to more water and energy conservations than the conventional process. This novel bio-treatment process resulted in cost reductions and more environmentally friendly production type for cotton fabrics and this new technique can shed light on other textile fibers in the industry [30].

Also bleaching is the most important pretreatment process, especially for natural fibers. Eren et al. [25] investigated the bleaching process on knitted cotton fabrics by supercritical carbon dioxide. The pressure and temperature were as follows: 180–250 bar at 80–120 °C for 20 min. Different auxiliaries were used such as hydrogen peroxide and caustic soda with different concentrations. The results were compared with traditional aqueous peroxide bleaching process. Bleaching of cotton fiber at 80 °C for 20 min in $scCO_2$ media exhibited higher whiteness outcomes than traditional water-based bleaching at 80 °C. The bleaching process with hydrogen peroxide participation in waterless supercritical carbon dioxide media caused around 30–50% whiteness increment on cellulosic cotton fiber knitted fabric. After the treatment process, following peroxide bleaching in $scCO_2$ media improved the moisture management characteristics of the bleached cotton fiber fabric. As a result, effective waterless hydrogen peroxide bleaching could be performed for cellulosic knitted fabrics in supercritical carbon dioxide media [25].

Surface modification of polyester fabrics is one of the pretreatment applications of supercritical carbon dioxide ($scCO_2$). Glycerol polyglycidyl ether was impregnated as a cross-linking agent to polyester fabric through supercritical carbon dioxide. Subsequently, immobilization operations, such as containing pad-dry-cure application and the solution process to finish the glycerol polyglycidyl ether-polyester fabric via natural functional agents such as sericin, collagen, or chitosan, were performed. After the supercritical carbon dioxide pretreatment process, polyester fibers exhibited progression in surface hydrophilicity and wettability, moisturization efficiency, and displayed antibacterial activities against *S. Aureus* bacteria. It was concluded that $scCO_2$ pretreatment resulted in powerful and more stable polyester surface via the subsequent chemical immobilization of functional agents [25, 31].

4.2 Dyeing Process by Utilizing $scCO_2$ (Waterless Dyeing)

The textile industry constantly keeps searching for better, cheaper, and more eco-friendly way of textile production. At this point, the reduction of water and chemical consumption by the textile sector comes to the forefront. Indeed, textile production utilizes a vast amount of water, mainly for wet processing and produces a noteworthy volume of contaminated wastewater [7]. In the literature, we find that many research studies performed textile dyeing processes with water-free productions, which released no effluent to the environment, as well as energy- and other resource-saving techniques [32]. For example, many research studies reported the advantages of supercritical carbon dioxide media usage, especially for PET dyeing. Carbon dioxide displays characteristics of both a liquid and a gas as mentioned in the critical point above. In that way, hydrophobic dyes are dissolved by supercritical CO_2 which has liquid-like densities and gas-like low viscosities and diffusion characteristics, which result in shorter dyeing times in comparison with an aqueous dyeing counterpart [33]. Supercritical carbon dioxide media usage, especially for dyeing, is the best choice for textile applications because the machine and process are partly easier [34]. The utilization of supercritical carbon dioxide instead of water in the dyeing process is an important step for the textile industry. The suitable conditions for textile dyeing in $scCO_2$ are 30 MPa and 120 °C, leading to a liquid-like CO_2 density of 585 kg/m^3. The most important advantage of dyeing in $scCO_2$ is the easy separation of solvent and residual dye. Depressurization after the dyeing causes precipitation of the dye and delivers clean, gaseous CO_2, so that both compounds can be reused [35]. Here, $scCO_2$ is used as solvent instead of water, thus this dyeing process is called "waterless dyeing" at the same time.

Dyeing in $scCO_2$ has an advantage that results from the physical features of the supercritical state: low-vapor pressure compounds, such as dyes, that can be dissolved by the liquid-like density. The viscosity is lower and the diffusion coefficient in a supercritical fluid is bigger than in a liquid, so this situation eases the mass transportation. When dyeing nonpolar textile materials such as polyester fiber in the $scCO_2$, the medium behaves like a swelling agent, plasticizing the polymer and increasing the rate of disperse dye diffusion inside the polyester fiber [35]. $ScCO_2$ was also utilized as an ecofriendly solvent substitution for hydrocarbons, chlorofluorocarbons, and other organics in other fields [36]. The best results of dyeing in $scCO_2$ media were obtained for polyester products. This originated from the structural compatibility of the polyester fiber and the $scCO_2$ medium. Hydrophobic disperse dyes could dissolve in $scCO_2$ due to hydrophobicity of CO_2 and penetrate the hydrophobic polyester fibers. It ensures easier polyester dyeing with disperse dyes [37].

The polyester dyeing process steps in $scCO_2$ media are shown below:

1. The dyeing process begins by dissolving the disperse dye in supercritical carbon dioxide.
2. Dissolving dye transfer to the polyester fiber.
3. Dyestuff absorption to the fiber.

4. Process finalizes with the diffusion of dyes into the fiber [38].

Excellent penetration to the fiber led to an increase in the color quality. One of the most important properties of polyester dyeing in the supercritical CO_2 medium is the absence of auxiliary chemicals such as dispersing agents. This is because CO_2 is a nonpolar solvent, and disperse dyes can be dissolved without the necessity of dispersing agent (i.e., simpler dye formulations could be utilized for scCO_2 dyeing than dye formulations for conventional aqueous dyeing) [35]. Waterless dyeing in scCO_2 is a very important topic for sustainability. Not only polyester fibers but also many other synthetic fibers such as polyamide, PTT, PBT, PP, PLA, and aramid fibers, and many natural fibers such as wool, cotton, and linen were dyed in scCO_2 media [39–45]. The influence of water serving as entrainer in the dyeing of wool fabrics in scCO_2 was examined [46]. It was reported that the addition of water in scCO_2 media made the dyeing process more effective under low temperature and low pressure when compared with earlier applied supercritical dyeing methods. It was claimed that dye could be uniformly distributed on the surface of fabrics because of water interaction. And therefore, coloration was increased while color difference was decreased [46].

Moreover, there are few papers on the dyeing property of cellulose fibers in supercritical carbon dioxide fluid. Dyeing of natural fibers at desired values is particularly related to the problem of solubility in scCO_2 medium. Fiber modifications and new fixation mechanisms are being developed to overcome this problem [21]. The world textile industry will shift in a positive direction with the solution of the problems in dyeing cellulosic fibers in scCO_2 media. Dyeing features of cellulose fabrics were explored using Reactive Golden Yellow K-2RA in supercritical carbon dioxide fluid with different humidity levels. The influence of dyeing parameters and especially humidity on color strength was examined. The outcomes showed that the color strength was improved significantly by scCO_2 medium dyeing. The success of the study is relevant to the monochloro triazine reactive group in the reactive dye and the nucleophilic substitution reaction of the hydroxyl functional groups in cotton. Reaction occurred in the moist supercritical carbon dioxide fluid. Dyeing trails of cellulosic products in the supercritical carbon dioxide medium take place under laboratory conditions but are not commercially available yet [47]. The use of scCO_2 in leather dyeing is also an innovative method and provides better penetration and evenness [48].

4.3 Finishing Processes by Utilizing scCO_2

Recently, some studies have been reported regarding the finishing applications in scCO_2 media to different textile fibers. Research studies made an attempt to utilize scCO_2 for impregnation and deposition of some additives to the textile materials such as water/oilrepellent and antifungal and antimicrobial applications. Many commercial applications of scCO_2 processes are involved in the extraction of chemicals, but $scCO_2$ processes might also be utilized to modify the surface and impregnate the bulk.

Textile materials can be used in several medical applications such as hospital uniforms, bed sheets, prosthetic valves, and wound dressings. Antibacterial properties obtained by transferring metals such as copper, gold, and silver to fabrics were investigated in the $scCO_2$ medium. These antibacterial/antifungal properties are provided by processes such as electroless plating, master batch impregnating, layer-by-layer deposition, RF-plasma-mediated deposition, dip-pad-dry, sol–gel coating, soaking in silver nanosols, and sonochemical coating. Supercritical CO_2 ($scCO_2$) is an innovative process to accord antimicrobial functionality to textile substrates. Supercritical CO_2 has lately been used for manufacturing silver nanoparticle suspensions. It is widely known that $scCO_2$ is a good solvent. It can be used to dissolve metal-organic precursors to form thin films of metals and metal oxides. In earlier works, $scCO_2$ process has been utilized to give antimicrobial polymers and porous structures with antimicrobial specialties by absorbing these materials with silver nanoparticles. Here, Ag(hepta) or Ag(cod)(hfac) was placed in the pre-heated reactor before it was filled with pressurized carbon dioxide. The pressure and temperature conditions of the dissolution processing were 21 MPa and 40 °C, respectively. After exposure to *C. Albicans* yeast, samples modified with Ag(hepta) and Ag(cod)(hfac) showed measurable inhibition zones. The outcomes of this work propose that $scCO_2$ process might be utilized to coat textiles with antifungal silver for medical applications. The utilization of $scCO_2$ to impart antimicrobial functionality to substrates exhibits several advantages comprising relatively low processing temperatures, nonflammable processing materials, and nontoxic reactants. Supercritical CO_2 processing might be utilized to bring antifungal functionality to textile materials utilized in wound dressings and has also been utilized for disinfection of medical fabrics [49]. Another method used to impart antimicrobial properties in supercritical carbon dioxide medium is by adding bioactive components such as chitosan to the process during dyeing [50].

After the end stages of wet processing, the leather was dried and prepared for subsequent finishing process. Water content of the leather drying via $scCO_2$ is approximately 16–18% less than that of conventional process. The drying process was rapid and uniform, as the leather samples could be dried at 60 °C and 20 MPa. Furthermore, no noteworthy shrinkage may occur, and thus, a high dimensional stability of the substrates could be attained. Briefly, $scCO_2$ can be utilized for drying with less energy consumption and with better leather quality. In the finishing process, leather is generally coated with finishing agents to make it usable and suitable. The products to be used for impregnation should penetrate adequately. It was reported that oil and silicones display better solubility in $scCO_2$ [48]. Different usage areas of $scCO_2$ were stated by Knittel et al. in 1993 that UV stabilizers and perfumes could be transferred to textile fibers such as dye applications [15].

Another study about textile finishing by assisted supercritical carbon dioxide is silicon-based finishing on cotton fabric. This study used $scCO_2$ as a medium for cotton fabric finishing with modified dimethylsiloxane polymers terminated with silanol groups. 3-isocyanatepropyltriethoxysilane and tetraethylorthosilicate were applied as crosslinkers for covalent bonding formation between silicon and cotton fiber cellulose polymers. It was stated that all cotton fibers applied with silicon (PDMS) and 3-isocyanatepropyltriethoxysilane exhibit larger silicon amounts than those applied with tetraethylorthosilicate. Supercritical carbon dioxide medium attains satisfying cotton surface coating via a 3-D network of DMS compound and crosslinker, leading to the highest DMS concentration formation in a layer between 1 and 2 microns under the cotton fiber surface [51].

In order to achieve high antibacterial property durable to washing, chitin and chitosan were impregnated to polyester (PET) fabric using supercritical carbon dioxide. Chitosan–lactic acid salt was effectively applied to polyester fabric in supercritical carbon dioxide media. But, chitin could not be impregnated successfully. Here, 70% of the chitosan still conserved on polyester fabrics after 50 home washing cycles, and therefore polyester fabric still continues to exhibit antimicrobial properties. Impregnating chitosan to polyester fabric permanently in an aqueous system is very difficult as it is known. In addition, it is important to state that chitosan could be fixed by impregnation onto polyester fabric strongly through the supercritical carbon dioxide medium [52].

The strong permeability of supercritical carbon dioxide renders it an ideal medium for fabric finishing. Supercritical carbon dioxide medium with a solution of organic fluorine was used to create water-/oil-repellent polyester fiber fabrics. The outcomes displayed that the fluorine was evenly spread on the polyester fiber surface. The treated fabrics displayed a good level of water-/oil-repellent characteristics and improved mechanical property while keeping well air permeability character. It is believed that the fluoropolymer layer formed on the surface of polyester fabric with fluoride coating significantly reduces the surface energy of polyester fabrics [53].

Another method in which $scCO_2$ is used in textile finishing is electroless plating. It has been reported in the studies that catalysis and metallization processes were performed via electroless plating in the $scCO_2$ medium. Polyamide as synthetic fiber and silk as natural fiber were mostly used in these studies. The electrical resistance measurement results of the coated fabrics showed that the electroless plating was successful in $scCO_2$. It has been reported that textile surfaces that were treated with electroless plating can be used in industries such as health, military, and space [54, 55].

In a nutshell, elimination of water consumption and therefore wastewater load, reduced energy consumption, lack of air pollution because of recovery of utilized carbon dioxide can be given as the advantages of working in a $scCO_2$ environment. On the other hand, the machines to be worked with $scCO_2$ according to conventional machinery should be more resistant to pressure; therefore, first investment costs are usually high. This can be given as the disadvantage of working in $scCO_2$ environment.

5 Commercial Developments About $scCO_2$ Usage in the Textile Industry

It is known that commercial applications of supercritical carbon dioxide in the textile sector are mainly related to the dyeing process. A commercially available supercritical carbon dioxide beam dyeing machine with a capacity of 100–200 kg of fabric, as fabric roll, per batch in an open width of 60–80 inches was produced by DyeCoo Textile Systems BV and these machinery have been used in their textile production by its partner FeyeCon Co. Ltd. for Yeh Group of Thailand since 2010 [10, 45].

Commercially utilized DyeCoo brand supercritical carbon dioxide dyeing machine is currently in use on an industrial scale. DyeCoo, a *Dutch engineering company,* is an important leader of waterless textile processing systems. *DyeCoo, a* supercritical carbon dioxide dyeing *technology, was commercially utilized in factories in Thailand in 2010.* As a pioneer in dyeing with $scCO_2$, this company has cooperated with many major brands in the textile industry such as Nike, Adidas, Ikea, and Peak Performance. Lately, Nike opened a novel fabric dyeing factory with the Taiwanese contract manufacturer Far Eastern Century Corp (FENC) and with the collaboration of DyeCoo Textile Systems in Taiwan, which uses a waterless dyeing technique. Nike called their ecofriendly process as "ColorDry process" which uses the supercritical carbon dioxide for polyester fabric dyeing, and described that 95% of the utilized CO_2 can be recycled. Kuenlin Ho, the executive vice president of FENC, stated that the ColorDry process decreases the dyeing time by 40% and energy utilization by around 60% [56].

IKEA also lately had an investment in DyeCoo company. DyeCoo company publicized that their customers who utilized their commercially available supercritical carbon dioxide dyeing machine dyed over 30 million meters of textile substrates per year leading to 100% water and process chemical-free dyeing operations. Unfortunately, countries such as China, India, Bangladesh, Vietnam, and Thailand are dealing with a vast amount of pollution caused by the fashion industry. The most recent waterless supercritical carbon dioxide technology is on the way to reach India for commercial industrial dyeing purposes. For instance, Tiruppur, India, has a very high share in textile exports and this may contribute to undesirable environmental pollution. It was announced that DyeCoo is in contact with many Indian textile companies and targets to establish this ecofriendly waterless dyeing technique in India in 2019 [10, 45].

The final partner of DyeCoo is Tong Siang Co. Ltd. (from Thailand), part of the Yeh Group. This polyester textile producer became the first textile factory to utilize the commercial-scale supercritical CO_2 machine in their production line. They call their process as DryDye. Presently, the process is limited to dyeing of scoured polyester fabric run in batches of 100–150 kg, though DyeCoo and its partners are creating dyes for cellulosic material to be available for utilization in this process in the not-too-distant future [10].

Many partners are required to carry out waterless processes in the medium of supercritical carbon dioxide. The dyestuffs are as important as the processes used in $scCO_2$. Disperse dyes utilized in the process were especially manufactured by Triade (Dutch company) responsible for the production and distribution of CO_2 dyes, and in partnership by Setex (Germany), responsible for the control system [10].

Huntsman (global chemical manufacturer) and DyeCoo joined to develop and grow supercritical CO_2 ($scCO_2$) textile processing technology. Huntsman Textile Effects is collaborating with the DyeCoo company in order to develop and deliver innovative dye and chemical products to promote the waterless dyeing process and to obtain a high level of color fastness and performance that consumers demand. For example, Uvitex SCPN, Uvitex SC-PB, and Uvitex SC-PR are suitable dyes in the $scCO_2$ dyeing process that are developed and launched by Huntsman Textile Effects which delivers brighter white shades and makes colors more vibrant [6].

6 Conclusion

The importance of water is increasing day by day. Water is the most important resource necessary for the survival of the world. However, it is forecasted that there will be a significant decrease in water resources in 2050 due to threats from human beings. The amount of water used in this sector and the amount of wastewater released are very high. Scientists are therefore working to change this negative state to positive by innovative and sustainable processes. In the measurement of sustainable textile processes, whether the process supports water and footprint, life cycle assessment and clean production is checked. Supercritical fluids technology, particularly $scCO_2$, has been replaced by the utilization of dangerous organic solvents. The unlimited world supply of carbon dioxide which has caused global warming could be controlled to provide a wide range of environmentally friendly, energy-efficient, economically attractive, sustainable processes. The supercritical carbon dioxide medium is suitable for both sustainability and clean production because of the absence of water and chemical use. The most common usage area of $scCO_2$ is in the textile dyeing processes. The application of $scCO_2$ in dyeing can be successfully applied for synthetics, particularly PET and PA fibers. It has achieved great success, especially in polyester dyeing due to hygroscopic property. In addition to dyeing, the use of $scCO_2$ in pretreatment and finishing processes has started to increase. The penetration rate is better in $scCO_2$ media than conventional processes because the fiber swells in the $scCO_2$ medium and the material becomes more porous. Thus, the process is more nested with the fiber. In order to solve the existing water-related problems, waterless processes with $scCO_2$ should be extended to a wider area of usage. It is expected that $scCO_2$ technology will be increasingly used in many different steps of the textile sector in the near future. The use of this technology will increase rapidly all over the world, especially when the dyeing of naturally sourced textile products such as cotton is carried out smoothly in the $scCO_2$ medium.

Moreover, the use of $scCO_2$ technology is expected to increase in the textile finishing of many different textile fibers. It is very substantial for the manufacturer and the consumer in environmental and economic terms that all processes (pretreatment, dyeing, finishing, etc.) can be performed without any water in the $scCO_2$ environment in textile enterprises. The fact that many large companies (Nike, Ikea, etc.) prefer products produced by this process emphasizes the importance of the issue. Consequently, it is technically feasible to utilize supercritical carbon dioxide instead of conventional aqueous methods in the textile processing with more water and energy conservation. Therefore, carbon dioxide is not just a "greenhouse gas" but also an abundant molecule with numerous potential application types for life.

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Sustainability in the Spinning Process

P. Senthil Kumar and G. Janet Joshiba

Abstract Spinning is a vital operation process that consumes more power and massive investment. It has been challenging now than during the 1990s in the textile sector. Unlike other industrial segments, spinning mills are a big concern due to the moderate net profit of 5%. The primary export of yarn to neighboring countries has seamlessly reduced the profitability in recent times. The price determination of world cotton is dependent on cotton sourcing whereby the type of single dependency occurs for a secured source, and it seems a big threat for the spinning sector. It must reassure the diversified source and sustainable robust growth in order to avoid direct collapse of the total textile supply chain if it lacks the above sources. Such a competitive price and so challenges increase in the mills to produce quality yarn using average cotton. Perhaps finding out the cotton import arena and their capacity utilization can bring a great deal of success. Despite that, inadequate gas supply due to unavailability of gas mills or captive generators, production cost per unit and the cost for alternative sources of power are driving up even higher. Originally, sustainable business relies on the increase in profitability with respect to quality tasks, consistency, and fast supply of products. This chapter identifies the key issues for sustainability, fast fashion, innovation and changes, product diversification, the right strategy to craft international textile and apparel bodies. Therefore, the textile sector can become more sustainable in the long run. Furthermore, product diversification becomes formidable which can help reduce the market risk. In short, appropriate policy and regulatory guidance to the textile sector would ensure a level playing ground.

Keywords Spinning · Sustainability · Traceability · Diversification · Yarn · Cotton

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1 Introduction

The textile industry is one of the important and essential sectors catering to the human needs and it plays a vital role in the lifestyle management of human beings. Even though the textile industry has utilized numerous applications, in another way, it results in vigorous damage to the natural ecosystem. Wet chemical processes such as pretreatment, dyeing, finishing, drying, and quality check play an important role in the textile industry and it consumes a large amount of water, resulting in generation of large amount of textile effluents containing toxic dyes, heavy metals, soda, acids, and chemicals as major contaminants which are highly toxic to the environment and living organisms. The discharge of textile effluents composed of harmful contaminants into the nearby water bodies causes deficit of freshwater and water pollution. All these textile production processes such as scouring, washing, dyeing, bleaching, sizing, and finishing generate large volumes of toxic effluents with profound color, odor, organic compounds, and toxic chemical compounds [6].

Fiber is the fundamental raw material of textiles based on which the processing technology, time consumption, application, and sustainability criteria are decided. In the year 2015, the demand for fiber in various industrial sectors was elevated to a higher level and it is estimated to be 95.6 million tons globally. The textile industry itself is an inescapable segment in our everyday life that is ceaselessly augmenting from restorative applications to the common designing applications and from nanofabrication advancements to space innovations [7]. In the dyeing and finishing sector of the textile industry, it is estimated that around 10–645 L/kg of water is utilized. Furthermore, it is reported that the water consumption range can increase up to 932 L/kg, depending on the type of technology used and material produced [6]. The graphical representation of the global consumption of fiber in the year 2015 is given in Fig. 1.

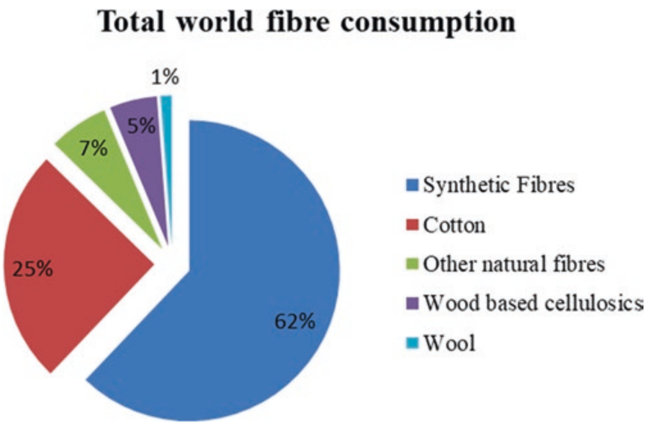

Fig. 1 Global consumption of different varieties of fiber. (Source: Palamutcu [7])

The cotton and polyester fibers are the two most important fibers used in various applications of industrial and domestic sectors. The manufacturing and production of clothing from cotton fibers are found to be ecofriendly, clean, and a sustainable technique. Be that as it may, it is not completely adequate. The pest control agents such as herbicides and pesticides used in the cultivation of crops exert a serious negative impact on the environment and human health; also, it gets released and accumulated in the environment, resulting in various consequences. Also, a large consumption of water for cultivation of cotton fibers is one of the main drawbacks. As days passed, the production and utilization of synthetic cotton dominated natural cotton and it is used effectively in the textile industry as raw material. In spite of its advantages, the enormous consumption of energy and generation of toxic chemicals into the environment during its synthesis process have raised as a major threat to the environment. Production of yarn using the spinning machine is the second most important processing step in the textile process. The spinning sector is one important sector in the textile industry which has advanced a great deal over the years and created a revolution in the field of clothing. Ring spinning method is found to be one of the effective methods utilized in yarn production to date. Implementation of advanced technology in spinning resulted in new variants in the spinning process such as friction spinning, rotor spinning, air-jet spinning, and air vortex spinning; also, these processes work at high speed and efficiency. As spinning is one of the high energy-intensive processes, the employment of sustainability technology in the spinning process is recommended by various researchers and governmental organizations to protect the environment [7]. This chapter reviews the mechanism of the spinning process in textile production and it also explains the various sustainable approaches implemented in the spinning process.

2 Evolution of the Textile Industry

Primitively, human beings used animal skins to cover their bodies for warmth, protection, and bedding. As the proteins present in the plant and animal sources are weak and capable of breaking down, there is almost no proof of their history. Initially, the sewing needles produced using animal bones were found close to Russia in the year 1988. These needles were dated back to around 18,000 BC and were likely used to sew animal skins together to frame a rough apparel. Several clay tablets have shown the existence of weaving in the Middle East Asian countries during 8000 BC. Around 6000 BC, clothing was woven by hand on looms and prepared from raw materials such as wool, linen, and flax. Around 2800 BC, China started silk production and turned it into a noteworthy fare, opening up exchange courses and associations with nations around the world. During the first century AD, both cotton and wool generation increased and it led to the mass production of clothes and garments in a simpler way. It was additionally around this time the principal spinning wheel was discovered. Through the Industrial Revolution of the nineteenth century, most of the texture production was done locally. The production of textile raw materials such as silk, cotton, and wool are progressively developed and utilized in the manufacture of textiles. The implementation of various advancements in the textile machinery resulted in increased production of textiles in Western Europe and North American countries.

The following enormous improvement in texture generation came in 1891 in France with the development of the world's first engineered strands. This cellulose item was obtained from wood and different plants and was first known as Chardonnet silk and later named rayon. The creation of rayon was immediately trailed by nylon during the 1930s and polyester before long. Today, a huge level of texture is made out of these strands, cutting down the expense of attire extensively (Textile school) [8].

3 Spinning Process in the Textile Industry

Spinning is generally defined as the process of conversion of fiber into yarns. In recent times, spinning has been known as a procedure of changing over crude materials such as cotton and wool into yarns for making material texture or items. Majorly, the textile spinning is classified into two types such as hand spinning and machine spinning. The size of yarn is dictated by the unit of Tex, Count, Worsted, Woolen, and Denier [2]. The spinning process is one of the fundamental sectors of the textile industries, which requires huge speculation. In recent times, there are more than 425 spinning factories that are in activity in Bangladesh and every year the nation is creating 2410 million kg yarn (Textile today). In ancient times, spinning was basically performed using hand spinning method with the help of a tool called carder. In the hand spinning method, the yarn is produced through serial processes such as carding, twisting, and roving. After the advancement of industries and technologies, numerous modifications have been furnished in the industries to facilitate the procedure with the application of machines and to ease the manual work done in industries. Ring spinning machine is one of the effective and significant spinning machines used widely in the production of filament and staple yarn in textile industries from the ancient days. The filament yarn is produced using various spinning techniques such as dry spinning, wet spinning, melt spinning, biconstituent spinning, and bicomponent spinning process.

The filament yarn spinning is a simpler and fundamental process when compared to the staple yarn spinning process. The production of staple yarns consists of several processing steps that require higher energy and cost-extensive procedures. The staple yarns are produced using various spinning processes such as air-jet spinning, ring spinning, vortex spinning, and rotor spinning [2]. Initially, the ring-spinning machine was discovered by Thorp, an American, in 1828. Later on, an American researcher called Jenk introduced the rotating ring in the spinner by 1830 (Textile learner). The ring spinning method was introduced by Samuel Crompton in 1779 with the discovery of the spinning mule. From that point forward, the standard of ring spinning has not changed; in any case, the apparel industry has attempted to create quicker, efficient, and adaptable spinning techniques.

Rotor spinning is the second most predominantly utilized spinning technology globally and in the working speed, the performance of the rotor spinning is found to be 10 times higher than that of rig spinning. Air-jet yarn spinning is the most innovative up-to-date technique that has been acknowledged by the textile industry over the most recent 20 years. The rate of textile production using the air-jet spinning line is shorter than the production line of the ring-spinning method [7].

4 Types of Spinning Processes

A wide variety of spinning processes is followed in the textile industry (Fig. 2). Commercially, there are three types of spinning processes followed in the textile industry:

- Ring spinning
- Rotor spinning
- Air-jet spinning

4.1 Ring Spinning

Ring spinning method is a high electrical energy-consuming process that takes up about 72% of the total monthly energy utilization rate for the conversion of fiber into yarn, and the usage of air conditioning in this sector alone consumes 16% of the total energy consumed. The amount of energy utilized by the spinning process

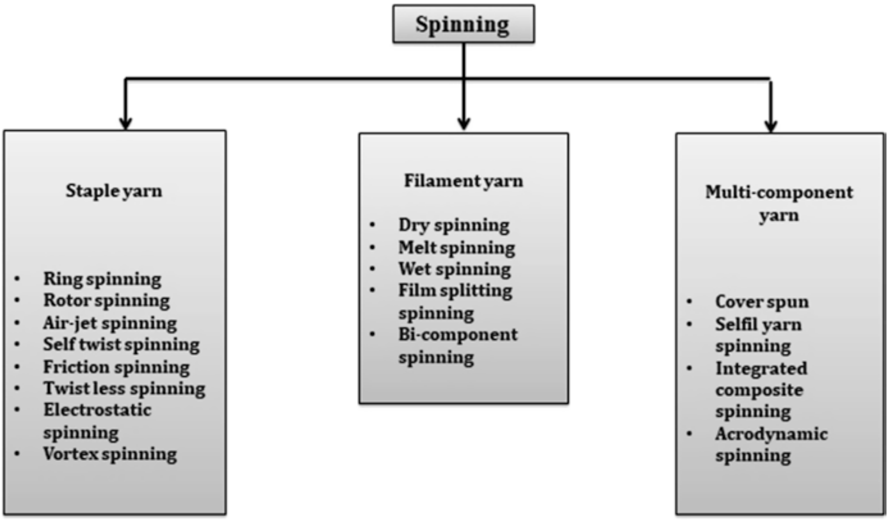

Fig. 2 Various types of spinning processes. (Source: Textile learner)

depends on factors such as type of yarn, thickness, twist level, and yarn morphology. This ring spinning process has the most abnormal amount of natural impact and it also includes the most abnormal amount of natural burden on the textile sector. From the sustainability point of view, the implementation of engines and technologies to consume less amount of energy in the spinning sector, usage of lesser weighing bobbin, adequate oiling of rings, and increasing speed of the spinning process will enhance the performance of the spinning process [7].

There have been numerous improvements in ring turning machines for the most recent years; however, the fundamental idea has stayed unaltered (Textile learner).

4.2 Rotor Spinning

Rotor spinning was discovered in the early 1970s and 1980s and it is otherwise called open-end spinning. Furthermore, it converts the fibers into yarn using the rotor spinner and it transmits a twist onto the yarn. Open-end turning requires fewer strides than ring spinning since the roving process is not required. Rotor turning is around seven times as quick as ring turning; however, it delivers more fragile yarn in a small scope of yarn counts [10].

4.3 Air-Jet Spinning

Air-jet spinning was initially discovered in the middle of 1980 and it has developed notoriety in light of its high profitability. The fiber is bolstered into a drafting framework that feeds the yarn into a vortex made by fast air jets, to confer false twist. This air-jet spinning is around multiple times as quick as ring turning [10]. The air-jet framework for all intents and purposes thoroughly incorporates the filaments into the yarn body and finishes turn addition into the yarn. Bend addition and fiber reconciliation onto the yarn strand are finished just when the air and no mechanical parts are straightforwardly associated with the curve addition process [7].

5 Process of Yarn Production

Initially, the cotton in bales is converted into cone winding using the technique called spinning. The tightly packed cotton in bales is converted into open, loose, and clear cotton; also, they are processed in the blow room. The processing of bales in the blow room is considered to be the first step of a spinning process. The blow room machinery exerts three different actions on the bales such as follows:

- The action of opposing spikes
- The action of air current
- Action of beaters

After the spinning process, the loosened fibers are subjected to a process called carding which enhances the yarn morphology. This carding process assists in clearing the impurities present in the fiber materials and production of untwisted fibers. In addition, it also helps in eliminating the neps and stretching of the yarn. It undergoes two different modes of action such as carding action and stripping action for processing the yarn. As the carded silver is irregular, they are subjected to treatment in the draw room in which doubling and drafting will take place. In the draw room, the equalization, parallelization, and blending of the yarn take place to enhance the quality of the yarn. Furthermore, roving helps in maintaining the strength of the fiber and it introduces a twist to the yarn through the processes such as drafting, winding, and twisting. Afterward, the yarn is subjected to a combing process in which the cotton is completely converted to yarn with satisfactory quality. The checked materials (bit) contain certain measures of neps, short strands, fine kitty and leaf particles. The short strands cause thick and uneven places in the yarn length and the yarn looks bushy. Aside from this, extremely short strands do not contribute anything to yarn quality. Short strands beneath a certain pre-decided length can be effectively isolated by utilizing a comber. Finally, the processed yarn is spun using the ring-spinning method; also, it helps in enhancing the texture and strength of the fiber. Processes such as drafting, creeling, winding, twisting, building, and doffing of the processed fiber are carried out in the ring-spinning. Then, the spun fiber is subjected to cone winding process which is the most important sector of the textile industry (Textile learner). The schematic representation of the methodology followed in the textile spinning process is given in Fig. 3.

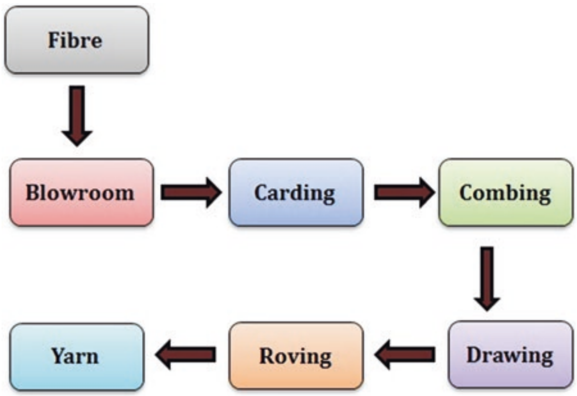

Fig. 3 Methodologies involved in the textile spinning process

6 Sustainability in the Textile Industry

Sustainable production in any industrial process aids in productive consumption of natural resources, reduction of production cost and waste generation. There are a few reference records that recommend systems to detect and alter the processes to diminish the utilization of water and vitality bringing about the decrease in the contamination [6]. Sustainable development focuses on cultural, social, economic, and technological aspects of any industrial process and production. Nowadays, new discoveries and technologies end in two ways such as comprehending the current issues and making some new issues. It implies that each new innovation brings its reactions among its preferences. Practical advancement is the mission of the society, and it is firmly connected to the utilization of innovation. In order to keep up a harmony between innovation for improving society and technology, sustainability serves as the main tool [7].

Sustainability is the management of constrained and limited natural sources for the upcoming generations. The progressive development of textile industries resulted in the improvement of a country's economy simultaneously and it has also resulted in various negative outcomes toward the environment. Textile industries faced many challenges in various sectors of production and manufacturing of textiles and garments. Sustainability is found to be the key factor that remains as a remedy for the various challenges posed by textile industries in managing the consumption of water, energy, and harmful chemicals (Lead innovation blog). Ecological issues play a vital role in the textile industry, from the perspective of government guidelines and customer desires. Nowadays, sustainability has arrived in every industrial process for fortifying the negative impacts of industries on the ecosystem. The textile industry is one of the biggest sectors which pollutes the environment vigorously and it requires the sustainability approaches in every single processing step in its manufacturing and production. According to the World Commission on Environment and development, sustainable development is defined as the one that meets the needs of the present without compromising the ability of future generations to meet their own needs [5].

7 Various Sustainable Strategies in Textile Spinning

Spinning is one of the traditional methods of producing yarn in the textile industry and it is one of the important methods utilizing higher energy in this sector. Basically, the yarn from the produced fiber is divided into two major categories such as staple and filamentous yarn spinning method. Staple yarn spinning method deals with the segregation, aeration, and processing of fiber which makes it suitable for mechanical coating and aerodynamic systems.

Some of the factors which strongly influence the sustainable spinning technique are as follows:

- Speed of the spinning machine
- Type of spinning equipment
- Type of fiber
- Energy consumption rate
- The thickness of the yarn obtained from fiber
- Pre- and postprocessing steps

During the texture development in garments, various processing methods such as heating, cooling, mechanical, and aerodynamic process are utilized in the spinning sector. In addition, staple and filamentous yarn production requires handling steps such as cooling, blowing, lighting, and cleaning apparatuses. The consumption of a higher amount of energy is found to be one of the critical issues in the spinning process. Furthermore, the implementation of sustainable technologies in the spinning process helps in efficient management of energy utilized in the textile sector. Traditionally, the ring-spinning method is considered to be one of the methods used in the spinning process and it is found to be more reliable and an effective spinning method among the various technologies used in the spinning process to date. Various types of spinning processes such as ring spinning, air-jet spinning, and rotor spinning consume a large volume of energy which plays a major role in influencing textile production parameters such as thickness, twist, and morphology of yarn. The present rotor spinning innovation has been reliably created for higher efficiency and lower vitality utilization. The improved rotor spinning enables a similar yarn quality to be created with less twist and littler rotors. Such methodologies help to build efficiency and spare vitality. The optimization process of spinning positions and integral parts results in less consumption of energy and space. Around 25% of the energy utilized per kilogram of yarn can be decreased with the implementation of sustainable principles to the spinning process and the yarn produced is of high quality and strength. The air-jet spinning system consolidates fibers into yarn and it imparts a false twist into the yarn. Due to the utilization of compressed air in the spinning process, a large amount of electrical energy is utilized in the spinning process. Since the expense of vitality is a significant and testing issue, particularly in certain nations, such favorable factor of spinning may turn into a restricting component for the determination of the air-jet spinning. Regardless of high vitality utilization of the air-jet spinning, it is always considered as the future of the textile spinning process. In recent times, around five million tons of air-jet, nine million tons of rotor, and twenty-six million tons of ring spin are utilized globally in the textile industries for the purpose of spinning. It is reported that by 2020, the textile production using the air jet spinning method will elevate to a net worth of two million tons [7].

All the assembling activities and innovations in the textile sector make hurtful effects on nature; be that as it may, a large portion of the procedures are crucial procedures that are traditionally acknowledged. There is no plausibility of zero effect, or altogether deleting of the natural burden, abandoned a material item. Just sustainable approaches to lessen the natural burden are innovation improvement, suitable innovation choice, and proficient management of technology. The advancement of technology in the textile industry offers a few chances to make a move toward new product innovation courses and models to fabricate maintainable material innovation conditions [7].

Talking about this point, we comprehend that the ring-spun yarn turns into the reference or a benchmark against which we judge the advancement of other turning frameworks. We have to take into account the advancement of new spinning frameworks in the light of how we can produce cost-effective spinning process as well as new items for wool processing. In such manner, the strength and appearance properties of the textile fabric are critical. Customarily, the wool business, especially in Western Europe, has been preservationist, which implies that new turning frameworks and their potential for processing wool have not been completely explored [11].

8 Innovative Approaches

The innovative idea was creative not just for its fast and imaginative way to deal with yarn fabricate; yet, it tested the very ideas of yarn and texture arrangement. The outcome was a progression of continuous generation all produced from the first self-twisting ideas such as sirospun, and solospun techniques. The integration of the self-twist method to the ring-spinning process is called as sirospun. This is a two-strand framework containing the physical properties required for weaving; however, interestingly at the time, it is produced in one stage. This implies that expenses are decreased considerably as a result of the lower number of transformation procedures, and Sirospun yarns are not exactly traditional delivered yarns.

Solospun is another energizing procedure where weavable singles yarn is created on a turning outline. This implies that a weavable, lighter weight strand than ordinary two-crease yarns is delivered in one stage. So, the leap forward is into lighter textures, yet additionally at a lower cost. This is altogether practiced with a generally minimal effort of the connection expected to produce the Solospun. Appropriation has been lower than anticipated most likely as a result of an absence of comprehension of the basic idea of the framework, especially in creating nations. This innovation is presently 5 or 6 years of age and has had a constrained entrance in the two markets. The yarns are smooth and lean with diminished hairs and pilling, and have some dismissal due to the absence of surface in the last item. With an expanded comprehension of fiber properties and yarn and texture building, there ought to be an extensively greater chance to abuse these yarns in specific pieces of the market; for instance, sports programs [11].

9 Conclusion and Future Perspectives

Textile spinning is one of the main sectors in the textile industry that is used to convert crude materials such as silk, cotton, and wool into yarn through the spinning process. The spinning process is a high-cost and energy-consuming spinning process. The utilization of a high amount of energy simultaneously increases the production cost and reduces the compatibility. In order to overcome the energy issues, various technologies and instrumentations have been integrated into the traditional spinning process. The advancement in the spinning technology results in enhancing the morphology and quality of the yarn. Also, it reduced the space requirements of large spinning machinery. Sustainability is a great tool for enhancing the efficiency of the spinning process in the textile industry. Faster working and efficient spinning techniques which consume less energy must be implemented in the spinning sector to reduce its negative impact on the environment.

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