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.

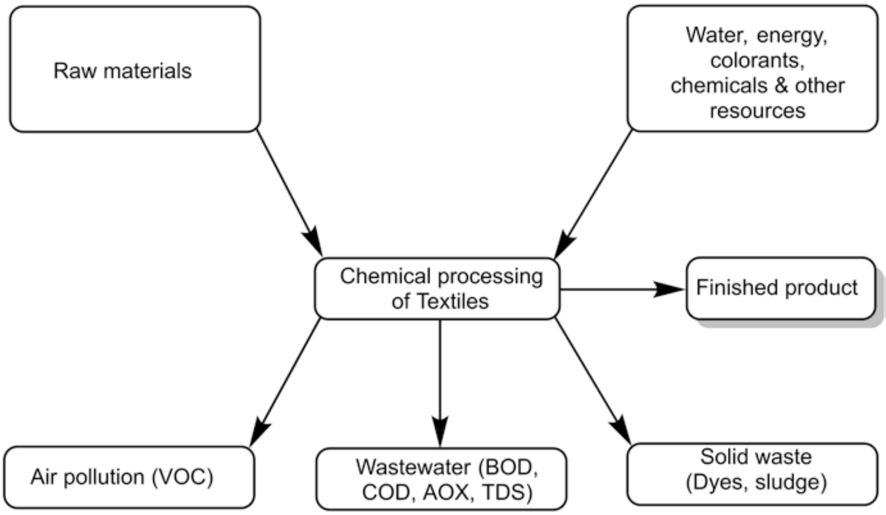

Fig. 1 The pollution route in the textile industry

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

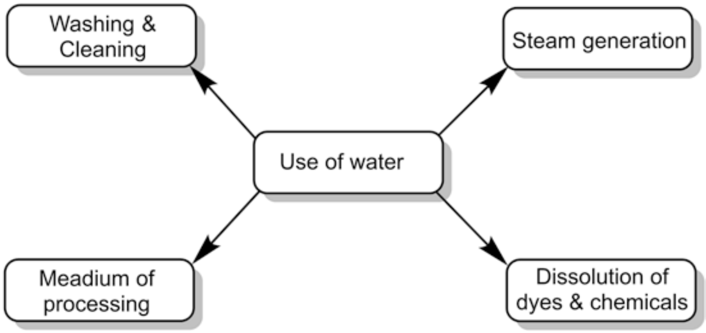

Fig. 3 Water consumption in chemical processing of textiles

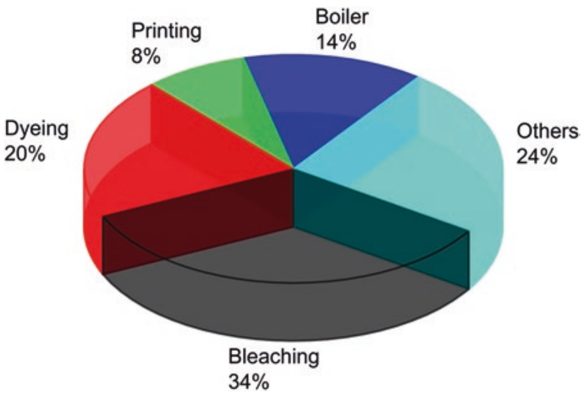

Fig. 4 Water consumption in wet processing of textiles

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

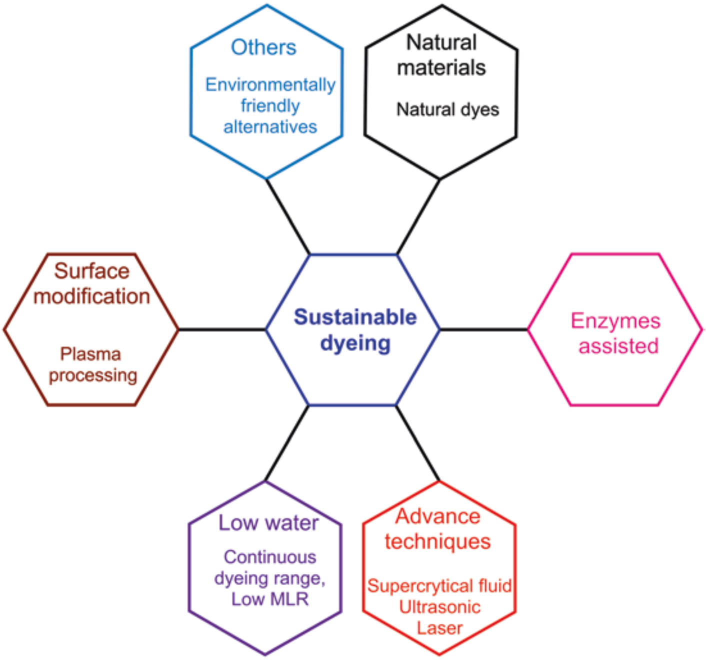

Fig. 6 Sustainable approaches in textile dyeing

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.

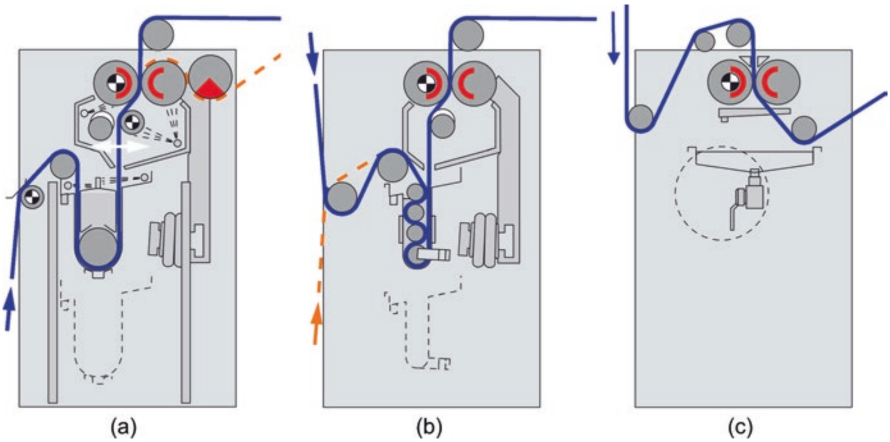

Fig. 8 (**a**, **b**) S-roller technology with quick cleaning (**a**) and without quick cleaning (**b**). (**c**) The nip dyeing method

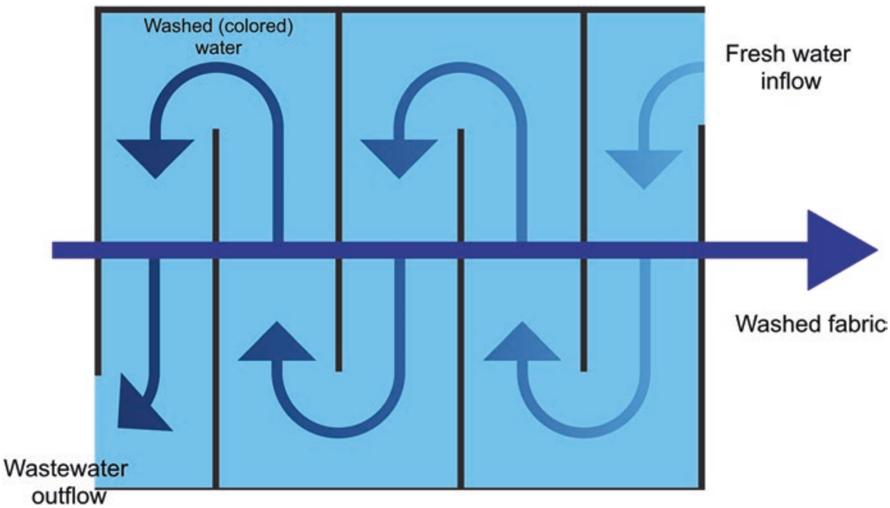

Fig. 9 Counterflow washing technology

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)

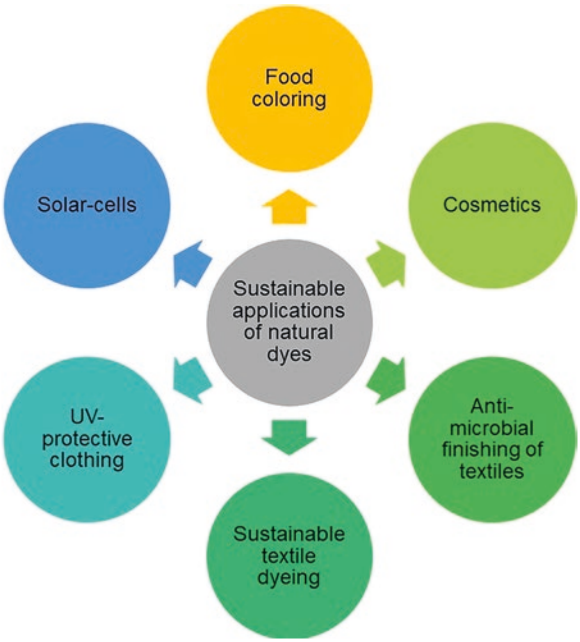

Table 11 Classification of natural dyes according to their chemical structure

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].

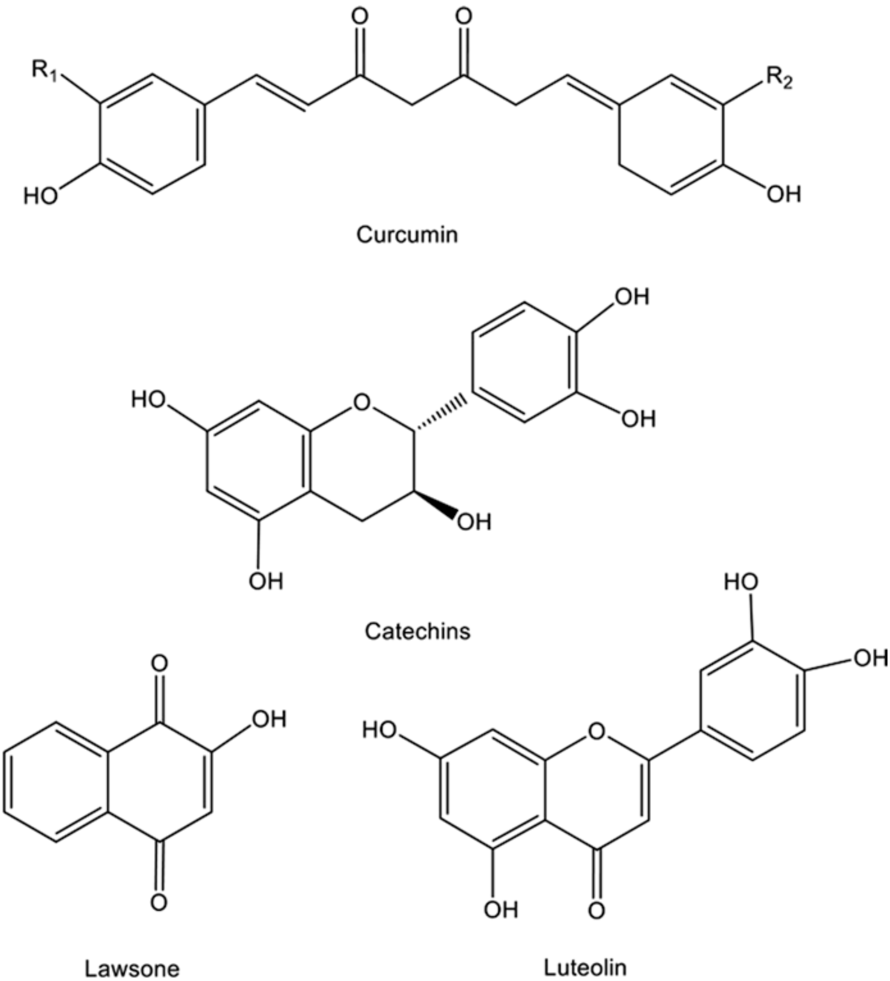

Fig. 11 Structures of curcumin, catechins, lawsone, and luteolin

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

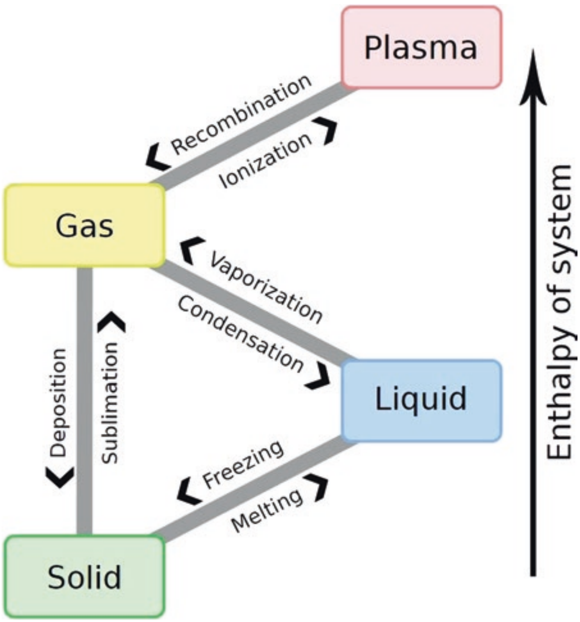

Fig. 12 Different states of matter

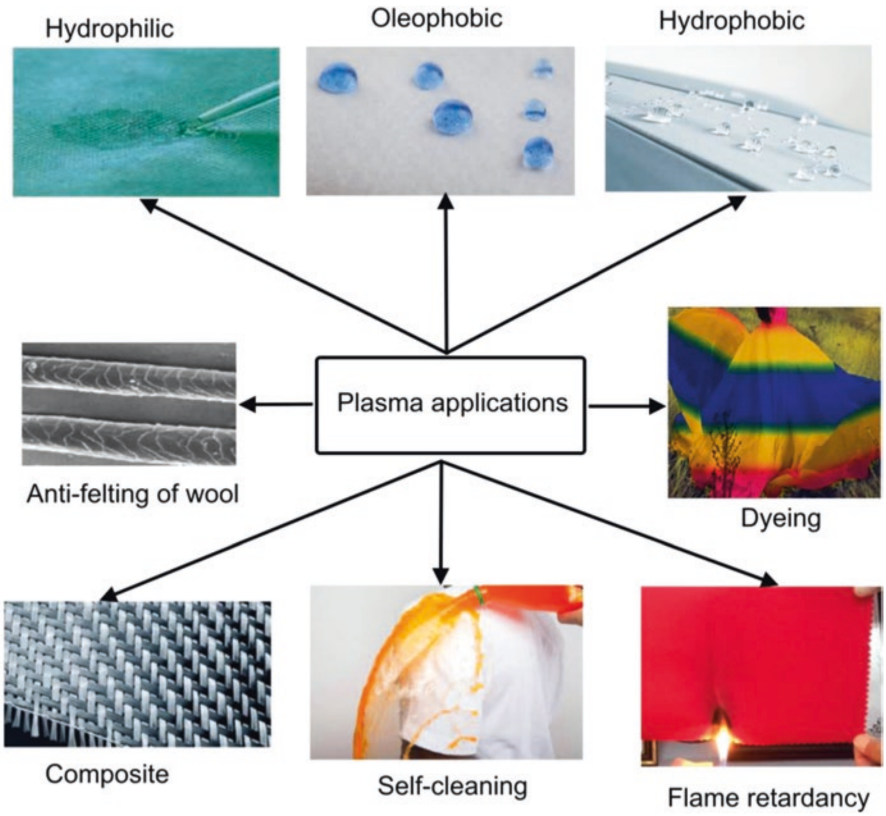

Fig. 13 Different applications of plasma in textiles

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.

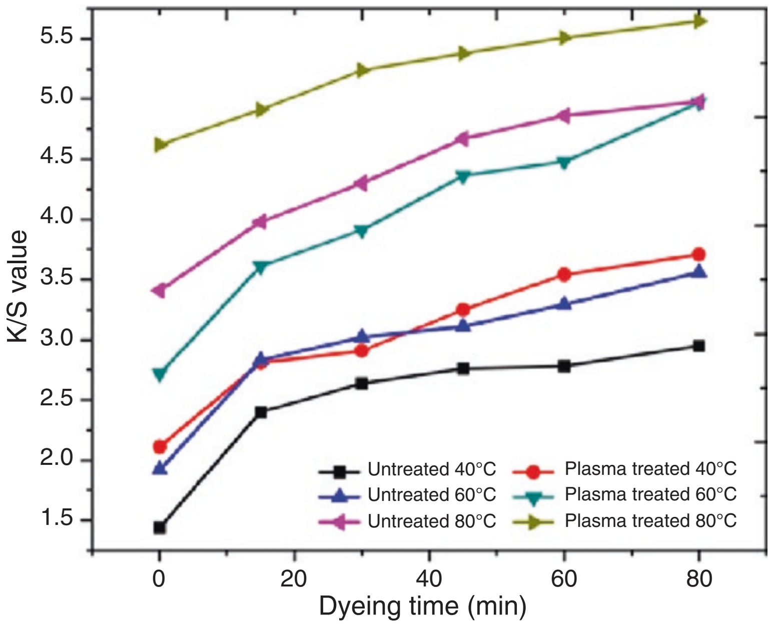

Fig. 14 K/S values of untreated and plasma-treated silk fabrics. (Reproduced from Teli et al. [83], with kind permission from Springer)

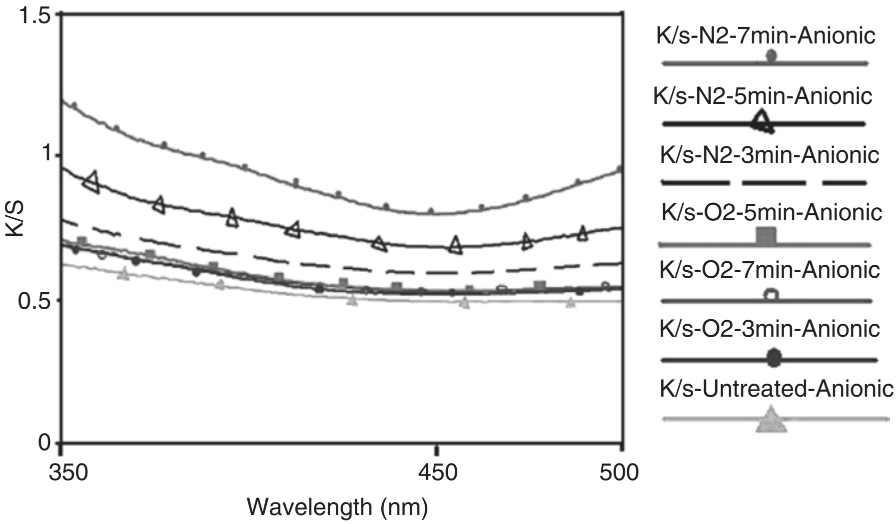

Fig. 15 Reflective spectrophotometry of anionic dyed samples. (Reproduced from Shahidi et al. [85], with kind permission from Springer)

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].

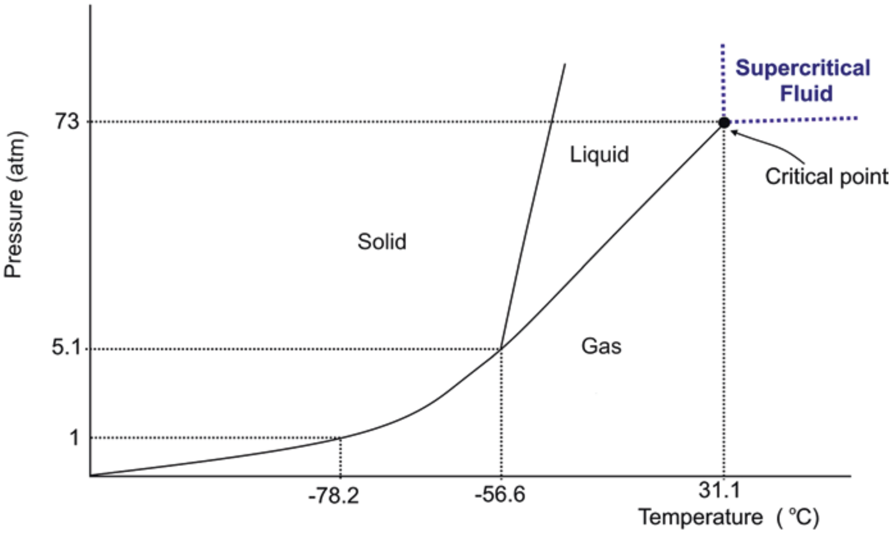

Fig. 16 Phase diagram of CO_2

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

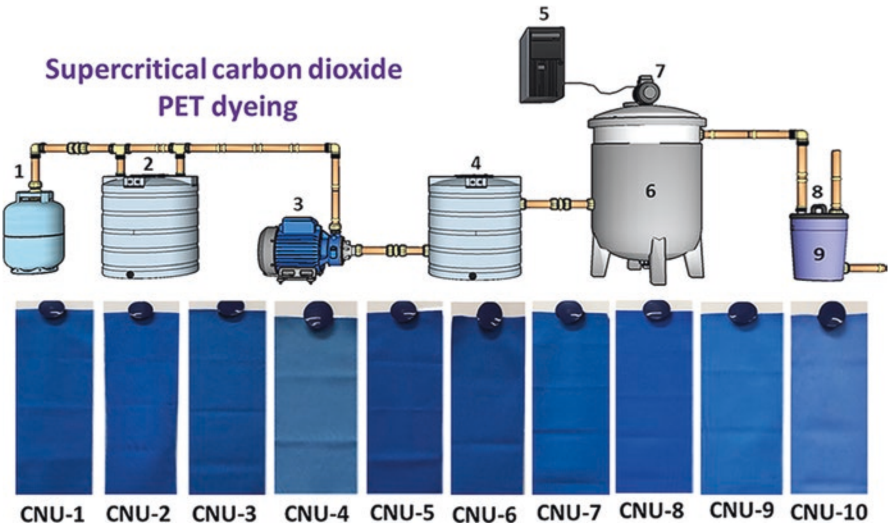

Fig. 17 Typical polyethylene terephthalate dyeing apparatus used in supercritical CO_2 conditions. (1) CO_2 cylinder, (2) circulated cooling bath, (3) CO_2 pump, (4) heating bath, (5) temperature controller, (6) stirrer, (7) dyebath, (8) pressure regulator, (9) separator. (Reproduced from Penthala et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

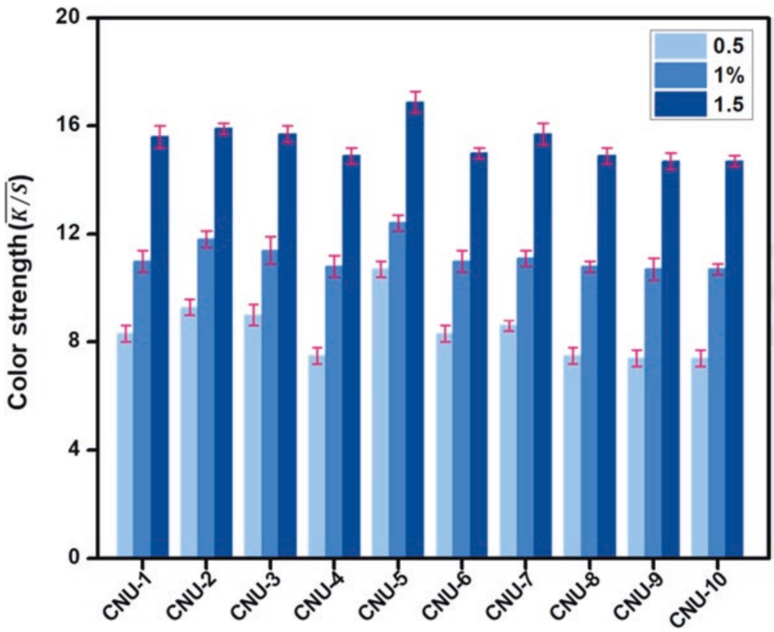

Fig. 18 Effect of dye concentration on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

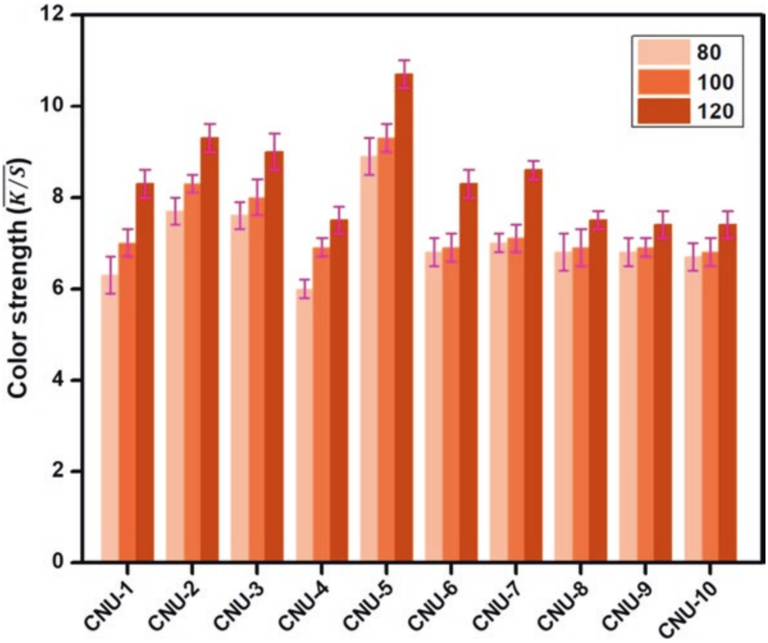

Fig. 19 Effect of process temperature (80, 100, or 120 °C) on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

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 micro-bubbles 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,

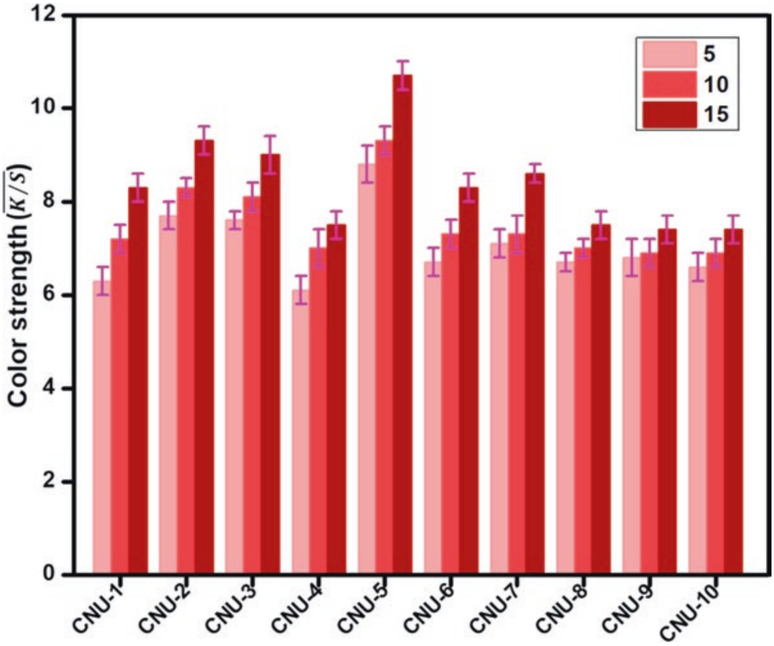

Fig. 20 Effect of process pressure (5, 10, or 15 MPa) on color strength values in supercritical CO_2 dyeing. (Reproduced from Penthala et al. [97], with kind permission from Elsevier)

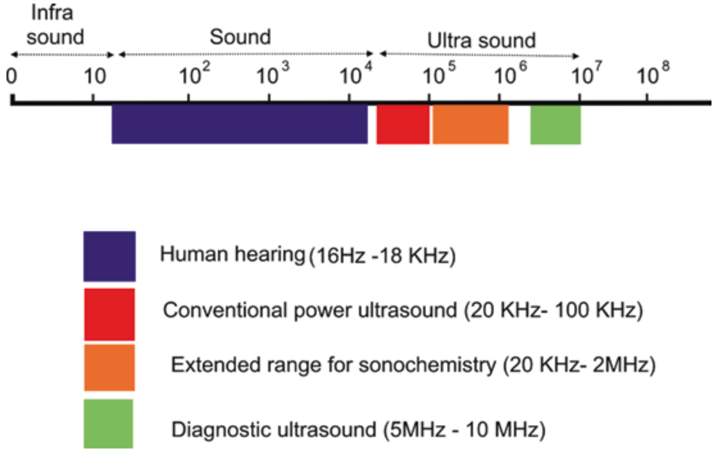

Fig. 21 Classification of sound according to its frequency

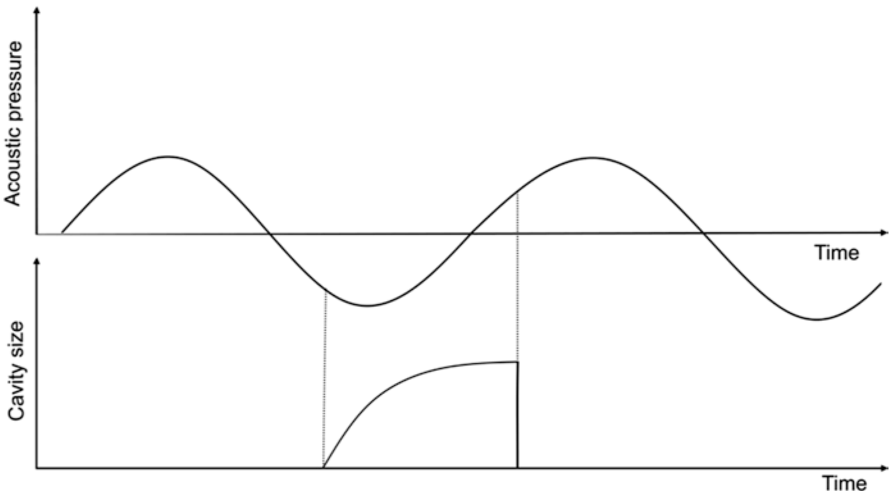

Fig. 22 Characteristics of an ultrasonic wave

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

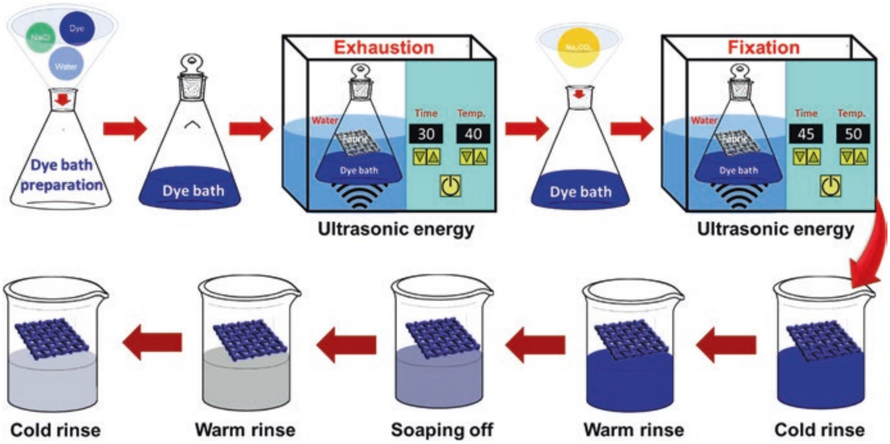

Fig. 23 The ultrasound-assisted exhaust dyeing process. (Reproduced from Babar et al. [98], with kind permission from Elsevier)

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:

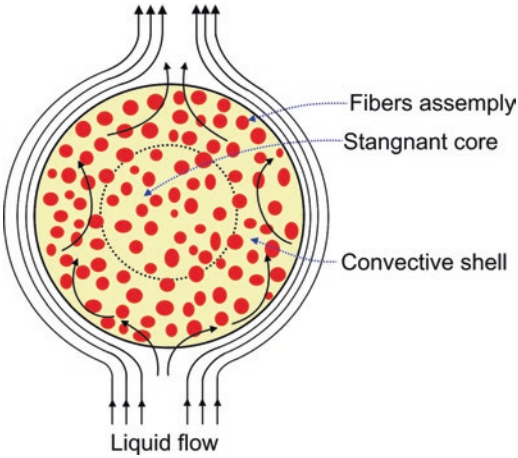

Fig. 24 Liquid flow in the yarn structure

- 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.

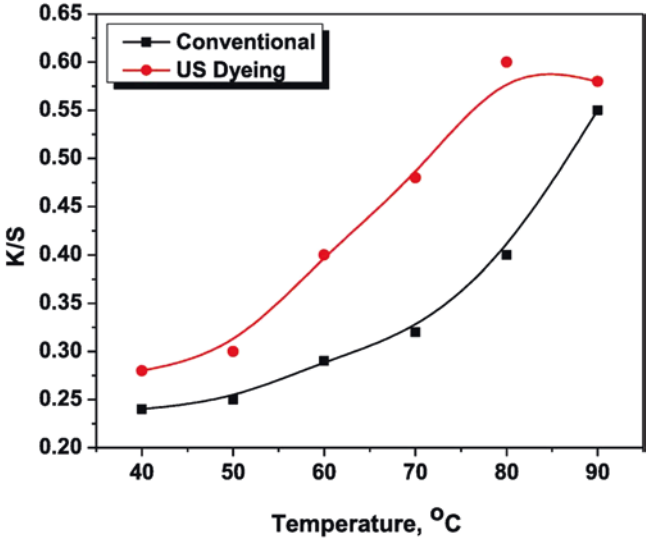

Fig. 25 Effect of dyeing temperature on coloration of nylon 6 nanofibers. (Reproduced from Jatoi et al. [104], with kind permission from Elsevier)

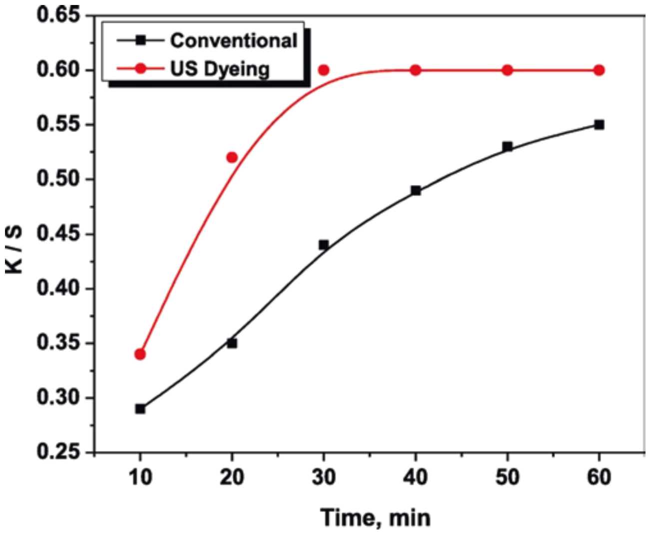

Fig. 26 Effect of dyeing time on coloration of nylon 6 nanofibers. (Reproduced from Jatoi et al. [104], with kind permission from Elsevier)

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

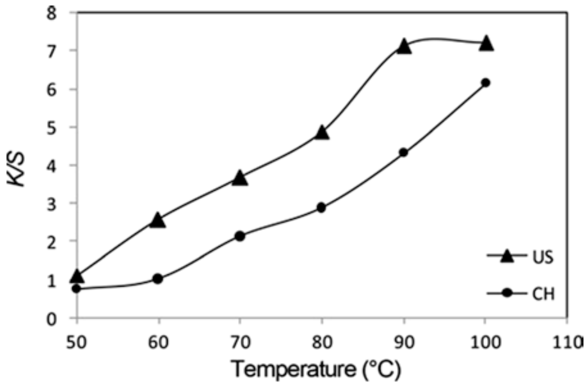

Fig. 27 K/S value versus dyeing temperature used for coloration of polyamide fabric. (Reproduced from Peng et al. [106], with kind permission from Springer)

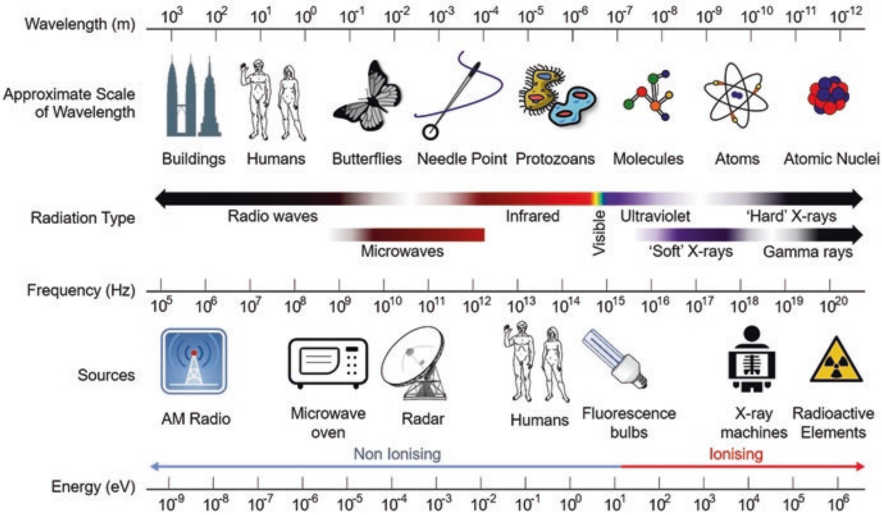

Fig. 28 The electromagnetic spectrum

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

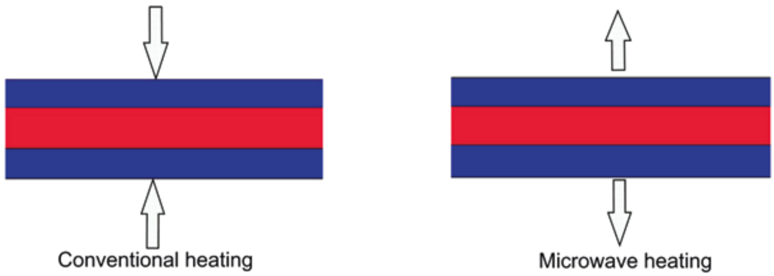

Fig. 29 Microwave (volumetric) heating versus conventional (surface) heating

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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