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REVIEW

The use of new technologies in coloration of textile fibers

Nahed S. E. Ahmed · Reda M. El-Shishtawy

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Abstract Textile coloration is a wet process that uses dyes, chemicals, and large volume of water. The chemical wet processing of textiles continues to expand each year using new technologies. The driving force being the need for cleaner, cost-effective, and value-added textile products. This review will provide a summary of recent developments in the coloration of textile fiber. Emphasis will be paid to the new technologies, in particular those based on physicochemical means such as nanotechnology, electrochemistry, supercritical carbon dioxide coloration, plasma, ultrasonic and microwave, and their uses in the coloration of textile fibers.

Introduction

Coloration is the aqueous application of color, mostly with synthetic organic dyes, to fiber, yarn or fabric. In this process, dye and auxiliary processing chemicals are introduced to the textile to obtain a uniform depth of coloration with color fastness properties suitable to the end use. Different fastness requirements may apply depending on the intended end use of the textile. Examples might include swimsuits that must not bleed in water and automotive fabrics that should not fade following prolonged exposure to sunlight. Different types of dyes and chemical additives are used to obtain these properties [1].

Dyes can be applied to textiles by various forms of continuous pad applications, or exhaust dyed in batch processing equipment. Knit fabrics are dyed by exhaust techniques in batch equipment and woven fabrics are most often dyed continuously. The chemical wet processing of textiles continues to expand each year as older products and processes are replaced by the technological diffusion of novel products and innovative processes. The driving force being the need for cleaner, cost-effective, and value-added textile products [2].

Aim

This article attempts to provide a summary of recent developments in the coloration of textile fiber. Emphasis will be paid to the new technologies, in particular those based on physicochemical means such as nanotechnology, electrochemistry, supercritical carbon dioxide coloration, plasma, ultrasonic and microwave, and their uses in the coloration of textile fibers.

Nanotechnology

The concept of nanotechnology is not new; it was started over 40 years ago. Nanotechnology is defined as the utilization of structures with at least one dimension of nanometer size for the construction of materials, devices, or systems with novel or significantly improved properties due to their nano-size. Nanotechnology can best be described as activities at the level of atoms and molecules that have applications in the real world. Nanoparticles

N. S. E. Ahmed · R. M. El-Shishtawy (✉)
Textile Research Division, National Research Centre,
El-Behouth St. Dokki, P.O. Box 12622, Cairo, Egypt
e-mail: elshishtawy@hotmail.com

R. M. El-Shishtawy
Chemistry Department, Faculty of Science,
King Abdul-Aziz University, P.O. Box 80203,
Jeddah 21589, Saudi Arabia

commonly used in commercial products are in the range of 1–100 nm. Nanotechnology is increasingly attracting worldwide attention because it is widely perceived as offering huge potential in a wide range of end uses. The unique and new properties of nanomaterials have attracted not only scientists and researchers but also businesses, due to their huge economical potential.

Nanotechnology also has real commercial potential for the textile industry. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanotechnology can provide high durability for fabrics, because nanoparticles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of nanoparticles on fabrics will not affect their breathability or hand feel. Therefore, the interest in using nanotechnologies in the textile industry is increasing [3].

The first study on nanotechnology in textiles was undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries [4]. Later, more and more textile companies began to invest in the development of nanotechnologies. Coating is a common technique used to apply nanoparticles onto textiles. Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing, and padding. Of these methods, padding is the most commonly used [5–7]. The nanoparticles are attached to the fabrics with the use of a padder adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dyeability, and more. As there are various potential applications of nanotechnology in the textile industry, only those related to textile coloration are critically highlighted below.

Nano-sized pigment particles in textile coloration

The development of nanotechnologies has stimulated research on applications of nano-sized pigment particles in textile processing. One possible application is to directly employ pigment nanoparticles in textile coloration. Such an approach could be achieved if the nanoparticles can be reduced to a small enough size and the particles can be dispersed well to avoid aggregation of the nanoparticles in dye baths (Fig. 1).

Exhaust dyeing of cationized cotton with nanoscale pigment dispersion has recently been achieved and the results indicated that the dyeings obtained have better soft handle and more brilliant shade with reduced pigment requirement than those obtained with a conventional pigment dispersion [8].

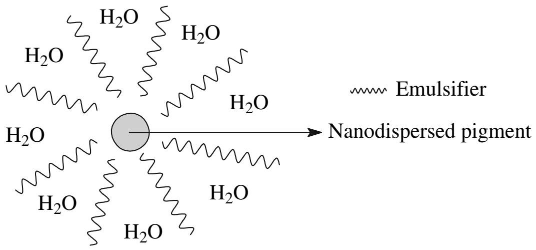


Fig. 1 Nanodispersion of an organic pigment

Langhals has recently reported the possibility of getting nanodispersion of lipophilic perylene bisimide pigments through studying the information about the direct environment of the pigment molecules in the nanoparticles using UV/Vis spectroscopy. The UV/Vis spectra of the nanodispersion of the pigment were identical with the spectra in homogeneous lipophilic solution such as in chloroform indicating the complete covering of the chromophore in its nano-size by the dispersant. The coloration of cellulose fiber with such dispersions was also demonstrated [9].

Previous research has shown that surfactant dispersed Carbon Black (CB) nanoparticles in nominal size of 8 nm were able to diffuse slowly into polyester and acrylic fibers at temperatures above their glass-transition temperatures (T_g) in a thermal coloration process [10]. However, in exhaustion coloration of cotton, wool, acrylic, and nylon fabrics, dispersion of CB nanoparticles in aqueous solutions and adsorption of the particles onto surface of the fibers was only achieved after modifying CB by oxidation to render it hydrophilic by virtue of the formation of carboxyl groups on the surface of the particles and thus leading it self dispersible without the need of dispersing agent [11].

Dyeability of nanocomposite fibers

Nanocomposites are materials that are created by introducing nanoparticles (often referred to as the filler) into a macroscopic sample material (often referred to as the matrix) (Fig. 2). This is part of the growing field of nanotechnology. After adding nanoparticles to the matrix material, the resulting nanocomposite may exhibit drastically enhanced properties [12].

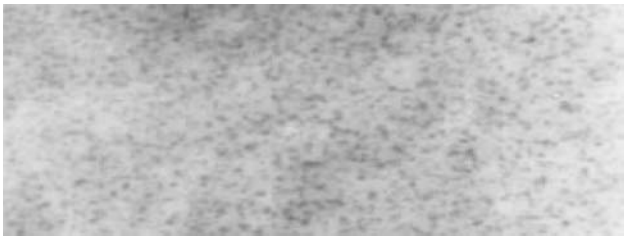


Fig. 2 Nanocomposite fiber

Polypropylene (PP) is cheaper than nylon and polyester, but its dyeability is a problem. There are few conventional processes which can improve the dyeability of PP, viz, copolymerization, polyblending, and grafting; however, all these processes are costly and in turn increases the overall cost of the PP fiber. Nanotechnology has solution for this problem. Nanoclays modified with quaternary ammonium salt were used to make nanocomposite polypropylene (nanoPP) [13].

This novel polypropylene is dyeable with both acid and disperse dyes. The acid dyeability of the nanoPP is due to the ionic attraction between the negatively charged acid dye and the positively charged quaternary ammonium salts in the nanoclay. Van der Waals forces, and perhaps hydrogen bonding, also play important roles in acid coloration of the nanoPP. For the coloration with disperse dye, it was proposed that the attraction between the disperse dye and nanoclay is mainly due to the van der Waals forces and hydrogen bonding. Also, the acid dyeability of nanoclay/PP nanocomposites using three distinct chemical structures, namely, anthraquinone, premetallized, and monoazo with four major colors, which are C.I Acid Blue 80, C.I Acid Orange 74, C.I Acid Red 266, and C.I Acid Yellow 135, was recently reported [14].

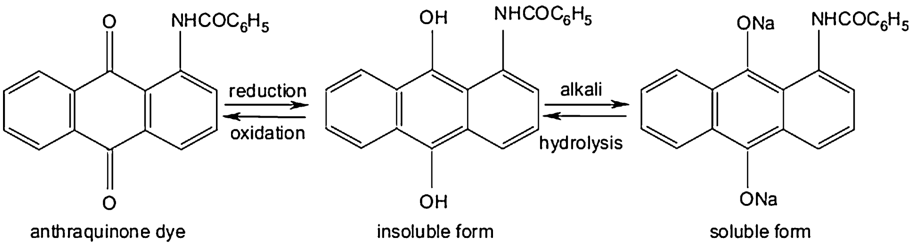
It was also reported that nanoclay/polyamide 6 (PA6) nanocomposite yarn dyes itself faster with disperse dyes than unfilled PA6 yarn, while it is the opposite with acid dyes and 2:1 metal complex dyes. In both latter cases the nanoclay fixes on the amino sites, preventing the fixation of the acid or the metal complex dyes [15].

Recently, polyester (PET) nanocomposite fiber was made from polyester and silica (SiO_2) nanoparticles aiming at getting a new-added value for PET and better dyeability with disperse dye. The results reported indicate that PET/SiO_2 nanocomposite fibers showed a greater degree of weight loss upon alkaline hydrolysis as compared with that of pure PET fibers. More and tougher superfine structures, such as cracks, craters, and cavities, were introduced, which would facilitate the certain application-like deep coloration [16].

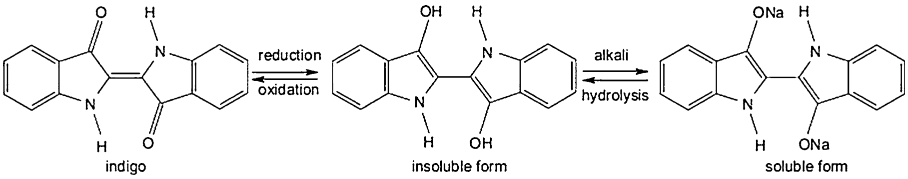
Electrochemical coloration

In the coloration of cellulose fibers, vat (including indigo) and sulfur dyes still represent a relatively large part of the dyestuff market (about 31%, Fig. 3). It seems that the situation will remain constant also in the near future mainly because vat dyes yield colored fibers of excellent all-round fastness, particularly to light, washing, and chlorine bleaching. Sulfur dyes are particularly important for the production of inexpensive products having average fastness requirements. The dyes are very fast to light and washing, but not to chlorine.

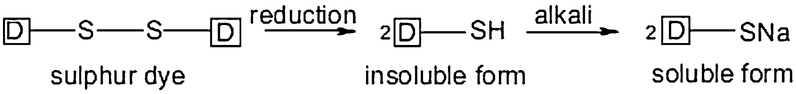
As shown below, these dyes have to be reduced (vatted) before coloration to be converted into the water-soluble form (leuco enolate dye form) which have substantivity toward fibers and which, after absorption into the fibers to be dyed, should be re-oxidized to the original water-insoluble dye pigment form in situ in the fibers [18].



Mechanism of reduction/oxidation of vat dyes



Mechanism of reduction/oxidation of indigo dyes



Mechanism of reduction/oxidation of sulfur dyes

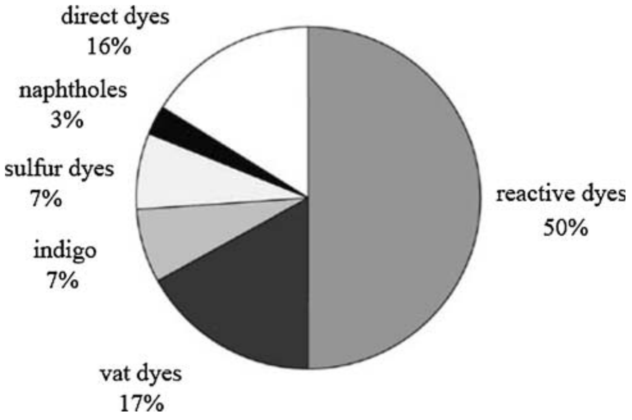


Fig. 3 Worldwide consumption of dyes for coloration of cellulose fibres [17]

The reducing agents required in the coloration process for vat and sulfur dyes cannot be recycled and lead to problematic waste products. In recent investigations to improve the biocompatibility of the vatting process even further, various electrochemical reducing methods have been described, such as indirect electrochemical reduction employing a redox mediator, direct electrochemical reduction of indigo via the indigo radical, electrocatalytic hydrogenation and direct electrochemical reduction of indigo itself on graphite. These methods offer tremendous environmental benefits, since they minimize the consumption of chemicals as well as effluent load [17, 19–23]. In this interest, The European research initiative EUREKA has extended the Lillehammer Award on June 2006 for the electrochemical dyeing project carried out by DyStar Textilfarben GmbH in collaboration with the University of Innsbruck's Institute for Textile Chemistry and Textile Physics (TID) in Dornbirn, Austria, and Getzner Textil AG. The patented technology combines an electric current with a recyclable mediator. It replaces the non-regenerative-reducing agents currently used to apply vat and sulfur dyes to textiles, which often prevent recycling of the dyebath and cause contamination of production effluent. The award-winning project represents a breakthrough in industrial use of electrochemical dyeing [24].

Indirect electrochemical reduction

The rate-limiting step of the electrochemical reduction is the electron-transfer from the cathode surface to the surface of the microcrystals of the dispersed dye pigment. This is especially the case if the electrons have to be transferred directly between the solid surfaces. Therefore, an indirect electrochemical reduction process employing a soluble redox mediator was developed to enhance the rate of the electron-transfer as shown Fig. 4.

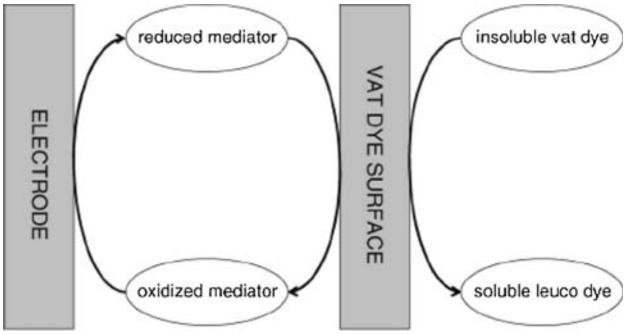


Fig. 4 Principle of the mediator technique

The mediators employed in this process are regenerable iron complexes with triethanolamine or gluconic acid as ligands. These mediators, however, are expensive and not entirely harmless from a toxicological point of view. In addition, after the reduction and prior to the coloration process the mediator has to be separated from the soluble leuco dye by ultrafiltration, which considerably increases the costs of this vatting process [17, 19].

Direct electrochemical reduction

Alternatively to the mediated electrochemical reduction, recently a novel electrochemical vatting process for vat and sulfur dyes has been described. This reduction does not require the permanent presence of a redox mediator. As shown Fig. 5, the leuco dye, acting as an electron-shuttle between the electrode and the surface of the dye pigment, has to be generated first in a small amount to initiate the reduction, which then proceeds by itself [17, 22] (Fig. 5).

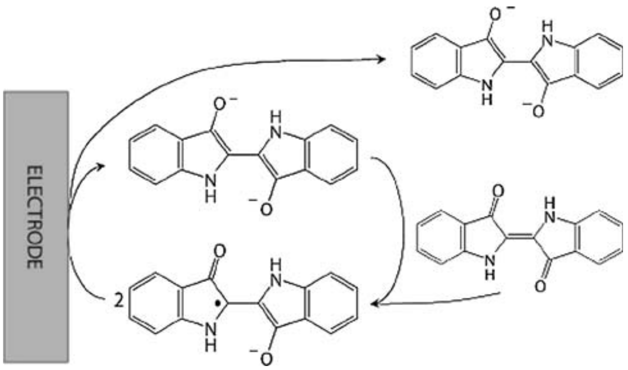


Fig. 5 Mechanism of the direct electrochemical reduction of indigo radical

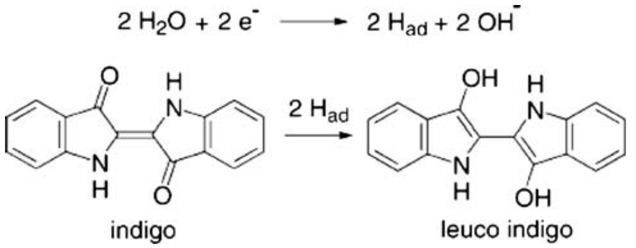


Fig. 6 Electrocatalytic hydrogenation of indigo

Electrocatalytic hydrogenation

The electrocatalytic hydrogenation is promising and attractive in view of economic and ecological aspects. The electrochemical hydrogenation is a process in which adsorbed hydrogen, produced in situ by electrolysis of water, reacts with adsorbed organic substrates (e.g., vat dye) at the electrode surface (Fig. 6) [17, 21].

The hydrogenation step is in competition with the hydrogen evolution reaction and the efficiency of the electrocatalytic hydrogenation is determined by this competition. The electrocatalytic hydrogenation has several advantages over the conventional catalytic hydrogenation (e.g., elevated temperatures and pressures can be avoided and the explosion risk is minimized).

In conclusion, from the point of stability, availability and costs, the latest development concerning direct electrochemical reduction on graphite granules seems to be the most attractive process and the results are obviously a promising basis for further development. The market introduction of the mediator process is imminent and the message is simple: electrochemistry in textile industry is coming our way.

Supercritical carbon dioxide coloration

The application of supercritical carbon dioxide ($scCO_2$) in the textile industry has recently become an alternative technology for developing a more environmentally friendly coloration process. $scCO_2$ coloration technology has the potential to overcome several environmental and technical issues in many commercial textile applications such as yarn preparation, coloration and finishing. $scCO_2$ represent a potentially unique media for either transporting chemical into or out of a polymeric substrate, because of their thermo-physical and transport properties. Supercritical fluids exhibit gas-like viscosities and diffusivities and liquid-like densities. Additionally, carbon dioxide is non-toxic, non-flammable, environmentally friendly, and chemically inert under many conditions [25]; however, its production is remained to be cost-effective.

The dissolving power of $scCO_2$ for disperse dyes and its use as the transport media for coloration polyester was studied from all theoretical aspects at DTNW in Krefeld, Germany [26, 27]. Cooperative research work between our laboratory and DTNW in Krefeld, Germany, has been conducted in 1995 up to 1997. These studies have revealed that the presence of intramolecular hydrogen bonds and/or the hydrophobicity of dye molecule are positive factors for better solubility in supercritical carbon dioxide, as indicated from its improved dye-uptake [28, 29].

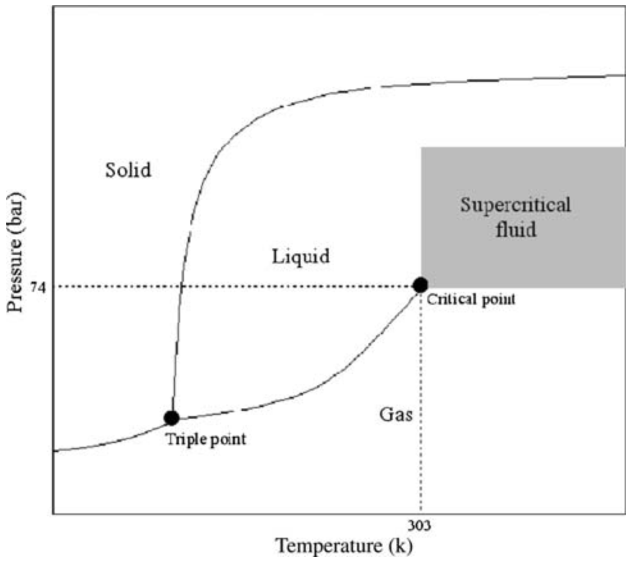


Fig. 7 Phase diagram of carbon dioxide

Theoretical background

Supercritical fluids are produced by the effects on gas and liquid changes in pressure and temperature, as illustrated in Fig. 7 [30]. The phase diagram of carbon dioxide shown in Fig. 7 represents the interfaces between phases; at the triple point all three phases may coexist. Above the triple point, an increase in temperature drives liquid into the vapor phase, while and increase in pressure drives vapor back to liquid. The critical point for carbon dioxide occurs at a pressure of 73.8 bar and a temperature of 31.1 °C.

Coloration approaches

The use of $scCO_2$ as a fluid medium for coloration of textile fibers, especially polyester, has been examined. This technology has become so promising that it has provided new opportunities to develop suitable dyes for this medium [31]. The coloration is conducted in a stainless steel high-pressure apparatus as shown in Fig. 8.

In a recent thesis on the Process and Equipment Development for Textile Dyeing in Supercritical Carbon Dioxide following observations have been made by the author of the thesis, van der Kraan [33].

A technical-scale, 100-L dyeing machine was designed and built to test polyester beam dyeing in $scCO_2$ at 300 bar

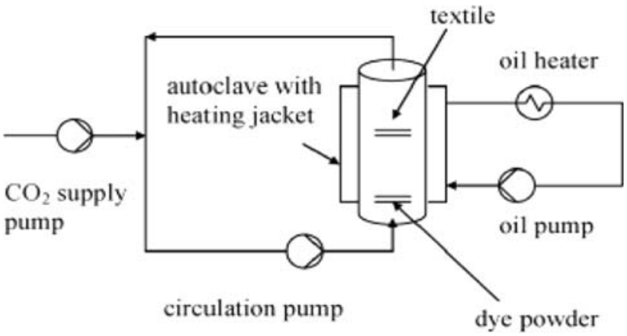


Fig. 8 Experimental set-up for textile coloration in $scCO_2$ [32]

and 120 °C. A new type of pressure vessel was used, consisting of a steel liner with carbon fibers wound around to take up the radial forces and a yoke construction for the axial forces. This configuration lowers the investment cost but also the operating cost, because the amount of steam required to heat the vessel is lower than for a completely steel vessel. Furthermore, because the carbon fiber vessel requires less heating due to the low heat capacity of the carbon fibers, the process time is shortened. To circulate the CO_2 with the dissolved dye through the textile, a low-pressure centrifugal pump was designed for service in $scCO_2$ and placed inside the dyeing vessel.

Also a commercial-scale, 1000-L supercritical dyeing machine was designed, for treating 300-kg polyester while recycling all dye and 96% of the CO_2. An economical analysis showed that, although the purchase cost for a supercritical machine is higher (500 k€) than for an aqueous machine (100 k€), the operating cost is lower (0.35 instead of 0.99 €/kg polyester). This is caused by the higher rate of dyeing and by the simpler dye formulations that can be used in $scCO_2$. The overall result is a 50% lower process cost for the supercritical process.

Attempts were made to modify cotton so as to be less hydrophilic and thus amenable to be dyed with disperse dyes in $scCO_2$ [34, 35]. Also, a possible coloration of cotton in $scCO_2$ without modification was achieved using disperse reactive dyes based on bromoacrylate and dichlorotriazine [36]. Further progress in this regard was recently reported to indicate that disperse reactive dyes based on fluorotriazine was found to be more reactive with cotton than chlorotriazine in the presence of methanol as a cosolvent in $scCO_2$ with fixation percentage 85 [37]. Moreover, deeper shades can be achieved with fluorotriazines since it is possible to increase the dye concentration up to 10% owf without damage of the cotton fibers.

Recently, the influence of water addition in the dyeability of polyester, nylon, silk, and wool with disperse reactive dyes in supercritical carbon dioxide ($scCO_2$) was investigated [32]. It was found that disperse dyes containing a reactive vinylsulphone or a dichlorotriazine group are suitable for coloration textiles containing polyester, nylon, silk, wool, or blends of these fibers in $scCO_2$. The dye uptake by polyester is independent of water addition. For the amino-containing textiles, the coloration increases with the concentration of water in the $scCO_2$ and the textiles. The positive effect of water was due to its ability to swell fibers or due to an effect of water on the reactivity of the dye–fiber system. At the saturation point, deep colors were obtained with both dyes for polyester, nylon, silk, and wool, with fixation percentages between 75 and 94.

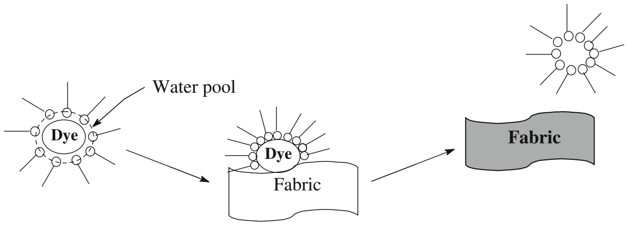


Fig. 9 Dyeing of natural fibers using reverse micelle

For water-soluble dyes, however, attempts were made to dye natural fibers using reverse micelle technique (Fig. 9) in which ionic dye, solubilized in the water-pool, passes into the fiber together with a small amount of water immediately after contact with it [38, 39]. Satisfactory results were obtained for proteinic fibers but not for cotton ones as a result of the electrostatic repulsion between the dye and the surface of the cotton fiber.

Plasma technology

Plasma is considered to be a partially ionized gas containing ions, electrons, and neutral particles produced by interaction of electromagnetic field with gas under appropriate pressure. Modern plasma-chemical techniques relate to environmentally clean technologies and are much superiors to chemical modification in which corrosive reagents, such as acids, hydroxides, alkaline-earth metals, and their compounds, are used. In this context, the pretreatment and finishing of textile fabrics by plasma technologies is increasingly replacing wet chemical applications.

One of the most promising and advanced polymer modification techniques is low-temperature plasma treatment, which allows the surface properties to be varied over a wide range and the area of application of polymeric materials to be considerably extended. This surface modification increases the hydrophilicity of the treated fiber. An important feature of plasma treatment is that it affects only the surface of a material subjected to treatment and a very thin near-surface layer whose thickness varies from 100 Å to several micrometers, according to different estimates. The bulk of the polymer remains intact under these conditions, retaining the mechanical, physicochemical, and electrophysical properties of the original material [40, 41].

The UV photons emitted by the plasma have sufficient energy to break chemical bonds (e.g., C–C, C–H) and to create radicals which can migrate along the chain and recombine. Depending on plasma conditions and on the nature of the polymer, the action of the plasma results in activation (radical formation), unsaturation (double-bond formation), chain scission, and cross-linking [42].

Coloration of plasma-treated polyester fibers

Polyester textiles are usually dyed with disperse dyes by a pad-dry-bake process (Thermosol process) or at high temperature and pressure. Otherwise, phenol-based carriers are needed to swell the fiber during coloration at atmospheric pressure, which may pollute the environment. Therefore, low-temperature plasma was used instead of the chemical method for the treatment of PET fibers. An increase in color depth upon coloration was obtained after treating PET fabrics with both argon and air plasma. This was attributed to the plasma-induced increase of surface roughness and surface area. Also, the introduction of hydrophilic groups, induced by both reactive and chemically inert plasmas, may increase the water swelling capability and the affinity of PET fibers for dyes containing polar groups which contributes to the increase of K/S values of dyed PET specimens [43].

Nanostructured surfaces are of great interest, since they provide a high surface area. A high functionality can thus be obtained by ultrathin coatings. Plasma polymerization of acetylene mixed with ammonia (C_2H_2/NH_3) onto PET fiber was used in a regime where both deposition and etching processes took place yielding a nanoporous, crosslinked network with accessible functional groups [44, 45] (Fig. 10).

Low-pressure plasma was used to deposit onto polyester fiber multi-functional thin film from ammonia/ethylene or acetylene mixture. The coated polyester showed fiber was acid dyeable and showed high color strength values per film thickness. Moreover, the plasma-deposited and dyed polyester fabrics showed a good rubbing and washing fastness demonstrating the coating-functional permanency. The excellent abrasion resistance confirmed that the coating was permanently adhered to the substrate [46]. Similarly, PET fibers were treated with two plasmas ($N_2 + H_2 + He$) and ($SO_2 + O_2$). It was found that the dyeability was significantly improved for water soluble acid dyes owing to the increased surface area as well as the hydrophilicity of the PET fiber [47].

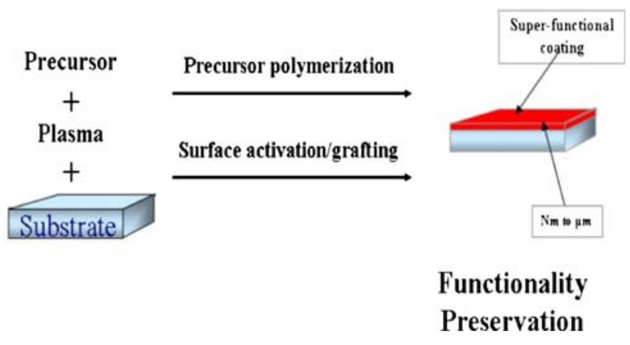


Fig. 10 Nanostructured plasma coating

Coloration of plasma-treated wool fibers

Wool, unlike other natural fibers, has a complicated surface structure and it is one of the important fibers in the textile industry. However, it has some technical problems such as wettability (which affects the dyeability). The wool fiber surface is hydrophobic in nature which is due to the presence of a high number of disulfide cystine crosslinkages (–S–S–) in the A-layer of the exocuticle, and of fatty acids on the fiber's surface. This surface morphology is thought to determine the diffusion in wool fiber [48].

Thus, low-temperature plasma (LTP) was used instead of the chemical method for the treatment of wool. It has been confirmed that LTP treatments improve the coloration behavior of wool fibers in different coloration systems. This can be due to plasma-induced cystine oxidation and thus to the reduced number of crosslinkages in the fiber surface which, in turn, facilitates a transcellular in addition to the intercellular dye diffusion [48–52].

Coloration of plasma-treated cotton fibers

Reactive dyes are often used for the application with cotton fibers as they provide a complete color range and are easily applied, particularly in exhaust coloration. However, reactive dyes have only a moderate affinity for cotton fiber. Several previous attempts have been made to overcome this limitation. One of the most feasible methods is to enhance dye–fiber interaction using cationized cotton [53]. In this interest, plasma-treated cotton fiber in the presence of amine compounds showed improved dyeability with reactive dyes when compared to the untreated fabric [54].

Ultrasonics

Power ultrasound can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitation in a liquid medium that is the growth and explosive collapse of microscopic bubbles (Fig. 11). Sudden and explosive collapse of these bubbles can generate ''hot spots'' [55, 56], i.e., localized high temperature,

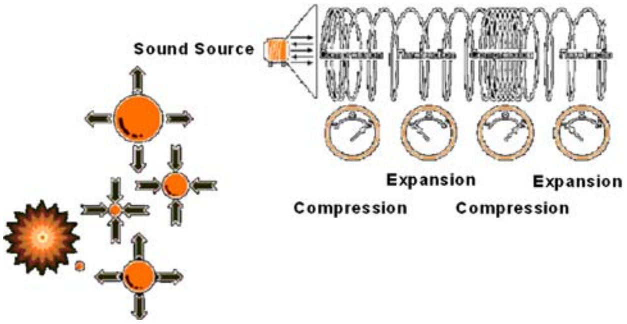


Fig. 11 Ultrasonic cavition in a liquid medium

high pressure, shock waves, and severe shear force capable of breaking chemical bonds.

Therefore, many efforts have been paid to explore this technique in the textile coloration as it is a major wet process, which consumes much energy and water and releases large effluent to the environment. Improvements observed in ultrasound-assisted coloration processes are generally attributed to cavitation phenomena and, as a consequence, other mechanical and chemical effects are produced such as:

- Dispersion (breaking up of aggregates with high relative molecular mass);
- Degassing (expulsion of dissolved or entrapped air from fiber capillaries);
- Diffusion (accelerating the rate of diffusion of dye inside the fiber);
- Intense agitation of the liquid;
- Destruction of the diffusion layer at dye/fiber interfaces;
- Generation of free radicals; and
- Dilation of polymeric amorphous regions.

The acceleration in coloration rates observed by many workers might be the cumulative effects of the above [57, 58].

Moreover, during last decade Marco Company of Korea had developed an ultrasonic retrofit module that has a generator, transducer, and electronic wire for jet-dyeing machine [59]. Other reported attempt to produce production machines is *ultrasounds*: an industrial solution to optimize costs, environmental requests, and quality for textile finishing [60].

Ultrasonic-assisted coloration of natural fibers

The pioneering work reported by Thakore in 1988 showed that cotton fabric could be ultrasonically dyed with direct dyes. The results indicated that the use of ultrasonic greatly reduced dyeing time, reduced dyeing temperature, reduced concentration of dyes, and electrolytes in the dyes-bath [61].

Ultrasonic-assisted coloration of cellulosic fabrics with C.I. Reactive Red 120 and C.I. Reactive Black 5 was studied [62]. The colorations were carried out conventionally, and with the use of ultrasonic techniques, were compared in terms of percentage exhaustion, total amount of dye transferred to the washing bath after coloration, fastness properties, and color values. Results obtained in this study indicate that ultrasound improved dye fixation and increased the percentage exhaustion for both reactive dyes, but had no effect on the fastness properties of the dyed materials.

Cotton was dyed with the direct dyes Solophenyl Blue FGL 220 and Solophenyl Scarlet BNL 200. Both dyes needed a relatively large amount of salt for exhaustion. The important facts of this study were that coloration with direct dyes at lower salt levels approaches the same final exhaustion as coloration at higher salt level without ultrasound, ultrasound has the greatest effect on coloration at low temperatures and, in addition, it can reduce the amount of salt and energy required when compared to a conventional process [63].

The coloration of cotton fabric using Eclipta as natural dye has been studied in both conventional and sonicator methods. The sonicator coloration shows 7–9% efficiency higher than conventional coloration [64]. Also, ultrasonic proved effectiveness in dye-uptake of cationized cotton fabric with lac natural dye, and the enhanced effect after equilibrium coloration was about 66.5% more than the conventional heating [65].

The coloration process of silk using cationic, acid, and metal–complex dyes at low temperatures, assisted by a low-frequency ultrasound of 26 kHz and compared the results of dye uptake with those obtained by conventional processes was studied [66]. The results show that silk coloration in the presence of ultrasound increases the dye uptake for all classes of dyes at lower coloration temperatures and a shorter coloration time as compared with conventional coloration. Furthermore, there was no apparent fiber damage caused by cavitation.

The coloration of wool fabrics using lac as a natural dye has been studied in both conventional and ultrasonic techniques. The extractability of lac dye from natural origin using power ultrasonic was also evaluated in comparison with conventional heating. Ultrasonics proved effectiveness in the dye extraction and dye-uptake of wool fibers with lac dye, the enhanced effect was about 41 and 47% more than conventional heating, respectively [67].

Ultrasonic-assisted coloration of synthetic fibers

A study on the effect of ultrasound on the coloration of polyester fibers with C.I. Disperse Orange 25 and C.I. Disperse Blue 79 dyes was investigated [68, 69]. Swollen and unswollen PBT and PET fibers were dyed with and without low-frequency ultrasound under different conditions regarding time and temperature. The results from this investigation show that ultrasound enhanced the diffusion of dye molecules into the fibers; although, the levels of coloration are not as high as in conventional commercial coloration processes. Also, a study of the influence of ultrasound on the coloration behavior of PET fibers was investigated using C.I. Disperse Red 60 which has a highly crystalline structure and C.I. Disperse Blue 56 with a poor crystalline structure [70, 71]. The results indicated that ultrasound has a significant effect on the reduction in particle size of C.I. Disperse Red 60, but it is very interesting that there is no significant influence attributed to ultrasound on dye uptake and coloration rate for C.I. Disperse Blue 56.

The ultrasound-assisted coloration of nylon-6 fibers was first investigated by Shimizu et al. [72] and later by Kamel et al. [73, 74]. It seems that nylon-6 fiber is very susceptible to low-frequency ultrasound-assisted coloration with various classes of dyes at different temperatures and under different reaction conditions, i.e., ultrasound power, pH of the medium, and initial dye concentration. Colorations with disperse, acid, acid mordant, and reactive dyes in a low ultrasound field (27 and 38.5 kHz) were investigated and, in all cases, increases in coloration rate and decreases in activation energies were observed. Furthermore, Kamel established that dye uptake is enhanced in the coloration diffusion phase. These experimental results confirm the observations of other authors that the enhancing effect is attributed to de-aggregation of the dye molecules, which leads to better dye diffusion and possible assistance for dye–fiber bond fixation.

Microwave

Microwave-promoted organic reactions as well known as environmentally benign methods that can accelerate a great number of chemical processes. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [75]. Microwave is a volumetric heating (fast), whereas conventional is a surface heating (slow) as shown Fig. 12.

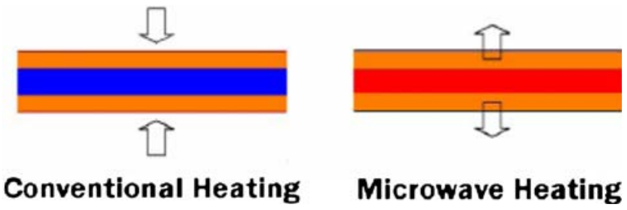


Fig. 12 Microwave heating (volumetric) versus conventional heating (surface)

This fact has been realized in textile coloration by many authors. In this regard, it has been reported that a short exposure time as low as 30–50 s for dichlorotriazine reactive dyes gives good results [76].

Using pad-batch method, the effect of batching time on coloration of cotton with monochlorotriazine reactive dyes using microwave irradiation and conventional heating was investigated. The results show that microwave in short time (2 min) was better than 12-h batching time under conventional heating [77].

Flax fiber due its poor dyeability, a recent method based on microwave treatment of flax fiber with urea to improve its dyeability with reactive dyes was recently reported. It was found that the treated flax fibers had significantly improved dyeability. The causes to the improvement of the dyeability of the flax fiber were found to be the increased absorption of dye on the fiber and the increased reaction probability between the dye and the fiber [78].

The possibility of coloration polyester fiber using microwave irradiation was studied. A high increase in dye uptake and acceleration in the coloration rate were observed [79]. A study on the effect of microwave irradiation on the extent of aqueous sodium hydroxide hydrolysis of PET fiber and the impact of this treatment on its coloration with disperse dyes was investigated. Comparison of the results obtained from the microwave irradiation and the conventional heating methods showed that the rate of hydrolysis was greater using microwave irradiation. The treated fabric was then dyed using microwave irradiation to heat the dyebath. Increased levels of dye uptake were observed with increasing weight loss of the hydrolyzed polyester fabric [80].

Future outlook

1. The interest in nanotechnology is growing very fast as this technology offers the production of new materials with smart functions. In particular, nanostructure coating by plasma technique as well as nanocomposite polymer will furnish fibers of certain properties and easy dyeable to meet the demands of the ever-growing market.
2. Also, the ongoing interest for cleaner production in textile industries will encourage more R&D investigation for the use of $ScCO_2$ in industrial scale for synthetic fibers using disperse and disperse reactive dyes. However, the way is yet long toward using water-soluble dyes by this technique.
3. From the point of stability, availability and costs, the latest development concerning direct electrochemical reduction on graphite granules seems to be the most

attractive process and the results are obviously a promising basis for further development. The market introduction of the mediator process is imminent and the message is simple: electrochemistry in textile industry is coming our way.

4. Furthermore, the interest of using ultrasonic and microwave in dying will continue wish special attention toward their possible uses for small-scale enterprises

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