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TEXTILE TECHNOLOGY

Cotton Textile Processing: Waste Generation and Effluent Treatment

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ABSTRACT

This review discusses cotton textile processing and methods of treating effluent in the textile industry. Several countries, including India, have introduced strict ecological standards for textile industries. With more stringent controls expected in the future, it is essential that control measures be implemented to minimize effluent problems. Industrial textile processing comprises pretreatment, dyeing, printing, and finishing operations. These production processes not only consume large amounts of energy and water, but they also produce substantial waste products. This manuscript combines a discussion of waste production from textile processes, such as desizing, mercerizing, bleaching, dyeing, finishing, and printing, with a discussion of advanced methods of effluent treatment, such as electro-oxidation, bio-treatment, photochemical, and membrane processes.

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. Increasing public concern about environmental issues has led to closure of several small-scale industries.

Interest in ecologically friendly, wet-processing textile techniques has increased in recent years because of increased awareness of environmental issues throughout the world. Consumers in developed countries are demanding biodegradable and ecologically friendly textiles (Chavan, 2001). Cotton provides an ecologically friendly textile, but more than 50% of its production volume is dyed with reactive dyes. Unfortunately, dyes are unfavorable from an ecological point of view, because the effluents generated are heavily colored, contain high concentrations of salts, and exhibit high biological oxygen demand/chemical oxygen demand (BOD/COD) values.

In dyeing textiles, ecological standards are strictly applied throughout processing from raw material selection to the final product. This has become more critical since the German environmental standards regarding dye effluents became effective (Robinson et al., 1997). The main challenge for the textile industry today is to modify production methods, so they are more ecologically friendly at a competitive price, by using safer dyes and chemicals and by reducing cost of effluent treatment/disposal. Recycling has become a necessary element, not because of the shortage of any item, but because of the need to control pollution. There are three ways to reduce pollution: (1) use of new, less polluting technologies; (2) effective treatment of effluent so that it conforms to specified discharge requirements; and (3) recycling waste several times over before discharge (Sule and Bardhan, 1999), which is considered the most practical solution.

The objective of this review is to discuss the various processing stages in the textile industry and the methodologies adopted for treating textile wastewater. A variety of water treatment techniques (Table 1) are discussed from an environmental point of view. Conventional and novel techniques discussed include electro-oxidation, biological treatment, photochemical processing, ion-exchange, and a variety of membrane techniques.

TEXTILE OPERATIONS

The textile industry comprises a diverse and fragmented group of establishments that produce and/or process textile-related products (fiber, yarn, and fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibers; transform fibers

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Table 1. Possible treatments for cotton textile wastes and their associated advantages and disadvantages

Processes	Advantages	Disadvantages	References
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes	Pala and Tokat, 2002; Ledakowicz et al., 2001.
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Gaehr et al., 1994.
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Arslan et al., 2000.
Ozone treatment	Good decolorization	No reduction of the COD	Adams et al., 1995; Scott and Ollis, 1995.
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge	Lin and Peng, 1994; Lin and Chen, 1997.
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Ghayeni et al., 1998.
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	-----	Erswell et al., 1998; Xu et al., 1999; Akbari et al., 2002; Tang and Chen, 2002.
Ultrafiltration–microfiltration	Low pressure	Insufficient quality of the treated wastewater	Watters et al., 1991; Rott and Mike, 1999; Ciardelli and Ranieri, 2001; Ghayeni et al., 1998.

into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production (Ghosh and Gangopadhyay, 2000).

The process of converting raw fibers into finished apparel and non-apparel textile products is complex, so most textile mills specialize. There is little difference between knitting and weaving in the production of man-made cotton and wool fabrics (Hashem et al., 2005). Textiles generally go through three or four stages of production that may include yarn formation, fabric formation, wet processing, and textile fabrication. Some of the steps in processing fibers into textile goods are shown in Figure 1. A list of some wastes that may be generated at each level of textile processing are provided in Table 2.

Desizing. The presence of sizing ingredients in the fabric hinders processes, such as dyeing, printing, and finishing. For example, the presence of starch can hinder the penetration of the dye into the fiber, which necessitates removal of starch prior to dyeing or printing. Starch is removed or converted into simple water-soluble products either by hydrolysis (by enzymatic preparations or dilute mineral acids) or by oxidation (by sodium bromide, sodium chlorite, etc.) (Batra, 1985).

In general, about 50% of the water pollution is due to waste water from desizing, which has a high BOD that renders it unusable. The problem can be mitigated by using enzymes that degrade starch into ethanol rather to anhydroglucose. The ethanol can be recovered by distillation for use as a solvent or fuel, thereby reducing the BOD load. Alternatively, an oxidative system like H_2O_2 can be used to fully degrade starch to CO_2 and H_2O.

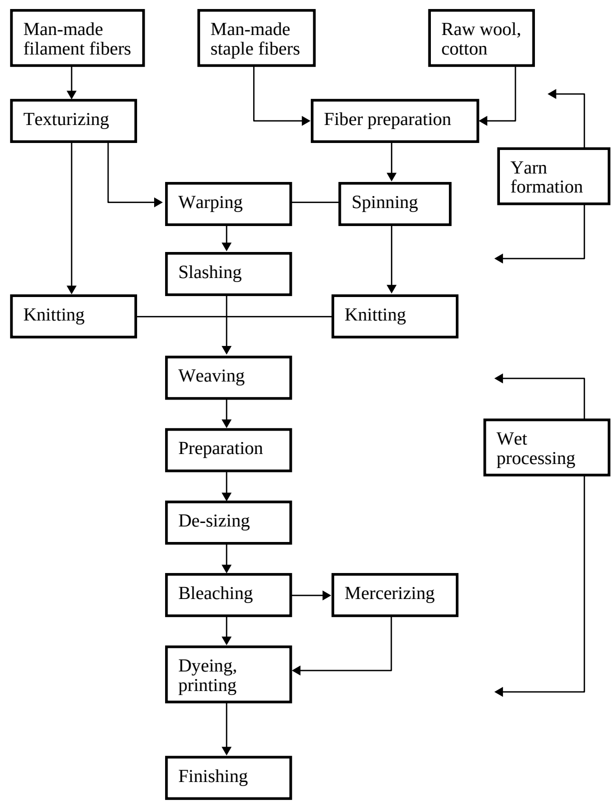

Figure 1. A flow diagram for various steps involved in processing textile in a cotton mill.

Electro-oxidation on RuO_2/Ti or PbO_2/Ti electrodes is an effective method for the treatment of starch effluent. An anaerobic plate-column reactor capable of retaining high concentrations of biomass was studied using a synthetic wastewater that contained starch. The total organic carbon (TOC)-loading rate, hydraulic retention time (HRT), and temperature were kept constant. The initial conditions were a biomass concentration of approximately 0.5 mg/ml N (5 mg/ml volatile suspended solids), 20 °C, an HRT of 30 h, and a TOC-loading rate of 0.8 g/l/day. A removal efficiency of dissolved organic carbon exceeding 90% was realized. At the end of the treatment, the removal efficiency reached a steady-state value of 98%, at which the biomass concentration in the reactor was 2.3 mg/ml N.

Table 2. List of some of the waste materials generated at each level of cotton textile processing

Process	Air emissions	Wastewater	Residual wastes
Fiber preparation	Little or no air emissions generated	Little or no wastewater generated	Fiber waste; packaging waste; hard waste.
Yarn spinning	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; sized yarn; fiber waste; cleaning and processing waste.
Slashing/sizing	Volatile organic compounds	BOD; COD; metals; cleaning waste, size	Fiber lint; yarn waste; packaging waste; unused starch-based sizes.
Weaving	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fabric scraps; off-spec fabric; used oil.
Knitting	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fabric scraps; off-spec fabric.
Tufting	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fabric scraps; off-spec fabric.
Desizing	Volatile organic compounds from glycol ethers	BOD from water-soluble sizes; synthetic size; lubricants; biocides; anti-static compounds	Packaging waste; fiber lint; yarn waste; cleaning materials, such as wipes, rags and filters; cleaning and maintenance wastes containing solvents.
Scouring	Volatile organic compounds from glycol ethers and scouring solvents	Disinfectants and insecticide residues; NaOH; detergents; fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents	Little or no residual waste generated.
Bleaching	Little or no air emissions generated	Hydrogen peroxide, sodium silicate or organic stabilizer; high pH	Little or no residual waste generated.
Singeing	Small amounts of exhaust gasses from the burners.	Little or no wastewater generated.	Little or no residual waste generated.
Mercerizing	Little or no air emissions generated.	High pH; NaOH.	Little or no residual waste generated.
Heat setting	Volatilization of spin finish agents applied during synthetic fiber manufacture.	Little or no wastewater generated.	Little or no residual waste generated.
Dyeing	Volatile organic compounds	Metals; salt; surfactants; toxics; organic processing assistance; cationic materials; color; BOD; sulfide; acidity/ alkalinity; spent solvents.	Little or no residual waste generated.
Printing	Solvents, acetic acid from dyeing and curing oven emissions; combustion gasses; particulate matter.	Suspended solids; urea; solvents; color; metals; heat; BOD; foam.	Little or no residual waste generated.
Finishing	Volatile organic compounds; contaminants in purchased chemicals; formaldehyde vapor; combustion gasses; particulate matter.	BOD; COD; suspended solids; toxics; spent solvents.	Fabric scraps and trimmings; packaging waste.
Product fabrication	Little or no air emissions generated.	Little or no wastewater generated.	Fabric scraps.

Cornstarch waste is easily degraded by treatment in a mixed activated sludge system. The bio-kinetic coefficients were calculated from the two-level activated sludge operational processes using influent COD concentrations and four values of solid retention time. The results indicate that the effluent COD is related to the influent COD concentration. It is also proportional to the product of the influent COD and the specific growth rate. A multiple-substrate model was developed to predict the effluent COD under variable influent COD concentrations (Bortone et al., 1995). There was no sludge-bulking problem apparently because of high dissolved oxygen (DO) concentrations, a buffered system, and a balanced C:N:P ratio; however, the critical DO concentration at which the sludge volume index began to rise increased as the food for microorganism (F/M) ratio increased. A cost analysis was provided for a hypothetical wastewater plant with a flow rate of $300m^3$/day (Vanndevivera and Bianchi, 1998). Synthetic sizing formulations based on polyvinyl acrylic (PVA) and acrylic resins, instead of starch, are expensive. Considering the cost of effluent treatment, the cost of synthetic sizing formulations is negligible. Today, advances in nano-filtration and ultra-filtration techniques allow recovery and reuse of PVA (Meier et al., 2002; Yu et al., 2001).

Compared with reverse osmosis, nanofiltration is less energy intensive and can be used for the treatment of various industrial effluents (Meier et al., 2002). Moreover, a higher retention of dyes and other low molecular weight organic compounds (MW: 200–1000) is achievable by nanofiltration. The salt-rich permeate can be reused in the preparation of dye baths, which minimizes the amount of wastewater that needs to be processed. The basic problems involved in any membrane-based process are a drop in flux and membrane fouling. To overcome this problem and to achieve a high quality separation, combinations of various separation methods have been adopted in recent years (Pigmon et al., 2003; Abdessemed and Nezzal, 2002; Dhale et al., 2000; Xu et al., 1999).

Mercerization. In order to impart luster, increase strength, and improve dye uptake, cotton fiber and fabric are mercerized in the gray state after bleaching. Essentially, mercerization is carried out by treating cotton material with a strong solution of sodium hydroxide (about 18–24%) and washing-off the caustic after 1 to 3 min, while holding the material under tension. Cotton is known to undergo a longitudinal shrinkage upon impregnation with this solution. This can be prevented by stretching it or holding it under tension. The material acquires the desired properties of luster, increased strength, dye uptake, and increased absorbency. The large concentrations of NaOH in the wash water can be recovered by membrane techniques. Use of $ZnCl_2$ as an alternative method leads to an increase in the weight of fabric and in dye uptake, and allows easy recovery of NaOH. Moreover, the process is ecologically friendly and does not require neutralization by acetic or formic acid (Karim et al., 2006).

Bleaching. Natural color matter in the yarn imparts a creamy appearance to the fabric. In order to obtain white yarn that facilitates producing pale and bright shades, it is necessary to decolorize the yarn by bleaching. Hypochlorite is one of the oldest industrial bleaching agents. The formation of highly toxic chlorinated organic by-products during the bleaching process is reduced by adsorbable organically bound halogen (AOX).

Over the last few years, hypochlorite is being replaced by other bleaching agents (Rott and Minke, 1999). An environmentally safe alternative to hypochlorite is peracetic acid. It decomposes to oxygen and acetic acid, which is completely biodegradable. One of the advantages of peracetic acid is higher brightness values with less fiber damage (Rott and Minke, 1999). Recently, a one-step preparatory process for desizing, scouring, and bleaching has helped to reduce the volume of water. The feasibility of a one-step process for desizing, scouring, bleaching, and mercerizing of cotton fabric followed by dyeing with direct dyes has been discussed by Slokar and Majcen (1997).

Cooper (1989) suggested an economical and pollution-free process for electrochemical mercerization (scouring) and bleaching of textiles. The process does not require conventional caustic soda, acids, and bleaching agents. The treatment is carried out in a low-voltage electrochemical cell. The base required for mercerization (scouring) is produced in the cathode chamber, while an equivalent amount of acid is produced in the anode chamber, which is used for neutralizing the fabric. Gas diffusion electrodes simultaneously generate hydrogen peroxide for bleaching. With a bipolar stack of electrodes, diffusion electrodes can be used as anode or cathode or both. The process does not produce hydrogen bubbles at the cathode, thereby avoiding hazards involving the gas (Lin and Peng, 1994).

An electrochemical treatment was developed for the treatment of cotton in aqueous solution containing sodium sulphate. In this technique, the current density was controlled between two electrodes. At the cathode, water is reduced to hydrogen and base, while at the anode it is oxidized to oxygen and acid. Favorable results on mercerization (scouring) and electrochemical sanitation of unmercerized (grey) cotton have been reported (Naumczyk et al., 1996).

Neutralization. According to Bradbury et al. (2000), replacement of acetic acid by formic acid for neutralization of fabric after scouring, mercerizing, bleaching, and reduction processes is effective, economical, and environment-friendly. The procedure also allows a sufficient level of neutralization in a short period of time, needs low volumes of water, and results in low levels of BOD.

Dyeing. Treatment of fiber or fabric with chemical pigments to impart color is called dyeing. The color arises from chromophore and auxochrome groups in the dyes, which also cause pollution (Azymezyk et al., 2007). In the dyeing process, water is used to transfer dyes and in the form of steam to heat the treatment baths. Cotton, which is the world's most widely used fiber, is a substrate that requires a large amount of water for processing. For example, to dye 1 kg of cotton with reactive dyes, 0.6–0.8 kg of NaCl, 30–60 g of dyestuff, and 70–150 L of water are required (Chakraborty et al., 2005). More than 80,000 tonnes of reactive dyes are produced and consumed each year. Once the dyeing operation is over, the various treatment baths are drained, including the highly colored dye bath, which has high concentrations of salt and organic substances. The wastewater must be treated before reuse. Coagulation and membrane processes (nanofiltration or reverse osmosis) are among processes suggested for treatment of this water; however, these treatments are effective only with very dilute dye baths. Dye baths are generally heavily polluted. For example, wastewater produced by reactive dyeing contains hydrolyzed reactive dyes not fixed on the substrate (representing 20 to 30% of the reactive dyes applied on an average of 2 g/L). This residual amount is responsible for the coloration of the effluents, and cannot be recycled. Dyeing auxiliaries or organic substances are non-recyclable and contribute to the high BOD/COD of the effluents.

Membrane technologies are increasingly being used in the treatment of textile wastewater for the recovery of valuable components from the waste stream, as well as for reusing the aqueous stream. A number of studies deal with application of various pressure-driven membrane filtration processes in the treatment wastewater from the dyeing and finishing process (Chen et al., 2005).

Measures adopted for the abatement of pollution by different dyes are 1) use of low material-to-liquor ratios, 2) use of trisodiumcitrate (Fiebig et al., 1992), 3) replacement of reducing agent (sodium hydrosulphite) with a reducing sugar or electrochemical reduction (Maier et al., 2004), and 4) use of suitable dye-fixing agents to reduce water pollution loads.

Padma et al. (2006) first reported the concept of totally ecologically friendly mordents or natural mordents during dyeing with natural dyes. Deo and Desai (1999) were the first to point out that natural dye shades could be built-up by a multiple dip method that renders natural dyeing more economical. Dyeing of natural and synthetic fibers with natural dyes has been the subject of several studies. Development of ecologically friendly non-formaldehyde dye fixative agents for reactive dyes was recently reported (Bechtold et al., 2005; Sekar, 1995).

Printing. Printing is a branch of dyeing. It is generally defined as 'localized dyeing,' i.e. dyeing that is confirmed to a certain portion of the fabric that constitutes the design. It is really a form of dyeing in which the essential reactions involved are the same as those in dyeing. In dyeing, color is applied in the form of a solution, whereas in printing color is applied in the form of a thick paste of the dye. Table 3 shows the pollution loads for a printing and finishing operation (50 polyester/50 cotton). The fixation of the color in printing is brought about by a suitable after-treatment of the printed material (El-Molla and Schneider, 2006).

Table 3. Pollution loads for printing and finishing operations for 50% polyester/50% cotton blend fabric

Process	pH	Biological oxygen demand		Total dissolvable solids	
		per 1000 kg of product			
Printing					
Pigment (woven goods)	6–8	1.26	5.0	0.13	2.5
Pigment (knot goods)	6–8	1.26	5.0	0.13	2.5
Vat dye (woven goods)	10.0	21.5	86	25	34
Vat dye (knit goods)	10.0	21.5	86	25	35
Resin finishing (woven goods)	6–8	-	-	-	22
Resin finishing flat curing (woven goods)	6–8	6.32	25	12	17.3

Textile fabric printing produces hydrocarbon effluents that must be removed before they reach the atmosphere. Limits on emissions will become more restrictive in the future, which makes cleaning exhausts an environmental necessity. In India, a majority of textile printing units prefer to use kerosene in printing because of the brilliant prints and ease of application. In India alone, about 122 million liters of kerosene is released into the atmosphere annually during printing, drying, and curing. The resulting pollution of the atmosphere and wastage of hydrocarbon products is colossal. Air-laden kerosene is harmful to human beings, as well as to the flora and fauna, in the neighborhood. Therefore, it is imperative that as much kerosene as possible is recovered from the exhaust pipes of the printing industry.

Zachariah (1995) developed a process for the recovery of thin kerosene vapor. In this process, the percentage of recovery of kerosene from the printing drier was 78.5%, and the total percentage of recovery of kerosene consumed for the preparation of print paste was 58.8%.

The most common chemical in reactive dye printing is urea, which leads to a high pollution load. A number of attempts have been made to limit or eliminate the use of urea in the print paste to reduce effluent load. Geeta et al. (2004) developed a urea-free process in which caprolactam, PEG-400, and PEG-600 partially or completely replaced urea in the dyeing and printing of reactive dyes on cotton fabrics. Caprolactam in many reactive dyes can fully replace urea, while PEG-400 and PEG-600 replaced approximately 50% of the dyes required for fixation. Other substitutes for urea include glycerin, cellosolve, sorbitol, polycarboxylic acid, PEG-200, and PEG-4000.

Printing is mainly done by a flat or rotary screen, and after every lot of printing some residual paste is left in the wastewater. This can be reused for printing of similar shades by adding new stock. Recently, screen-free printing methods, such as ink-jet printing and electrostatic printing, have been developed that make use of an electronic control of color distribution on fabric. Screen-free printing methods are attractive for pollution mitigation (Lukanova and Ganchev, 2005).

Finishing. Both natural and synthetic textiles are subjected to a variety of finishing processes. This is done to improve specific properties in the finished fabric and involves the use of a large number of finishing agents for softening, cross-linking, and waterproofing. All of the finishing processes contribute to water pollution.

Among the products that are used in textile finishing, the most ecologically friendly ones are formaldehyde-based cross-linking agents that bestow desired properties, such as softness and stiffness that impart bulk and drape properties, smoothness, and handle, to cellulosic textiles. It can also lead to enhanced dimensional stability. A free surface characteristic of the fabric shows the evolution of un-reacted formaldehyde. This obviates the use of formaldehyde in the product and liberation of chemical products, and results in considerable reduction in the amount of formaldehyde during the cross-linking reaction that leads to toxicity and stream pollution. Generation of formaldehyde during vacuum extraction has been used in the storage of resin-finished fabrics and garments. The formaldehyde resin used as a cross-linking agent is a pollutant and a known carcinogen. Much effort has been expended in the search for a substitute for formaldehyde (Hashem et al., 2005).

Since the late 1980s, there has been an increase in the demand for easy-care, wrinkle-resistant (durable press), 100% cotton apparel. Formaldehyde-based chemical finishes, such as dimethylol dihydroxyethylene urea and its etherified derivative with lower formaldehyde concentrations, are used to impart ease-of-care characteristics and durable-press properties to cotton apparel. They are cost-effective and efficient (Hashem et al., 2005). The free formaldehyde on the finished fabric is a major drawback given the adverse effects of formaldehyde, which ranges from a strong irritant to carcinogenic. In addition, washing the apparel pollutes the washing liquor. Because of its carcinogenic properties, the concentration of formaldehyde allowed in the workplace air space is limited to 0.1 ppm. Furthermore, worker health must be monitored in the textile industry when formaldehyde is used. This is strictly stated in recent actions by federal regulatory agencies in most industrialized countries. The restrictions have sprouted renewed interest in non-formaldehyde textile finishing substances in the cotton textile industry (El-Tahlawya et al., 2005). Moreover, formaldehyde-based finishing is energy-intensive. A variety of cellulose cross-linking agents, such as polycarboxylic acids, have been investigated to provide non-formaldehyde easy-care finishing.

Natural polymeric substances, such as natural oil and wax, have been used for water-proofing; however, textiles made from natural fibers are generally more susceptible to biodeterioration compared with those made from synthetic fibers. Products, such as starch, protein derivatives, fats, and oils, used in the finishing or sizing bath can also promote microbial growth. An ideal anti-bacterial finish should 1) not support growth of bacteria or fungi on the cloth, 2) be effective over the lifetime of the treated sample, 3) be durable against wash and bleaching, 4) pose no risk of adverse dermal or systemic effects, 5) have no detrimental influence on fabric properties, such as yellowing, handle, and strength, 6) be compatible with colorants and other finishes, such as softeners and resins, and 7) have low environmental impact of heavy metals, formaldehyde, phenols, and organic halogens.

There are few anti-bacterial fibers. There are a number of antibacterial chemicals are available (Son et al., 2006; Singh et al., 2005; El-Tahlawya et al., 2005), but they are man-made. There are many natural plant products that are known to slow down bacterial growth. Anti-bacterial properties have been detected in chemicals extracted from the root, stem, leaves, flowers, fruits, and seeds of diverse species of plants (Kannan and Geethamalini, 2005). Sachan and Kapoor (2004) used natural herbal extracts for developing bacteria-resistant finishes for cotton fabric and wool felting. Years ago, wool was treated with chlorine, hypochlorite, and sulfuryl chloride. Bio-polishing using cellulose enzymes is an environmentally friendly method to improve soft handling of cellulose fibers with reduced piling, less fuzz, and improved drape (Thilagavathi et al., 2005).

EFFLUENT TREATMENTS

Dyes in wastewater can be eliminated by various methods. The wastewater from the dye house is generally multi-colored. The dye effluent disposed into the land and river water reduces the depth of penetration of sunlight into the water environment, which in turn decreases photosynthetic activity and dissolved oxygen (DO) (Table 4). The adverse effects can spell disaster for aquatic life and the soil. Figure 2 shows a flow diagram for treatment of cotton textiles, and the water and COD balance are depicted in Figure 3. Many dyes contain organic compounds with functional groups, such as carboxylic (–COOH), amine ($–NH_2$), and azo (–N=N–) groups, so treatment methods must be tailored to the chemistry of the dyes. Wastewaters resulting from dyeing cotton with reactive dyes are highly polluted and have high BOD/COD, coloration, and salt load. For example, this ratio for Drimaren HF (a cellulosic product from Clariant Chemicals, India) is constant and around 0.35 for each dyeing step (bleaching step BOD: 1850 mg/l; bleaching step COD: 5700 mg/l; neutralization step BOD: 290 mg/l; neutralization COD: 830 mg/l; dyeing step BOD: 500 mg/l; dyeing step COD: 1440 mg/l; soaping step BOD: 310 mg/l; soaping step COD: 960 mg/l). Because aquatic organisms need light in order to develop, any deficit in the light reaching the aquatic life due to water coloration results in an imbalance in the ecosystem. Moreover, river water meant for human consumption that is colored will increase treatment costs. Obviously, when legal limits are specified (although not in all countries), they are justified.

Table 4. Composition of cotton textile mill waste

Characteristics	Values
pH	**9.8–11.8**
Total alkalinity	**17–22 mg/l as $CaCO_3$**
BOD	**760–900 mg/l**
COD	**1400–1700 mg/l**
Total solids	**6000–7000 mg/l**
Total chromium	**10–13 mg/l**

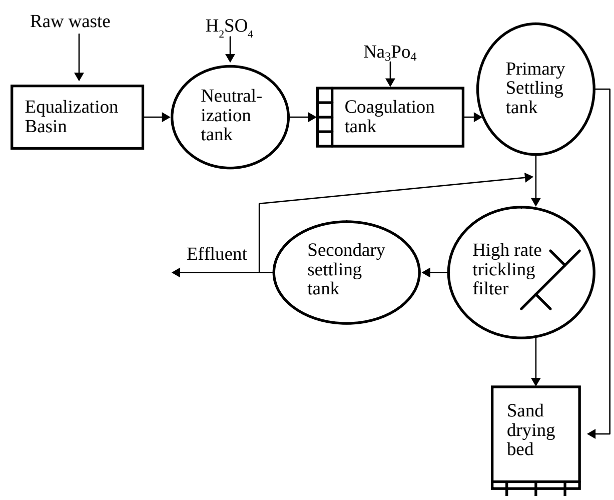

Figure 2. A flow diagram for treatment of cotton textile mill waste.

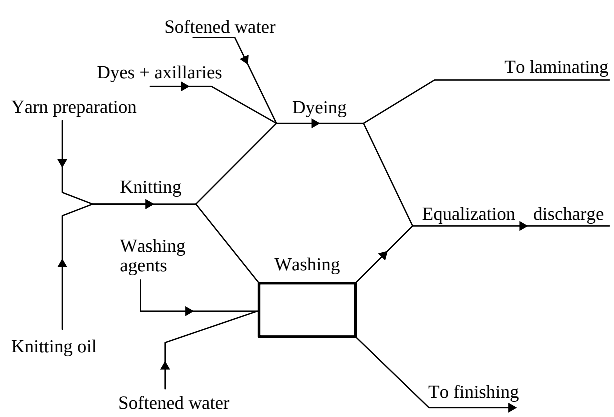

Figure 3. Activites involving water in textile processing.

Marrot and Roche (2002) have given more than 100 references in a bibliographical review of textile wastewater treatment. Treatment operation and decision structure are shown in Figure 4. The physical methods include precipitation (coagulation, flocculation, sedimentation) (Lin and Peng, 1996; Solozhenko et al., 1995; Lin and Liu, 1994; McKay et al., 1987), adsorption (on activated carbon, biological sludges) (Pala and Tokat, 2002), filtration, or reverse osmosis membrane processes (Ghayeni et al., 1998; Treffry-Goatley et al., 1983, Tinghui et al., 1983).

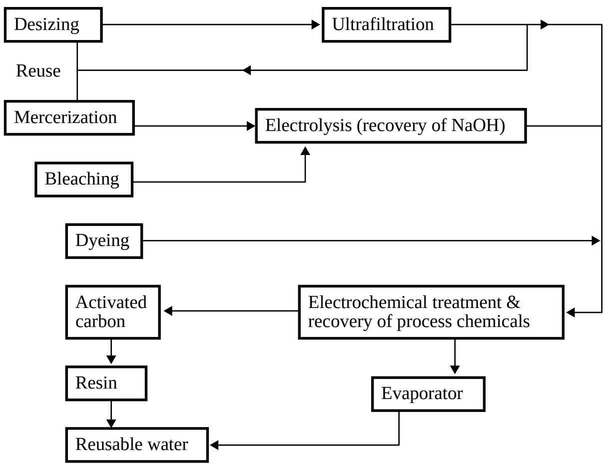

Figure 4. Electrochemical treatment and recovery of chemicals from the textile effluent.

Azo dyes constitute the largest and the most important class of commercial dyes used in textile, printing, tannery, paper manufacture, and photography industries. These dyes are inevitably discharged in industrial effluents. Azo dyes have a serious environmental impact, because their precursors and degradation products (such as aromatic amines) are highly carcinogenic (Szymczyk et al., 2007). Numerous biodegradability studies on dyes have shown that azo dyes are not prone to biodegradation under aerobic conditions (O'Neill et al., 2000; Basibuyuk and Forster, 1997). These dyes are either adsorbed or trapped in bioflocs, which affects the ecosystem of streams, so they need to be removed from wastewater before discharge. Removal of dyes from wastewater can be effected by chemical coagulation, air flotation, and adsorption methods (Malik and Sanyal, 2004; Seshadri et al., 1994). These traditional methods mainly transfer the contaminants from one phase to another phase without effecting any reduction in toxicity. Therefore, advance oxidation is a potential alternative to degrade azo dyes into harmless species.

Biological treatments. Biological treatments reproduce, artificially or otherwise, the phenomena of self-purification that exists in nature. Self-purification is the process by which an aquatic environment achieves the re-establishment of its original quality after pollution. Biological treatments are different depending on the presence or absence of oxygen (Bl'anquez et al., 2006). 'Activated sludge' is a common process by which rates of elimination by oxidizable substances of the order of 90% can be realized (Pala and Tokat, 2002). Because of the low biodegradability of most of the dyes and chemicals used in the textile industry, their biological treatment by the activated sludge process does not always achieve great success. It is remarkable that most of these dyes resist aerobic biological treatment, so adsorbents, such as bentonite clay or activated carbon, are added to biological treatment systems in order to eliminate non-biodegradable or microorganism-toxic organic substances produced by the textile industry (Pala and Tokat, 2002; Marquez and Costa, 1996; Speccia and Gianetto, 1984).

Oxidative chemical treatment, or sometimes the use of organic flocculants (Pala and Tokat, 2002), is often resorted to after the biological treatment (Ledakowic et al., 2001). These methods, which only release effluents into the environment per legal requirements, are expensive (around €2.5/kg for polyamide coagulant: a factor 10 compared with mineral coagulants).

Biological aerated filters (BAF) involve the growth of an organism on media that are held stationary during normal operation and exposed to aeration. In recent years, several BAF-based technologies have been developed to treat wastewater. Effluents from textile industry are among wastewaters that are hard to treat satisfactorily, because their compositions are highly variable. The strong color is most striking characteristic of textile wastewater. If unchecked, colored wastewater can cause a significantly negative impact on the aquatic environment primarily arising from increased turbidity and pollutant concentrations.

Coagulation–flocculation treatments. Coagulation–flocculation treatments are generally used to eliminate organic substances, but the chemicals normally used in this process have no effect on the elimination of soluble dyestuffs. Although this process effectively eliminates insoluble dyes (Gaehr et al., 1994), its value is doubtful because of the cost of treating the sludge and the increasing number of restrictions concerning the disposal of sludge.

Adsorption on powdered activated carbon. The adsorption on activated carbon without pretreatment is impossible because the suspended solids rapidly clog the filter (Matsui et al., 2005). This procedure is therefore only feasible in combination with flocculation–decantation treatment or a biological treatment. The combination permits a reduction of suspended solids and organic substances, as well as a slight reduction in the color (Rozzi et al., 1999), but the cost of activated carbon is high.

Electrochemical processes. Electrochemical techniques for the treatment of dye waste are more efficient than other treatments (Naumczyk et al., 1996). Electrochemical technology has been applied to effectively remove acids, as well as dispersed and metal complex dyes. The removal of dyes from aqueous solutions results from adsorption and degradation of the dye-stuff following interaction with iron electrodes. If metal complex dyes are present, dye solubility and charge are important factors that determine the successful removal of heavy metals. In order to maximize dye insolubility, pH control is crucial (Chakarborty et al., 2003; Vedavyasam, 2000; Nowak et al., 1996; Calabro et al., 1990). Conventional methods involve generation of secondary pollutants (sludge), but sludge formation is absent in the electrochemical method (Ganesh et al., 1994). Electrochemical treatment and recovery of chemicals from the effluent are shown in Fig. 4. In this process, the recovery of metals or chemicals is easily carried out. At the same time, the following environmental advantages are realized; emission of gases, solid waste, and liquid effluent are minimized.

The use of an electrolytic cell in which the dye house wastewater is recirculated has been described (Lin and Chen, 1997; Lin and Peng, 1994). The advantage of this process seems to be its capacity for adaptation to different volumes and pollution loads. Its main disadvantage is that it generates iron hydroxide sludge (from the iron electrodes in the cell), which limits its use. Electro-coagulation has been successfully used to treat textile industrial wastewaters. The goal is to form flocs of metal hydroxides within the effluent to be cleaned by electro-dissolution of soluble anodes. Three main processes occur during electro-coagulation; electrolytic reactions at the electrodes; formation of coagulants in the aqueous phase and adsorption of soluble or colloidal pollutants on coagulants; and removal by sedimentation and floatation. Electro-coagulation is an efficient process, even at high pH, for the removal of color and total organic carbon. The efficiency of the process is strongly influenced by the current density and duration of the reaction. Under optimal conditions, decolorization yields between 90 and 95%, and COD removal between 30 and 36% can be achieved.

Ozone treatment. Widely used in water treatment, ozone (either singly or in combinations, such as O_3-UV or O_3-H_2O_2) is now used in the treatment of industrial effluents (Langlais et al., 2001). Ozone especially attacks the double bonds that bestow color. For this reason, decolorization of wastewater by ozone alone does not lead to a significant reduction in COD (Coste et al., 1996; Adams et al., 1995). Moreover, installation of ozonation plants can entail additional costs (Scott and Ollis, 1995).

MEMBRANE PROCESSES

Increasing cost of water and its profligate consumption necessitate a treatment process that is integrated with in-plant water circuits rather than as a subsequent treatment (Machenbach, 1998). From this standpoint, membrane filtration offers potential applications. Processes using membranes provide very interesting possibilities for the separation of hydrolyzed dye-stuffs and dyeing auxiliaries that simultaneously reduce coloration and BOD/COD of the wastewater. The choice of the membrane process, whether it is reverse osmosis, nanofiltration, ultrafiltration or microfiltration, must be guided by the quality of the final product.

Reverse osmosis. Reverse osmosis membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate (Ghayeni et al., 1998; Treffry-Goatley et al., 1983; Tinghui et al., 1983). Decoloration and elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step by reverse osmosis. Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes, and chemical auxiliaries. It must be noted that higher the concentration of dissolved salt, the more important the osmotic pressure becomes; therefore, the greater the energy required for the separation process.

Nanofiltration. Nanofiltration has been applied for the treatment of colored effluents from the textile industry. A combination of adsorption and nanofiltration can be adopted for the treatment of textile dye effluents. The adsorption step precedes nanofiltration, because this sequence decreases concentration polarization during the filtration process, which increases the process output (Chakraborty et al., 2003). Nanofiltration membranes retain low-molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries. Harmful effects of high concentrations of dye and salts in dye house effluents have frequently been reported (Tang and Chen, 2002; Koyuncu, 2002; Bruggen et al., 2001; Jiraratananon et al., 2000; Xu et al., 1999; Erswell et al., 1988). In most published studies concerning dye house effluents, the concentration of mineral salts does not exceed 20 g/L, and the concentration of dyestuff does not exceed 1.5 g/L (Tang and Chen, 2002). Generally, the effluents are reconstituted with only one dye (Tang and Chen, 2002; Koyuncu, 2002; Akbari et al., 2002), and the volume studied is also low (Akbari et al., 2002). The treatment of dyeing wastewater by nanofiltration represents one of the rare applications possible for the treatment of solutions with highly concentrated and complex solutions (Rossignol et al., 2000; Freger et al., 2000; Knauf et al., 1998; Peuchot, 1997; Kelly and Kelly, 1995).

A major problem is the accumulation of dissolved solids, which makes discharging the treated effluents into water streams impossible. Various research groups have tried to develop economically feasible technologies for effective treatment of dye effluents (Karim et al., 2006; Cairne et al., 2004; Rott and Mike, 1999). Nanofiltration treatment as an alternative has been found to be fairly satisfactory. The technique is also favorable in terms of environmental regulation.

Ultrafiltration. Ultrafiltration enables elimination of macromolecules and particles, but the elimination of polluting substances, such as dyes, is never complete (it is only between 31% and 76%) (Watters et al., 1991). Even in the best of cases, the quality of the treated wastewater does not permit its reuse for sensitive processes, such as dyeing of textile. Rott and Minke (1999) emphasize that 40% of the water treated by ultrafiltration can be recycled to feed processes termed “minor” in the textile industry (rinsing, washing) in which salinity is not a problem. Ultrafiltration can only be used as a pretreatment for reverse osmosis (Ciardelli and Ranieri, 2001) or in combination with a biological reactor (Mignani et al., 1999).

Microfiltration. Microfiltration is suitable for treating dye baths containing pigment dyes (Al-Malack and Anderson, 1997), as well as for subsequent rinsing baths. The chemicals used in dye bath, which are not filtered by microfiltration, will remain in the bath. Microfiltration can also be used as a pretreatment for nanofiltration or reverse osmosis (Ghayeni et al., 1998).

CONCLUSIONS

Waste minimization is of great importance in decreasing pollution load and production costs. This review has shown that various methods can be applied to treat cotton textile effluents and to minimize pollution load. Traditional technologies to treat textile wastewater include various combinations of biological, physical, and chemical methods, but these methods require high capital and operating costs. Technologies based on membrane systems are among the best alternative methods that can be adopted for large-scale ecologically friendly treatment processes. A combination methods involving adsorption followed by nanofiltration has also been advocated, although a major drawback in direct nanofiltration is a substantial reduction in pollutants, which causes permeation through flux.

It appears that an ideal treatment process for satisfactory recycling and reuse of textile effluent water should involve the following steps. Initially, refractory organic compounds and dyes may be electrochemically oxidized to biodegradable constituents before the wastewater is subjected to biological treatment under aerobic conditions. Color and odor removal may be accomplished by a second electro-oxidation process. Microbial life, if any, may be destroyed by a photochemical treatment. The treated water at this stage may be used for rinsing and washing purposes; however, an ion-exchange step may be introduced if the water is desired to be used for industrial processing.

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