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Improvements in permeate flux by aluminum electroflotation pretreatment during microfiltration of surface water

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Abstract

Cathodic production of fine hydrogen bubbles over relatively long durations during aluminum electrochemical treatment of natural waters was empirically observed to induce floc flotation. Such electrochemically assisted flotation, termed electroflotation, was employed for microfiltration (MF) pretreatment by skimming off the surficial floc layer and drawing water from near the bottom of the electroflotation cell. This approach significantly increased permeate fluxes during surface water dead-end MF by reducing both the cake mass and the cumulative hydraulic resistance. These results were compared with a closely related process – electrocoagulation – wherein the entire destabilized suspension was sent to MF. Electrocoagulation pretreatment also improved MF fluxes compared with raw water, but not as much as electroflotation. In both pretreatment scenarios, amorphous $Al(OH)_3$ was dominant as revealed by X-ray photoelectron spectroscopy. The absence of an intermediate particle removal step in electrocoagulation contributed to a higher cake mass and greater total cake resistance even though it reduced the specific resistance by forming larger aggregates. In addition to improving MF flux during forward filtration, electroflotation pretreatment appears to form largely reversible fouling layers that may lead to more effective MF backwashing. In contrast, nitrogen and silicon detected on membranes, even after cake removal suggests a greater extent of irreversible MF fouling following electrocoagulation pretreatment. Significant improvements in flux and potential improvements in backwashing effectiveness following aluminum electroflotation of surface water in laboratory-scale experiments points to the need for larger-scale evaluations before a hybrid electroflotation-MF process can be implemented for drinking water treatment.

Highlights

► Cathodic release of hydrogen gas facilitates floc flotation during Al electrolysis. ► Electroflotation pretreatment significantly reduces mass loading and MF fouling. ► Electroflotation outperforms electrocoagulation for fouling reduction. ► Largely

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Review Article

Electrochemical Techniques in Textile Processes and Wastewater Treatment

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The textile industry uses the electrochemical techniques both in textile processes (such as manufacturing fibers, dyeing processes, and decolorizing fabrics) and in wastewaters treatments (color removal). Electrochemical reduction reactions are mostly used in sulfur and vat dyeing, but in some cases, they are applied to effluents discoloration. However, the main applications of electrochemical treatments in the textile sector are based on oxidation reactions. Most of electrochemical oxidation processes involve indirect reactions which imply the generation of hypochlorite or hydroxyl radical in situ. These electrogenerated species are able to bleach indigo-dyed denim fabrics and to degrade dyes in wastewater in order to achieve the effluent color removal. The aim of this paper is to review the electrochemical techniques applied to textile industry. In particular, they are an efficient method to remove color of textile effluents. The reuse of the discolored effluent is possible, which implies an important saving of salt and water (i.e., by means of the "UVEC Cell").

1. Introduction

Traditionally, the electrochemical techniques have been used for the synthesis of compounds or for metal recovery treatments. But more recently, a wide range of other applications have been proposed. Some of them are proposed to solve several technical problems of the textile industry. This is the case of a recent application to produce smart textiles [1–28] by obtaining functionalized fabrics. These textiles with specific properties are prepared by using the electrochemistry in the synthesis of conductive polymers, especially conductive fibers.

Another interesting use of the electrochemical techniques is the bleaching of cotton fibers [29] and the bleaching of finished denim fabrics [30–37]. In order to achieve the visual effect in jeans, the generation in situ of hypochlorite by electrochemical reaction has been proposed, instead of its addition.

Their application in sulfur- and vat-dyeing processes [38–61] is also interesting. In this case, dyes are reduced by means of an electrochemical reaction (instead of sodium dithionite). In this way, sulfur and vat dyeing become cleaner processes as the addition of chemical reagents is not required.

Although the electrochemical methods play an important role in the different textile processes listed above, their wider range of applications are related to color removal in wastewater treatments [62–115], in particular, in the degradation of nonbiodegradable dyes (such as reactive dyes). This kind of dyes requires additional treatments to obtain uncolored effluents. In general, the electrochemical methods are cleaner than physicochemical and membrane technologies (the current methods for color removal) because they use the electron as unique reagent and they do not produce solid residues.

The objective of this paper is to review the main applications of electrochemical techniques in textile industry (production processes and wastewater treatments). Nowadays, there are only few applications at industrial scale as most of electrochemical treatments are still being studied at laboratory scale. Therefore, it is convenient to encourage the research on new applications of these techniques because they provide some important benefits. As far as we know,

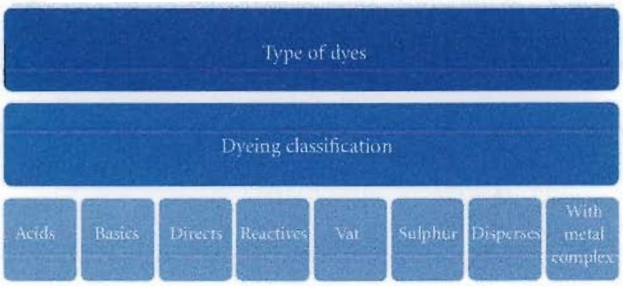

Figure 4: Dyes classification.

that is, several reviews [59, 60] are available on functionalizing the surface of carbon electrodes to obtain higher reduction rates with the same color intensity and washing fastness than traditional methods [61]. Furthermore the possibility of reusing these electrodes is a subject of the study.

The reuse of the reducing agent (by regeneration in a cathodic reduction) and also the dyeing bath in the indirect reduction electrochemical method, using a mediator, has been studied [53] but the final color was poorer than the one obtained by the traditional method with sodium dithionite.

Taking into account all these studies, we can conclude that the use of electrochemical techniques constitute a promising field for the different steps of textile process, but their application to the dyeing of vat and sulfur dyes is specially interesting to avoid the use of reducing reagents.

3. Wastewater Color Removal

3.1. Textile Wastewater Concern. The textile industry produces large volumes of wastewater in its dyeing and finishing processes. These effluents have as common characteristic their high coloration. Colorants, the additive substances that cause a variation in color, can be divided in dyes or pigments. Pigments in general are insoluble substances which have not the chemical affinity to the substrate to be colored; otherwise, dyes are generally soluble (or partially soluble) organic compounds, which interact with the fiber or leather imparting color [62]. Figure 4 summarizes the different textile dyes according to their dyeing behavior.

Most of electrochemical discoloration studies are focused on reactive dyes. They represent about 20–30% of the total market [63], because of their solidity and brilliant color. Their structure consists on a *reactive group* (which reacts with the fiber), and a *chromophore group* (which gives the color). The most used chromophore group is the "azo" (R–N=N–R′), followed by the anthraquinone group [64]. Azo group constitute, more than half of worldwide production [65], approximately 65% [66–68]. Moreover, this kind of dyes produces toxic aromatic products in their degradation.

The dyeing reaction, when a triazine is the reactive group, occurs by a nucleophilic displacement of the chlorine atom from the reactive group to the hydroxyl group from the cellulose in alkaline medium, as it is shown below [69].

Reaction 2:

$$\text{dye-Cl} + \text{HO-cellulose} \longrightarrow \text{dye-O-cellulose} + \text{HCl} \qquad (1)$$

The competitive reaction between dye and water produces dyes hydrolysis (reaction 3). The hydrolyzed dyes cannot react with the fiber, being the element responsible for the colored effluents.

Reaction 3:

$$\text{dye-Cl} + \text{H}_2\text{O} \longrightarrow \text{dye-OH} + \text{HCl} \qquad (2)$$

The high consumption of reactive dyes, mainly in the cotton industry, increases this environmental and aesthetic problem, due to their low degree of exhaustion, and their presence both in dyeing and soaping effluents.

Other chemical products present in the dyeing process (such as Na_2CO_3 used to set the pH in the dyeing bath which has an important role in dyes fixation to the fiber and color fastness; or NaCl added to transfer the dyestuff to the fabric) can influence the electrochemistry process as they can scavenge $^{\bullet}OH$ and $h_{\gamma b}{}^{+}$) [70].

Several methods are used for the removal of organic dyes from wastewaters. Most of dyes are only partially removed under aerobic conditions in conventional biological treatments. As biological treatment is insufficient to remove color and to accomplish with current regulations, the application of specific treatments is required. The effluent color regulations are very variable depending on the Country. In UK, the color value is calculated from some absorbance measurements. State and USA federal agencies have been requiring low effluent color limits (<200 units of the American Dye Manufacturers Institute, ADMI). While the implementation of the Cluster Rules did not place regulatory limits on color, the U.S. EPA left the option open for regulatory authorities to establish limits on color based on the individual circumstances of each holder and watershed. In Spain, the colored effluents are allowed to be discharged if no color is observed after a 1/20 dilution (Real Decreto 849/1986), although each regional authority can restrict this value.

The different techniques to achieve effective color removal, according to Martínez-Huitle and Brillas [71], are schematically indicated in Figure 5.

Some electrochemical color removal methods have been applied to industrial effluents. The current physico-chemical methods, based on the separation of dyes from the effluents, produce a residue which requires an additional treatment to be destroyed. Also, the absorbent materials (such as active carbon, silica gel, or alumina) require their regeneration after several treatments [72], and the filtration and membranes methods need cleaning treatments. Chemical oxidation methods are rather expensive and involve some operational difficulties [73, 74]. Biological treatments are a simple method but supply inefficient results in discoloration because dyes have aromatic rings in their large molecules that provide them chemical stability and resistance to the microbiological attack [75]. Enzymatic decomposition requires

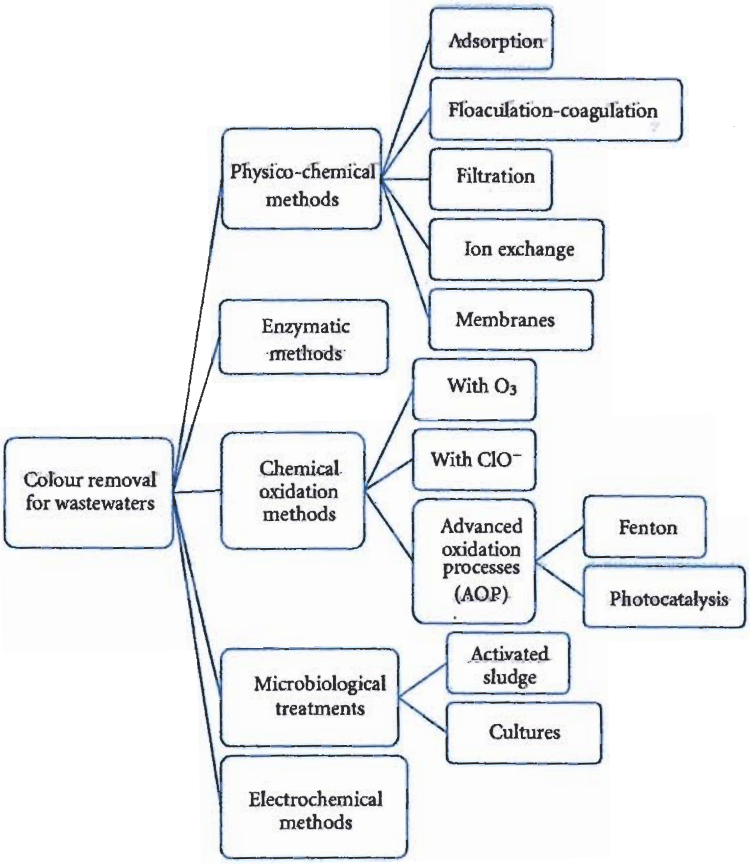

Figure 5: Methods for textile wastewater color removal.

further investigation in order to know which enzymatic process takes place [76]; moreover, temperature and pressure have to be controlled to avoid enzymes denaturalization.

For these reasons, the electrochemical methods are nowadays the subject of a wide range of investigations at laboratory and pilot-plant scale. The advantage of these electrochemical techniques is that electron is a clean reagent. They also have good versatility and high-energy efficiency. They are easy for automation and safety because it is possible to operate at smooth conditions [77]. Figure 6 represents the main types of electrochemical methods applied to wastewater treatment, briefly described below.

3.2. Electrocoagulation Methods. Electrocoagulation systems provide electrochemical aggregation of heavy metals, organic and inorganic pollutants, to produce a coagulated residue to be separated or removed from water.

This technique is an indirect electrochemical method which produces coagulant agents (Fe^{3+} or Al^{3+}) from the electrode material (Fe or Al) in hydroxide medium. These species, that is, $Fe(OH)_3$, can remove dissolved dyes by precipitation or by flotation [78, 79]. These complexed compounds are attached to the bubbles of $H_{2(gas)}$ evolved at the cathode and transported to the top of solution. The inconvenient of the electrocoagualtion in comparison to the other electrochemical methods is that it produces secondary residues (the complex formed with pollutant and hydroxide) which implies the use of tertiary treatments.

3.3. Electrochemical Reduction Methods. The electrochemical reduction method has been discussed in a restricted number of papers because its yield in pollutants degradation is poor in comparison to direct and indirect electro-oxidation methods [71]. Bechtold et al. [80], consider that this method is particularly suitable for the treatment of highly colored wastewaters such as the residual pad-batch dyeing bath with reactive dyes. The dye reduction takes place producing hydrazine (in the partial reduction) and its total reduction generates amino compounds (scheme in Figure 7). They remark the importance of a divided cell in the case of dye baths containing chlorides; this division is important to avoid the formation of chlorine and chlorinated products.

In the same way, Vanerkova et al. [81] proposed a reduction mechanism for the azo dyes degradation with platinated titanium electrodes (Pt/Ti) in the presence of NaCl. In this study, the action of hypochlorite generated by oxidation of chloride is also discussed Zanoni et al. [69] studied the hydrolysis under reduction process of two anthraquinone reactive dyes. They demonstrate that the acidic medium provides the best conditions, and that the presence of borate in the solution modifies the reduction process.

a high amount of acid has to be added before the treatment. Subsequently, the treated effluent must be neutralized to be discharged. Consequently, the whole process produces a high increase of the wastewater salinity.

As some industrial wastewaters contain large amounts of chloride, the first approach is more suitable to treat this kind of effluents, because the addition of any chemical product is not required whereas in second case, Fenton reagent is needed. In contrast, the combination of electrochemistry and chloride can produce haloforms such as chloroform, although it is not an inconvenient if the treated water is degraded lately in a biological plant to accomplish its mineralization. In fact, it has been verified that the concentration of haloforms is very low and they do not show any toxic effect on the plant microorganisms [98]. Otherwise it is possible to remove the haloform generated by placing a UV lamp in the electrochemical cell where the reaction takes place [99], or by adding H_2O_2 into the wastewater before the reaction had started. The first approach was studied by López-Grimau and Gutiérrez [100] and it was found to improve the kinetic rates of electrochemical degradation of some reactive azo dyes with Ti/PtO_x electrodes. The electrochemistry method using chlorine has been noted to be effective in other kind of dyes, such as acid dyes [101] or disperse dyes [102], and combined with photoelectrochemistry has also obtained good results for phtalocyanine dyes degradation [103], but in this case, the metal ions liberated (as copper) have to be removed.

3.6. *Photo-Assisted Methods.*

The photoassisted electrochemical methods are based on the exposure of the effluent to a UV light source during the electrochemical treatment. In these procedures, the intensity and the wavelength of the incident light plays an important role on the mineralization rate.

The most studied photoassisted method is the photoFenton [105], which consists in the simultaneous use of UV light and H_2O_2 (electrogenerated in situ with the presence of Fe^{2+}); followed by the heterogeneous TiO_2 photocatalysis method [106]. Although several photocatalysts (TiO_2, WO_3, SnO_2, ZnO, CdS...) act via hydroxyl radical and generate powerful oxidants, the TiO_2 under UV radiation has been the preferred catalyst, due to its low cost, nontoxicity, water insolubility and wide band gap, which consequently implies a good stability and prevents photocorrosion [62, 70, 107–112]).

Moreover, Carneiro et al. [70] noted that the use of photocatalysis with Ti/TiO_2 electrodes achieves efficiently discoloration with both electrolytes, NaCl and Na_2SO_4. Their efficiency depend on the pH.

Xie and Li [113] reported the coupling of electro-Fenton with electrocatalysis for the removal of an azo dye. With respect to other electro-oxidation and photoassisted methods, their results showed a better removal of the dye in the coupled system. The major disadvantage of these methods was the excessive energy cost of the artificial UV light used. However, this problem is easy to solve by using sunlight [114, 115] as inexpensive energy source although it had less catalytic power.

Additionally, the combination between the indirect oxidation methods with the UV irradiation has been the subject of recent investigations. According to Sala [116], the energy consumption is around $5.7\,\text{kW}\cdot\text{h/m}^3$ to achieve discoloration higher than 90% when the photoelectrochemical treatment is applied to real industrial effluents by means of a semi-industrial pilot. The discoloration process follows a pseudo-first-order kinetic in the case of monochromies and a second order kinetics in the case of trichromie, evaluated at the maximum absorbance wavelength of the trichromie, which corresponds mainly to the contribution of two dyes (due to the low absorbance of the third dye at the selected wavelength).

By another hand, the actual policies concerning water and energy consumption conduce to recycling and reuse treatments. In this sense, recent studies [104] demonstrate the possibility of reusing these discolored effluents for new dyeing processes. The reuse of 70% of discolored dyebaths, after electrochemical treatment assisted by UV irradiation, provides in most of cases, low color differences ($\text{DE}_{\text{CMC}(2:1)} \leq 1$) with respect to the original dyeing with decalcified tap water. This value increases from the first step until the 4th or 5th cycle of electrochemical treatment and reuse, where $\text{DE}_{\text{CMC}(2:1)}$ become constant. In some cases, when the bath is reused, an extra amount of dye must be added to obtain the required color.

Numerous studies can be found about the electrochemical discoloration of textile wastewater, but some authors have advanced a further step: in the case of indirect oxidation with active chlorine, the conditions for the effluents reutilization have also been optimized [99, 100, 104]. In this sense, Gutierrez-Bouzan et al. in a recent patent (ES201131159) claimed a process "UVEC Cell" for the discoloration and reuse of reactive dyes effluents in a new dyeing process. Both prototype and procedure are patented, based on an electrochemical cell combined with UV source for the treatment and reuse of textile effluents saving more than 60% water and electrolyte.

4. Conclusions

The electrochemical techniques have been proved to be efficient in different oxidation or reduction steps of the textile processes such as: bleaching denim fabrics or reduction of sulfur and vat dyes, where their applications are available in both natural and synthetic fibers. They constitute a less harmful alternative than the traditional processes. They also have been studied in new textile fields, such as in the production of conductive polymers used as fibers which are applied in smart textiles to produce fabrics with new functions.

In addition, the electrochemical treatments have been extensively applied to the decontamination of wastewaters from the textile processes. They have been mainly used in the removal of residual reactive dyes, but also in the discoloration of acid and disperse dyes effluents. Taking into account the considerable amount of salt contained in the reactive dyes residual dyebath, the best method for the treatment of these

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TEXTILE TECHNOLOGY

Cotton Textile Processing: Waste Generation and Effluent Treatment

B. Ramesh Babu*, A.K. Parande, S. Raghu, and T. Prem Kumar

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).

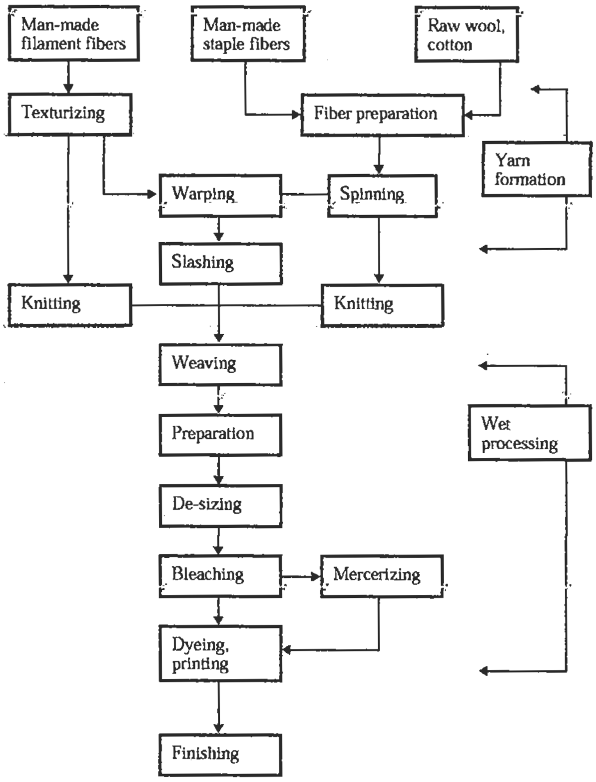

Figure 1. A flow diagram for various steps involved in processing textile in a cotton mill.

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.

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).

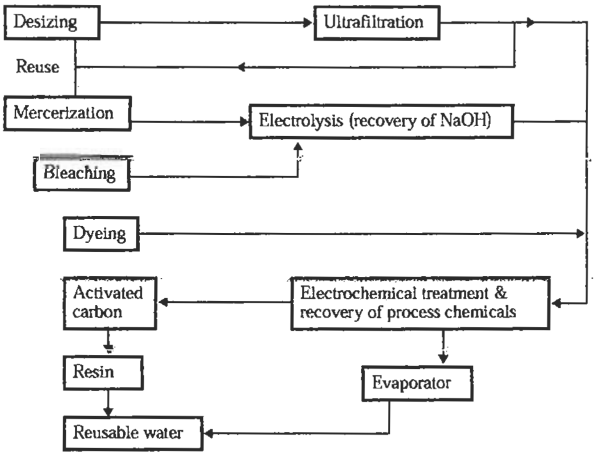

Figure 4. Electrochemical treatment and recovery of chemicals from the textile effluent.

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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