Chemistry: Bulgarian Journal of Science Education, Volume 21, Number 3, 2012
Природни науки в образованието

From the Research Laboratories
В изследователските лаборатории

TEXTILE EFFLUENT TREATMENT AND DECOLORIZATION TECHNIQUES – A REVIEW

Bizuneh Adinew
Mizan-Tepi University, ETHIOPIA

Abstract. Dyes and pigments are widely used, mostly in the textile, paper, plastics, leathers, food and cosmetics industry to color products. Textile industry consumes large volume of water and produce large amount of wastewater during all phases of textile production and finishing. The release of colored effluents represents a serious green pollution and a human health concern particularly in developing countries like Ethiopia (East Africa). Color removal, especially from textile effluents, has gargantuan challenge over the last decades, and up to now there is no single and cost-effectively attractive treatment that can effectively decolourise as well as treat the dyes effluents. The objective of this review article is to discuss a variety of textile wastewater treatment techniques (physical, chemical and biological techniques) from the environmental point of view.

Keywords: textile effluent, color removal, adsorption, green pollution, dyes

Introduction

The world's ever increasing population and the progressive adoption of an industrial based life style has inevitably led to an increased anthropogenic impact on the biosphere. Textile industries are the most important industries in Ethiopia and their numbers have increased. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The global consumption of textiles is currently around 30 million tones with expected growth at 3% per annum (Walker & Weatherly, 1997). The coloration of this total needs approximately 8×10^5 tons of dyes (Walker & Weatherly, 1997) and it is estimated that 10,000 different types of dyes and pigments are produced worldwide annually.[1)] Out of which a large number of dyes are azo compounds (-N=N-), which are linked by an azo bridge and are used by a wide number of industries. While textile mills predominantly use them, azo dyes can also be found in the food, pharmaceutical, paper and printing, leather, and cosmetics industries (Asamudo et al., 2005). Synthetic textile dyes used each year are lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters.[1)] 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 effluent produced by a reactive dye contains hydrolyzed reactive dyes not fixed on the substrate, representing 20-30% of the reactive dyes applied (on average 2 gL^{-1}), this residual amount is responsible for the coloration of the effluents and cannot be recycled, dyed organic substances, which are non recyclable and responsible for the high biological oxygen demand (BOD) and chemical oxygen demand (COD) of the effluents, Textile fibers, 60-100 gL^{-1} electrolytes, essentially sodium chloride and sodium carbonate, which are responsible for the very high saline content of the wastewater (Allegre et al., 2006). In addition to dyes, textile wastewater also contains solids, oil, and halogenated organics from processes such as bleaching. Moreover, some compounds may be applied to fibers in processes preceding the final step of washing to improve the properties of the fibers. These compounds may be released to effluent water during washing. Examples of these compounds include surfactants, sizing, coating, and finishing additives. Sizing compounds such as starch contribute to increased biological oxygen demand (BOD) and chemical oxygen demand (COD) of wastewater stream. Synthetic sizing additives, which are not as biodegradable as starches, can pass through conventional wastewater treatment system, and are often linked to aquatic toxicity in receiving water.[2)]

Although Ethiopia does not have the industries that flourished in the developed countries, textile and leather industries are given more attention due to the availability of raw materials and further expansion of such industries is expected. However, almost all of the available industries (textile, paper, plastic, leather, food, cosmetic, etc) release their untreated or partially treated wastewaters into municipal sewers, or directly into nearby drains, rivers, stagnant, ponds, lagoons, or lakes. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic bionetwork and the environment at large (Pala et al., 2003). 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 forced to wind up 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 environmental 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 & Bardhan, 1999), which is considered the most practical solution.

Dyes

According to Allen (1971), dye is a colored substance that can be applied in solution or dispersion to a substrate, thus giving it a colored appearance. Usually a substrate is a textile fiber, but it may be paper, leather, hair, fur, plastic material, wax, a cosmetic base or a foodstuff. Dyes may be classified in several ways, according to its chemical constitutions, application class, or end-use. The primary classification of dyes is based on the fibers to which they can be applied and the chemical nature of dye.

Table 1. Typical characteristics of dyes used in textile dyeing operations

Application Class	Characteristics
Acid dyes	Highly water-soluble due to the presence of sulphonic acid groups. Form ionic interactions between the protonated functionalities of the fibers (-NH_3^+) and the negative charge of the dyes. Also Van-der-Waals, dipolar and hydrogen bonds are formed. The most common structures are azo, anthraquinone and triarylmethane.
Reactive dyes	Form covalent bonds with -OH, -NH or -SH groups in cotton, wool, silk and nylon. The problem of colored effluents associated to the use of these dyes is due to the hydrolysis of the reactive groups that occurs during the dyeing process. The most common structures are azo, metal complex azo, anthraquinone and phthalocyanine.
Direct dyes	Their flat shape and length enables them to bind along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds. Only 30% of the 1600 structures are still in production due to their lack of fastness during washing. The most common structures are almost always sulphonated azo dyes.

Basic dyes	Basic dyes work very well on acrylics due to the strong ionic interaction between dye functional groups such as $-NR_3^+$ or $=NR_2^+$ and the negative charges in the copolymer. The most common structures are azo, diarylmethane, triarylmethane and anthraquinone.
Mordant dyes	Mordant are usually metal salts such as sodium or potassium dichromate. They act as "fixing agent" to improve the color fastness. They are used with wool, leather, silk and modified cellulose fibers. The most common structures are azo, oxazine or triarylmethane.
Disperse dyes	Non-ionic structure, with polar functionality like $-NO_2$ and –CN that improve water solubility, Van-der-Waals forces, dipole forces and the color. They are usually used with polyester. The most common structures are azo, nitro, anthraquinones or metal complex azo.
Pigment dyes	These insoluble, non-ionic compounds or salts, representing 25% of all commercial dye names, retain their crystalline or particulate structure throughout their application. The most common structures are azo or metal complex phthalocyanines.
Vat dyes	Vat dyes are insoluble in water, but may become solubilized by alkali reduction (sodium dithionite in the presence of sodium hydroxide). The produced *leuco* form is absorbed by the cellulose (Van-der-Waals forces) and can be oxidized back, usually with hydrogen peroxide, to its insoluble form. The most common structures are anthraquinones or indigoids.
Ingrain dyes	The term ingrain is applicable to all dyes formed *in situ*, in or on the substrate by the development, or coupling, of one or more intermediate compounds and a diazotized aromatic amine. In the Color Index the sub-section designated Ingrain is limited to tetra-azaporphin derivatives or precursors.
Sulphur dyes	Sulphur dyes are complex polymeric aromatics with heterocyclic S- containing rings representing about 15% of the global dye production. Dyeing with sulphur dyes (mainly on cellulose fibers) involves reduction and oxidation processes, comparable to vat dyeing.
Solvent dyes	Non-ionic dyes that are used for dyeing substrates in which they can dissolve as plastics, varnish, ink and waxes. They are not often used for textile processing. The most common structures are diazo compounds that undergo some molecular rearrangement, triarylmethane, anthraquinone and phthalocyanine.
Other dye classes	Food dyes are not used as textile dyes. Natural dyes use in textile processing operations is very limited. Fluorescent brighteners mask the yellowish tint of natural fibers by absorbing ultraviolet light and weakly emitting blue light. Not listed in a separate class in the Color Index, many metal complex dyes can be found (generally chromium, copper, cobalt or nickel). The metal complex dyes are generally azo compounds.

Types of synthetic dyes

Synthetic dyes have many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes, that fall into either the cationic, nonionic or anionic type (Table 1). Anionic dyes include the direct, and the most problematic water-soluble acid and reactive dyes. Nonionic dyes refer to disperse dyes that do not ionize in aqueous medium and some of them have the ability of bioaccumulation. Whereas anthroquinone based dyes are the most resistant to degradation due to their fused aromatic ring structure (Robinson et al., 2001b).

The color of dye is combined effects of chromophores, delocalized electron system with conjugated double bonds, and auxochrome – electron withdrawing or electron donating substituent that enhance the color of chromophore by changing the overall energy of electron system. Some of the important chromophores are –N= N- , -C= O, $-NO_2$ and quinoid groups, and important auxochromes are $-NH_3$, -OH, $-SO_3H$ and $-CO_2H$. Both chromophore and auxochrome increase the bath chromic effect – shifting adsorption bands to longer wavelength, on a conjugated system of dye. In addition to enhancing the chromophore in production of color, auxochromes are also responsible for the solubility of dye and increase its reactivity towards fibers.[3-5)]

The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone type. Toxic amines result when azo groups undergo reductive cleavage. Reactive dyes are azo-based chromopores that contain different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, diflurochloropyrimidine. In contrast to other classes of dyes, they form covalent bonds to the textile fibers such as cotton. The uses of reactive dyes are highly favored in the textile industries owing to their bright color, water fast, simple application techniques with low energy consumption and, thus reactive dyes are among the dyes most commonly in use today (Aksu, 2005). Reactive dyes are used primarily on cotton and rayon. They are highly soluble in water and with the help of large amount of salt; the exhaustion of the dyes is improved.

Metals in dyes

Metals found as integral parts of the dye chromophores (e.g., phthalocyanine); comprise mainly cobalt, copper, and chromium. However, some dyes have low-level metal impurities that are present incidentally, rather than necessity in terms of functionality and color. When mercury-based compounds are used as catalysts in dye manufacturing, there is a possibility of its presence as trace residue. Very few (e.g., only 2% commercial direct dyes) have metal as an integral part of the dye chromophore (Al-Ghouti et al., 2003; Andrady, 2003). Unless textile effluent is treated properly, as a result of extensive use of dyes and pigments throughout the world, toxic metals associated with the dyes and pigments inevitably reach to aquatic environments, and pose serious treats to aquatic lives and the system (Waranusantigul et al., 2003).

Textile effluent treatment dye decolorization techniques

Water pollution by textile industry

Water is one of the major elements essential for sustenance of all forms of life. The chemical nature of water is one of the most important criteria that determine its usefulness for specific needs and as such not all waters are fit for drinking. Many water sources contain harmful substances in concentrations that make the water unsafe to drink or unfit for domestic use. Water pollution problems in any part of the world are far worse from day to day. What are the causes of these problems? The answer is due to human activity and unbalanced development. Water that has been withdrawn, used for some purposed and returned will be polluted in one-way or another way. Agricultural return water containing pesticides fertilizes and salts, municipal return water contain chemical. All of this is due to human activity.

Table 2. Industrial source of water pollution

Type of industry	Percentage, %
Palm oil	11.6
Raw natural rubber	8.6
Rubber and product	14.1
Food and beverage	40.5
Textile and leather	9.0
Paper	4.4
Chemical	11.8
Total	100

When water is polluted the water becomes unsuitable for drink water and habitat for aquatic life. Wastewater discharged from textile industry characterized by high chemical demand (COD), low biodegradability, high salt content and is the source of aesthetic pollution related to color (Alinsafi et al., 2005). The salt and heavy metal from highly colored wastewater are toxic to aquatic life (Wu et al., 2004). While some of the dyes such as azo dye are carcinogenic and then cause serious health problems such as cancer.[6)] This caused the treatment of dye before discharged are important to ensure sustainable development able to achieve. Textile industry is the fifth major industry that becomes source of environmental problem (Table 2).

However, in term of coloring effluent, textile industry is the largest industry discharging coloring effluent. So it is important to study a treatment process that is efficient to treat the color and chemical in the effluent in order to ensure our water be safe for the future generation.

In accordance with the development of textile industry, the pollution of environment by the industry has become obvious. Especially colored wastewater discharged from dyeing factory. Many factories discharge colored wastewater without any treatment because color is outside the scope of regulation. For Small to middle size factories they don't have treatment facilities to reduce pH, COD, BOD and the entire hazardous chemicals. This makes the pollution caused by the textile industry worst. Typical pollutants generated by synthetic dyes are discussed in Table 3. To reduce water pollution caused by textile industry, investigation in this regard must be done in search of efficient means for treatment of effluents prior to discharging them to the surrounding environment.

Table 3. Typical pollutants generated by synthetic dyes

Dye Class	Typical pollutants associated with the dyes
Acid	Color, organic acids, and unfixed dyes
Basic	N/A
Direct	Color, salt, unfixed dye, cationic, fixing agents, surfactant, leveling, retarding agents, finish, diluents
Disperse	Color, organic acids, carriers, leveling agents, phosphates, lubricants, and dispersants
Reactive	Color, alkali, oxidizing agent, reducing agent, and unfixed dye
Sulfur	Color, alkali, oxidizing agent, reducing agent, and unfixed dye
Vat	Color, alkali, oxidizing agents, and reducing agents

In water reuse technology, various physical, chemical and biological per-treatments and post treatment can be used to treat textile effluent. Physico-chemical techniques including membrane filtration, coagulation, flocculation, precipitation, floatation, adsorption, ion exchange, mineralization, advanced oxidation, electrolysis and chemical reduction are known. Biological treatment systems that can effectively remove dyes from large volumes of wastewater at low cost are preferable alternatives (Robinson et al., 2001). Biological techniques including biosorption and biodegradation in aerobic, anaerobic or combined aerobic/ anaerobic treatment processes with bacteria, fungi, plants, yeasts, algae and enzymes are known (Mohan et al., 2005; Shrivastawa et al., 2005). Textile dye effluents are complexes, containing a wide variety of dyes, natural impurities extracted from the fibers and other products such as acids, alkalis, salts and sometimes heavy metals (Laing, 1991). In general, the effluent is highly colored with high biological oxygen demand (BOD) and chemical oxygen demand (COD), has a high conductivity and is alkaline in nature. For this reason, several factors determine the technical and economic feasibility of each single dye removal technique as the dye type, wastewater composition, dose and costs of required chemicals, operation cost (energy and material), Environmental fate, and handling and cost of generated waste products. Usually the use of one of the individual processes may not be sufficient to obtain complete decolorization because each technique has its limitations. Dye removal strategies consist of therefore, mostly of a combination of different techniques. In choosing types of treatment several factors need to be considered such as type of dye to be treated, composition of wastewater, cost of required chemical, and cost of operation, handling and cost of waste product generated. It is up to the industry to choose which treatment is suitable for the factory.[5)]

Physicochemical methods of textile effluent treatment

Membrane filtration

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; usually used to treat reactive dye bath effluent, because it could potentially reduce waste volume and simultaneously recovering salt (Sen & Demirer, 2003). Moreover, it can be separated in to two or more components from liquid stream by their molecular size. The advantages of membrane filtration are because it is a quick method with low spatial requirement and the saturate can be reused. The disadvantage with the membrane filtration method that it has a limited life time before membrane fouling occurs and the cost is also high.[5)] 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 membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate (Sadrghayeni 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 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 & Chen, 2002; Koyuncu, 2002; Van der 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 & Chen, 2002). [31]. In general, the effluents are reconstituted with only one dye (Tang & Chen, 2002; Koyuncu, 2002; Akbari et al., 2002), and the volume studied is also low. 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; Mietton-Peuchot et al., 1997; Kelly & 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; Cerón-Rivera et al., 2004; Roth & Minke, 1999). Nanofiltration treatment as an alternative has been found to be fairly satisfactory. The technique is also favorable in terms of environmental regulation.

Ultrafiltration enables elimination of macromolecules and particles, but the elimination of polluting substances, such as dyes, is never complete (Watters et al., 1991) - it is only between 31% and 76%. 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. Roth & 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 & Ranieri, 2001) or in combination with a biological reactor (Mignani et al., 1999).

Microfiltration is suitable for treating dye baths containing pigment dyes (Al-Malack & 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).

Coagulation and flocculation of the inorganic coagulants such as, lime, aluminum, magnesium and iron salts have been used for coagulation in the treatment of wastewater to partly removed total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and color over many years (Aguilar et al., 2005). The principle in this process is the addition of a coagulant followed by a general rapid association between the coagulant and the pollutants. Finally they form coagulate or flock and subsequently precipitate. The precipitate is then removed by flotation, settling, filtration or other physical techniques to generate a sludge that is normally further treated to reduce its toxicity (Golob & Ojstrek, 2005; Mishra & Bajpai, 2005). Although these processes effectively eliminate insoluble dyes (Gaehr et al., 1994), its value is doubtful because of the cost of treating the sludge and the increasing number of restriction concerning the disposal of sludge. Organic anionic, cationic or non-ionic coagulant polymers have been developed in the last years for color removal treatments and in general they offer advantages over inorganic: such as lower sludge production, lower toxicity and improved color removal ability (Zouboulis et al., 2004).

Adsorption is the other alternative which is a physico-chemical technique. It is the process by which ions or molecules present in one phase tend to accumulate and concentrate on the surface of another phase. Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are Van der Walls' interactions, hydrogen bonding and dipole-dipole interactions. In the majority of cases, physical adsorption is easily reversible. *Chemical adsorption* occurs when strong interspecies bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorption is deemed to be irreversible in the majority of cases. Suzuki (1997) discussed the role of adsorption in water environmental processes and also evaluated the development of newer adsorbents to modernize the treatment, systems and the role modeling of the findings plays in their development. Most adsorbents are highly porous materials. As the pores are generally very small, the internal surface area is in the order of magnitude greater than the external area. Amongst the numerous techniques of dye removal, this technique gives the paramount results as it can be used to remove different types of coloring materials (Jain et al., 2003). Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants that are not easily biodegradable. Adsorption can produce high quality water while also being a process that is cost-effectively feasible. Decolorization is a result of two mechanisms - adsorption and ion exchange and is influenced by many factors including dye/adsorbent interaction, adsorbent surface area, particle size, temperature, pH and contact time. If the adsorption system is designed correctly, it will produce a high-quality treated effluent.

Activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies.

However, the disadvantage associated with is its high cost (Slokar & Majcen Le Marechal, 1998). The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively inexpensive starting materials is also unjustified for most pollution control applications (Streat et al., 1995). Various carbonaceous materials, such as coal, lignite, coconut shells, wood and peat are used in the production of commercial activated carbons (Bansode et al., 2003). However, the abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Agricultural by products are renewable sources of raw materials for activated carbon production because the development of methods to reuse waste materials is greatly desired (Anuar et al., 2001). Residues from agriculture and agro-industries are the non-product outputs from the growing and processing of raw agricultural products such as rice, corn, beans and peanuts (Tsai et al., 2001). Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to adsorbents, such as activated carbon, represents a possible outlet.

Electrolysis - the electrochemical technique is very efficient to remove the color from a wide variety of dyes and pigments. Biological oxygen demand (BOD) and Chemical oxygen demand (COD) reduction and coagulation of the total suspended solid present in the wastewater are also obtained (Carneiro, 2005). The process is very simple based on applying an electric current through to the wastewater by using sacrificial iron electrode to produce ferrous hydroxide in solution. These sacrificial iron electrodes generate Fe(II) - ion and –OH. The $Fe(OH)_2$ is formed and soluble and insoluble acid dyes are removed from the effluent. Moreover Fe(II) can reduce azo-dyes to aryl amines. Water can also be oxidized resulting in the formation of O_2 and O_3. The efficiency of the electrochemical system in pollutant removal can often reach 90%. However, the process is expensive due to large energy requirements, limited life time of the electrode and uncontrolled radical reactions (Cerón-Rivera et al., 2004).

Ozone is a very powerful and rapid oxidizing agent that can react with most species containing multiple bond (such as C=C, C=N, N=N, etc) and with simple oxidizable ions such as S^{-2}, to form oxyanions such as SO_3^{-2} and SO_4^{-2} (Gogate & Pandit, 2004a). Ozone rapidly decolorizes water-soluble dyes but with non-soluble dyes (Vat and Disperse dyes) react much slower. Furthermore, textile processing wastewater usually contains other refractory constituents that will react with ozone, thereby increasing its demand (Muthukumar et al., 2005). Decomposition of ozone requires high pH value (pH>10). In alkaline solutions ozone reacts almost indiscriminately with all compounds present in the reacting medium (Aksu, 2005; Chu & Ma, 2000), converting organic compounds into smaller and biodegradable molecules (Park et al., 1999). Consequently, after ozone treatment seems logical the use of biological methods for reaching a complete mineralization (Krull et al., 1998; Krull & Hempel, 2001). A major limitation of the ozonation process is the relatively high cost of ozone generation process coupled with its very short half-life (Gogate & Pandit. 2004).

Fenton reagents - the oxidation system based on the Fenton's reagent (hydrogen peroxide in the presence of a ferrous salt) has been used for the treatment of both organic and inorganic substances. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream (Hao et al., 2000). It is accepted that both hydroxyl as well as ferryl complex coexist in Fenton's mechanism and depending on the operating conditions (substrate nature, metal –peroxide ratio etc), one of these will predominate (Bossmann et al., 1998). The oxidation system can be effectively used for the destruction of non-biodegradable toxic waste effluents (Nesheiwat & Swanson, 2000). Fenton oxidation process can decolorize a wide range of dyes and in comparison to ozonation; the process is relatively cheap and results generally in a larger COD reduction (Park et al., 1999). Fenton oxidation is limited to the fact that the textile process wastewaters usually have high pH, while the Fenton process requires low pH. At higher pH, large volumes of waste sludge are generated by the precipitation of ferric iron salts and the process loss its effectiveness.[5)]

Photocatalytic or photochemical degradation processes are gaining importance in the area of wastewater treatment, since these processes result in complete mineralization with operation at mild conditions of temperature and pressure. The photo-activated chemical reaction are characterized by free radical mechanism initiated by the interaction of photons of proper energy levels with the molecules of chemical species present in the solution, with or without the presence of the catalyst (Gogate & Pandit, 2004a). The radical can be easily produced using UV radiation. UV light has been tested in combination with H_2O_2, TiO_2, Fenton reagents, O_3 and other solid catalysts such as for the decolorization of dye solution (Wang et al., 2005). While the UV/H_2O_2 process appeared to be slow, pricey and little effective for potential full-scale application. The combination of UV/TiO_2 seems more promising. With UV/TiO_2 treatment a wide range of dyes can be oxidized and generally not only decolorized but highly mineralized (Freger et al., 2000). Because UV penetration in dye solutions is limited due to the highly colored nature of the effluents, the best use of UV technology is post treatment after ozonation (Vandevivere et al., 1998).

Advanced oxidation process can be used to remove dyes from waste water based on the generation of highly reactive radical (e.g. hydroxide radical) species that can react with wide range of compounds that is difficult to degrade. This process includes chlorination, bleaching, photo catalytic oxidation (Gogate & Pandit, 2004b). Such methods, that use compounds with an oxidation potential (E_O) higher than oxygen (1.23V) as hydrogen peroxide ($E_O = 1.78$V) and hydroxide radical ($E_O = 2.28$V), are often very costly and accumulation of concentrated sludge creates a disposal problems (Robinson et al., 2001a). There is also the possibility that a secondary pollution will arise due to excessive chemical use.

Biological methods

Dyestuffs and polymers are generally difficult to biodegrade and many substances are totally unsuitable for conventional biological treatment. For textiles in particular the emphasis is on physical, chemical and biological treatment systems. Biodegradation method such as fungal decolorization, microbial degradation, and adsorption by living or dead systems is commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae, and fungi are able to accumulate and degrade different pollutants (McMullan et al., 2001), and all biological systems require a continuous input of effluent. Therefore, where the aqueous process discharge is relatively small or likely to be discontinuous, then physical and or chemical treatments are more appropriate (Walker & Weatherly, 1997). Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, the biodegradability of azo dyes is very limited.

Bacterial biodegradation

The ability of bacteria to metabolize azo dyes has been investigated by a number or research groups (McMullan et al., 2001; Cao et al., 1993; Claus et al., 2002; Bhaskar et al., 2003). Under aerobic conditions, azo dyes are not readily metabolized, although the ability of bacteria with specialized reducing enzymes to aerobically degrade certain azo dyes was reported (Stolz, 2001). In contrast, under anaerobic conditions many bacteria reduce azo dyes by the activity of unspecific, soluble, cytoplasmatic reductase, known as azo reductases. The anaerobic reduction degrades the azo dyes that are converted into aromatic amines (Blümel et al., 2002), which may be toxic, mutagenic, and possibly carcinogenic to mammalians Pinheiro et al., 2004). Therefore, to achieve complete degradation of azo dyes, another stage that involves aerobic biodegradation of the produced aromatic amines is necessary (Haug et al., 1991; Libra et al., 2004; Sponza & Isik, 2005).

Bacterial biodegradation of non-azo dyes has only recently been studied. It has been observed that several bacteria can degrade anthraquinone dyes (Robinson et al., 2001a). Aerobic decolorization of triphenylmethane dyes has also been demonstrated (Sani & Banerjee, 1999). In phtalocyanine dyes, reversible reduction and decolorization under anaerobic conditions have been observed.[5)]

Fungal biodegradation

The most widely researched fungi in regard to dye degradation are the ligninolytic fungi. White-rot fungi in particular produced enzymes as lignin peroxidase, manganese peroxidase and laccase that degrade many aromatic compounds due to their non-specific activity (Toh et al., 2003). Large literature exists regarding the potential of these fungi to oxidize phenolic, non-phenolic, soluble and non-soluble dyes (Libra et al., 2004). In particular laccase from *Pleurotus ostreatus, Schizophyllum commune, Sclerotium rolfsii* and *Neurospora crassa*, seemed to increase up to 25% the degree of decolorization of individual commercial triarylmethane, anthraquinonic, and indigoid textile dyes using enzyme preparations (Abadula et al., 2000). On the contrary, manganese peroxidase was reported as the main enzyme involved in dye decolorization by *Phanerochaete chrysosporium* (Chagas & Durrant, 2001), and lignin peroxidase for *Bjerkandera adusta* (Robinson et al., 2001). Some non-white-rot fungi that can fruitfully decolorize dyes have also been reported (Tetsch et al., 2005). Fungal degradation of aromatic structures is a secondary metabolic event that starts when nutrients (C, N and S) become limiting (Kirk & Farrell, 1987). The influence of the substitution pattern on the dye mineralization rates and between dye structure and fungal dye biodegradability is a matter of controversy (Fu & Viraraghavan, 2002). However, these difficulties are even greater if one considers that complex mixed effluents are extremely variable in composition even from the same factory, as is often the case of the textile industry. Other important factors for cultivation of white-rot fungi and expression of ligninolytic activity are the availability of enzyme cofactors and the pH of the environment (Swamy & Ramsay, 1999).

Although stable operation of continuous fungal bioreactors for the treatment of synthetic dye solutions has been achieved, application of white-rot fungi for the removal of dyes from textile wastewater faces many problems as the nature of synthetic dyes, the control of the produced biomass and the great treating volumes (Mielgo et al., 2001).

Conclusion

This article provides a critical review on the current technologies available for decolouration as well as treatment of textile effluents and it suggests effective and economically attractive alternatives. Textile wastewater treatment before discharging is of great importance in decreasing pollution load and production costs. Conventional technologies to treat textile wastewater include various combinations of biological, physical, and chemical methods, but these methods require high capital and operating costs. Up to now there is no single and economically attractive treatment that can effectively decolourise dyes effluents. In the past years, notable achievements were made in the use of biotechnological applications to textile effluents not only for color removal but also for the complete degradation of dyes. Different microorganisms, such as, aerobic and anaerobic bacteria, fungi and physicochemical methods have been found to catalyse dye decolouration. As compared to physicochemical, biological treatment systems that can efficiently remove dyes from large volumes of wastewater at low cost are preferable alternatives.

APPENDIX

Advantages and disadvantages of some of the physicochemical methods of textile effluent treatment

Processes	Advantages	Disadvantages	References
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Aguilar et al., 2005; Golob & Ojstrsek, 2005
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Slokar & Majcen Le Marechal, 1998
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge	Carneiro et al., 2005
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Sadrghayeni et al., 1998; Treffry-Goatley et al., 1983; Tinghui et al., 1983
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	-------------	Chakraborty et al., 2003
Ultrafiltration–microfiltration	Low pressure	Insufficient quality of the treated wastewater	Sadrghayeni et al., 1998; Watters et al., 1991
Fenton's reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge production	Hao et al., 2000; Nesheiwat & Swanson, 2000
Ozonation	Applied in gaseous state: no alteration of volume	Short half–life (20 min) of O_3	Muthukumar et al., 2005; Aplin & Wait, 2000
Photochemical	No sludge production	Formation of by-products	Gogate & Pandit, 2004; Forgacs et al., 2004
NaOCl	Initiates and accelerates azo bond cleavage	Release of aromatic amines	Robinson et al., 2001

Electrochemical destruction	Breakdown compound are non-hazardous	High cost of electricity	Muthukumar et al., 2005; Aplin & Wait, 2000

Advantages and disadvantages of some of the biological methods of textile effluent treatment

Organism (process)	Advantages	Disadvantages	References
Bacteria (aerobic)	-decolorize both azo and anthraquinone dyes, -production of biogas	-low decolorization rates, -requires specific oxygen catalyzed enzymes, -requires additional carbon and energy sources	Stolz, 2001
Bacteria (anaerobic)	-suitable for large scale application, -takes place at neutral pH for sludge treatment system, -allows obligate and facultative bacteria to reduce azo dyes	-generation of toxic substance, -requires post treatment, -immobilization and recovery of redox mediator presents a challenge	Blumel et al., 2002; Pinheiro et al., 2004
Fungi	-decolorize anthraquinone and indigo-based dyes at higher rates	-decolorization rate is very low for azo dyes, -requires especial bioreactor and external carbon source, -needs acidic pH (4.5-5), -inhibition by mixture of dyes and chemical in textile effluents	Libra et al., 2004; Toh et al., 2003

NOTES

1. http://scholar.lib.vt.edu/theses/available/etd-07232001-225716/unrestricted/ThesisMasterDocument.PDF
2. Provisional standards for industrial pollution control in Ethiopia: a draft, 2003.
3. http://eprints.ru.ac.za/869/1/Mutambanengwe-TR07-30.pdf
4. http://library.wur.nl/WebQuery/edepot/121632
5. http://library.wur.nl/WebQuery/edepot/121282
6. Maarit, H., Ollikka, P. & Suominen, I. (2000). Decolurasition of azo dye crocerien orange by phanerochate chrysosporium ligning peroxidases. University of Jyvaskyl, Finland.

REFERENCES

Abadulla, E., Tzanov, T., Costa, S., Robra, K.H., Cavaco-Paulo, A. & Gübitz, G.M. (2000). Decolourization and detoxification of textile dyes with laccase from *Trametes hirsute. Appl. & Environ. Microbiology, 66,* 3357-3362.

Aguilar, M.I., Sáez, J., Lloréns, M., Soler, A., Ortuno, J.F., Meseguer, V. & Fuentes, A. (2005). Improvement of coagulation-flocculation process using anionic polyacryl amide as coagulant aid. *Chemosphere, 58,* 47-56.

Akbari, A., Remigy, J.C. & Aptel, P. (2002). Treatment of textile dye effluent using a polyamide-based nanofiltration membrane. *Chemical Engineering & Processing: Process Intensification, 41,* 601-609.

Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry, 40,* 997-1026.

Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J. & Ahmed, M.N. (2003). The removal of dyes from textile wastewater: a study of Physical characteristics and adsorption mechanisms of diatomaceous earth. *J. Environ. Management, 69,* 229-238.

Al-Malack, M.H. & Anderson, G.K. (1997). Use of cross flow microfiltration in wastewater treatment. *Water Research, 31,* 3064-3072.

Alinsafi, A., Khemis, M., Pons, M.N., Leclerc, J.P., Yaacoubi, A., Benthammou, A. & Nejmeddine, A. (2005). Electro-coagulation of reactive textile dyes and textile wastewater. *Chemical Engineering & Processing: Process Intensification, 44,* 461-470.

Allegre, C., Mouline, P., Maissey, M. & Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. *J. Membrane Sci., 269,* 15-34.

Allen, R.L.M. (1971). *Color chemistry.* London: Pitman Press.

Andrady, A.L. (2003). *Plastic and the environment.* New Yourk: Wiley Interscience.

Anuar, K., Joseph, C.J., Ahmad, F.B.H., Zulkarnian, Z., Hussein, Z.M. & Abdullah, H.A. (2001). Preparation and characterization of activated carbon from Resak wood. *Res.. J. Chemistry & Environment, 5*(3), 21-24.

Aplin, R. & Wait, T.D. (2000). Comparison of three advanced oxidation processes for degradation of textile dyes. *Water Science & Technology, 42,* 345-354.

Asamudo, N.U., Daba, A.S. & Ezeronyel, O.U. (2005). Bioremediation of textile effluent using *Phanerochaete chrysosporium*. *African J. Biotechnology, 4,* 1548-1553.

Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M. & Portier, R.J. (2003). Adsorption of metal ions by pecan shell-based granular activated carbons. *Bioresource Technology, 89,* 115-119.

Bhaskar, M., Granamani, A., Ganeshjeevan, R.J., Chandresekar, R., Sadulla, S. & Radhakrishnan, G. (2003). Analysis of carcinogenic aromatic amines released from harmfull azo colorants by *Streptomyces* SP.SS07. *J. Chromatography A, 1018,* 117-123.

Blümel, S., Knackmuss, H.-J. & Stolz, A. (2002). Molecular cloning and characterization of the gene coding for the aerobic azoreductase from *Xenophilus azovorans* KF46F. *Appl. & Environ. Microbiology, 68,* 3948-3955.

Bossmann, S.H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E.P., Payawan, Jr., L., Straub, M., Wörner, M. & Braun, A.M. (1998). New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. *J. Phys. Chem. A, 102,* 5542-5550.

Cao, W., Mahadevan, B., Crawford, D.L. & Crawford, R.L. (1993). Characterization of an extracellular azo dye-oxidizing peroxidase from *Flavobacterium sp.* ATCC 39723. *Enzyme & Microbial Technology, 15,* 810-817.

Carneiro, P.A., Osugi, M.E., Fugivara, C.S., Boralle, N., Furlan, M. & B. Zanoni, M.V. (2005). Evaluation of different electrochemical methods on the oxidation and degradation of Reactive Blue 4 in aqueous solution. *Chemosphere, 59,* 431-439.

Cerón-Rivera, M., Dávila-Jiménez, M.M. & Elizalde-González, M.P. (2004). Degradation of the textile dyes Basic yellow 28 and Reactive black 5 using diamond and metal alloys electrodes. *Chemosphere, 55*, 1-10.

Chagas, E.P. & Durrant, L.R. (2001). Decolorization of azo dyes by *Phanerochaete chrysosporium* and *Pleurotus sajorcaju. Enzyme & Microbial Technology, 29,* 473-477.

Chakraborty, S., Purkait, M.K., DasGupta, S., De, S. & Basu, J.K. (2003). Nanofiltration of textile plant effluent for color removal and reduction in COD. *Separation & Purification Technology, 31,* 141-151.

Chavan, R.B. (2001). Environment-friendly dyeing processing for cotton. *Indian J. Fibre & Textile Res., 4,* 239-242.

Chu, W. & Ma, C.-W. (2000). Quantitative prediction of direct and indirect dye ozonation kinetics. *Water Research, 34,* 3153-3160.

Ciardelli, G. & Ranieri, N. (2001). The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. *Water Research, 35,* 567-572.

Claus, H., Faber, G. & König, H. (2002). Redox-mediated decolorization of synthetic dyes by fungal laccases. *Appl. Microbiology & Biotechnology, 59,* 672-678.

Erswell, A., Brouchaert, C,J. & Buckley, C.A. (1988). The reuse of reactive dye liquors using charges ultrafiltration membrane technology. *Desalination, 70,* 157-167.

Forgacs, E., Cserhati, T. & Oros, G. (2004). Removal of synthetic dyes from wastewaters: e review. *Environment International, 30,* 953-971.

Freger, V., Arnot, T.C. & Howell, J.A. (2000). Separation of concentrated organic/inorganic salt mixtures by nanofiltration. *J. Membrane Sci., 178,* 185-193.

Fu, Y. & Viraraghavan, T. (2002). Dye biosotption sites in *Aspergillus niger. Bioresource Technology, 82,* 139-145.

Gaehr, F., Hermanutz, F. & Oppermann, W. (1994). Ozonation an important technique to comply with new German laws for textile wastewater treatment. *Water Science & Technology, 30,* 255-263.

Golob, V. & Ojstršek, A. (2005). Removal of vat and disperse dyes from residual pad liquors. *Dyes & Pigments, 64,* 57-61.

Gogate, P.R. & Pandit, A.B. (2004a). Reviews of imperative technologies for wastewater treatment. I: oxidation technologies at ambient conditions. *Adv. Environ. Res., 8,* 501-551.

Gogate, P.R. & Pandit, A.B. (2004b). A review of imperative technologies for wastewater treatment. II: hybrid methods. *Adv. Environ. Res., 8,* 553-597.

Hao, O., Kim, H. & Chiang, P.-C. (2000). Decolorization of wastewater. *Crit. Rev. Environ. Sci. & Technol., 30,* 449-505.

Haug, W., Schmidt, A., Nörtemann, B., Hempel, D.C., Stolz, A. & Knackmuss, H.J. (1991). Mineralization of the sulfonated azo dye Mordant Yellow 3 by a 6-aminonaphtalene-2-sulfonate-degrading bacterial consortium. *Appl. Environ. Microbiol., 57,* 3144-3149.

Jain, A.K., Gupta, V.K. & Bhatnagar, A. (2003). Utilization of adsorption techniques for removal of dyes. *J. Hazard. Mater., 101,* 31-42.

Jiraratananon, R., Sungpet, A. & Luangsowan, P. (2000). Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt. *Desalination, 130,* 177-183.

Karim, M.M., Dasa, A.K. & Lee, S.H. (2006). Treatment of colored effluents of the textile industry in Bangladesh using zinc chloride treated indigenous activated carbons. *Analytica Chimica Acta, 576,* 37-42.

Kelly, J. & Kelly, P. (1995). Nanofiltration of whey: quality, environmental and economic aspects. *Intern. J. Dairy Technology, 48,* 20-24.

Kirk, T.K. & Farrell, R.L. (1987). Enzymatic "combustion." The microbial degradation of lignin. *Ann. Rev. Microbiol., 41,* 465-505.

Knauf, R., Meyer-Blumenroth, U. & Semel, J. (1998). Einsatz von Membrantrennverfahren in der chemischen Industrie. *Chemie Ingenieur Technik, 70,* 1265-1270.

Koyuncu, I. (2002). Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dye: effects of feed concentration and cross flow velocity. *Desalination, 143,* 243-253.

Krull, R., Hemmi, M., Otto, P. & Hempel, D.C. (1998). Combined biological and chemical treatment of highly concentrated residual dyehouse liquors. *Water Science & Technology, 38,* 339-346.

Krull, R. & Hempel, D.C. (2001). Treatment of dyehouse liquors in a biological sequencing batch reactor with recursive chemical oxidation. *Water Science & Technology, 44,* 85-92.

Laing, I.G. (1991). The impact of effluent regulations on the dyeing industry. *Review Progress Coloration & Related Topics. 21,* 56-71.

Libra, A.J., Borchert, M., Vigelahn, L. & Storm, T. (2004). Two stage biological treatment of a diazo reactive textile dye and the fate of the dye metabolites. *Chemosphere, 56,* 167-180.

Machenbach, I. (1998). Membrane technology for dyehouse effluent treatment. *Membrane Technology, 96,* 7-10.

McMullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., Banat, I.M., Marchant, R. & Smyth, W.F. (2001). Microbial decolourization and degradation of textile dyes. *Appl. Microbiology & Biotechnology, 56,* 81-87.

Mielgo, I., Moreira, M.T., Feijoo, G. & Lema, J.M. (2001). A packed-bed fungal bioreactor for the continuous decolourisation of azo-dyes (Orange II). *J. Biotechnology, 89,* 99-106.

Mietton-Peuchot, M., Peuchot, C. & Courtois, T. (1997). Nanofiltration d'effluents industriels. *L'eau, l'industrie, les nuisances, 201,* 26-30.

Mignani, M., Nosenzo, G. & Gualdi, A. (1999). Innovative ultrafiltration for wastewater reuse. *Desalination, 124,* 287-292.

Mishra, A. & Bajpai, M. (2005). Floccolation behaviour of model textile wastewater trated with a food grade polysaccharide. *J. Hazard. Mater., 118,* 213-217.

Mohan, S.V., Prasad, K.K., Rao, N.C. & Sharma, P.N. (2005). Acid azo degradation by free and immobilized horseradish peroxidase (HRP) catalyzed process. *Chemosphere, 58,* 1097-1105.

Muthukumar, M., Sargunamani, D., Senthilkumar, M. & Selvakumai, N. (2005). Studies on decolouration, toxity and the possibility for recycling of acid dye effluents using ozone treatment. *Dyes & Pigments, 64,* 39-44.

Nesheiwat, F.K. & Swanson, A.G. (2000). Clean contaminated sites using Fenton's reagent. *Chemical Engineering Progress, 96,* 61-66.

Pala, A., Tokat, E. & Erkaya, H. (2003). Removal of some reactive dyes from textile processing using powdered activated carbon. *Intern. J. Chem. Eng., 2003,* 114-122.

Park, T.J., Lee, K.H., Jung, E.J. & Kim, C.W. (1999). Removal of refractory organics and color in pigment wastewater with Fenton oxidation. *Water Science & Technology, 39,* 189-192.

Pinheiro, H.M., Tourand, E. & Thomas, O. (2004). Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. *Dyes & Pigments, 61,* 121-139.

Robinson, T., Chandran, B. & Nigam, P. (2001a). Studies on the production of enzymes by white-rot fungi for the decolorization of textile dyes. *Enzyme & Microbial Technology, 29,* 575-579.

Robinson, T., McMullan, G., Marchant, R. & Nigam, P. (1997). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Colourage, 46,* 247-255.

Robinson, T., McMullan, G., Marchant, R. & Nigam, P. (2001b). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology, 77,* 247-255.

Rossignol, N., Jaouen, P., Robert, J.-M. & Quéméneur, F. (2000). Production of exocellular pigment by the marine diatom *Haslea ostrearia* Simonsen in a photobioreactor equipped with immersed ultrafiltration membranes. *Bioresource Technology, 73,* 197-200.

Roth, U. & Minke, R. (1999). Overview of wastewater treatment and recycling in the textile processing industry. *Water Science & Technology, 40,* 137-144.

Sadrghayeni, S., Beatson, P., Schneider, R. & Fane, A. (1998). Water reclamation from municipal wastewater using combined microfiltration-reverse osmosis (ME-RO): preliminary performance data and microbiological aspects of system operation. *Desalination, 116,* 65-80.

Sani, R.K. & Banerjee, U.C. (1999). Decolorization of triphenylmethane dyes and textile and dye-stuff effluent by *Kurthia sp. Enzyme & Microbial Technology, 24,* 433-437

Sen, S. & Demirer, G.N. (2003). Anaerobic treatment of synthetic textile wastewater containing a reactive azo dye. *J. Environ. Eng., 129,* 595-601.

Shrivastava, R., Christian, V. & Vyas, B.R.M. (2005). Enzymatic decolorization of sulfonphatelein dyes. *Enzyme & Microbial Technology, 36,* 333-337.

Slokar, Y.M. & Majcen Le Marechal, A. (1998). Methods of decoloration of textile wastewater. *Dyes & Pigments, 37,* 335-356.

Sponza, D. & Isik, M. (2005). Reactor performances and fate of aromatic amines through decolorization of Direct Black 38 dye under anaerobic/aerobic sequentials. *Process Biochemistry, 40,* 35-44.

Stolz, A. (2001). Basic and applied aspects in the microbial degradation of azo dyes. *Appl. Microbiology & Biotechnology, 56,* 69-80.

Streat, M., Patrick, J.W. & Camporro Perez, M.J. (1995). Sorption of phenol and parachlorphenol from water using conventional and novel activated carbons. *Water Research, 29,* 467-472.

Sule, A.D. & Bardhan, M.K. (1999). Objective evaluation of feel and handle, appearance and tailorability of fabrics. Part II: the KES-FB system of Kawabata. *Colourage, 46,* 23-35.

Suzuki, M. (1997). Role of adsorption in water environment processes. *Water Science & Technology, 35*(7), 1-11.

Swamy, J. & Ramsay, J.A. (1999). The evaluation of white rot fungi in the decoloration of textile dyes. *Enzyme & Microbial Technology, 24,* 130-137.

Tang, C. & Chen, V. (2002). Nanofiltration of textile wastewater for water reuse. *Desalination, 143,* 11-20.

Tetsch, L., Bend, J., Janssen, M. & Hölker, U. (2005). Evidence for functional laccases in the acidophilic ascomycete *Hortaea acidophila* and isolation of laccase-specific gene fragments. *FEMS Microbiology Lett., 245*, 161-168.

Tinghui, L., Matsuura, T. & Sourirajan, S. (1983). Effect of membrane materials and average pore sizes on reverse osmosis separation of dyes. *Ind. & Eng. Chem. Prod. Res. & Development, 22,* 77-85.

Toh, Y.C., Yen, J.J.L., Obbard, J.P. & Ting, Y.P. (2003). Decolourization of azo dyes by white-rot fungi (WRF) isolated in Singapore. *Enzyme & Microbial Technology, 33*, 569-575.

Treffry-Goatley, K., Buckley, C.A. & Groves, G.R. (1983). Reverse osmosis treatment and reuse of textile dyehouse effluents. *Desalination, 47,* 313-320.

Tsai, W.T., Chang, C.Y., Wang, S.Y., Chang, C.F., Chien, S,F. & Sun, H.F. (2001). Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob. *Resources, Conservation & Recycling, 32,* 43-55.

Vandevivere, P.C., Bianchi, R. & Verstaete, W. (1998). Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *J. Chem. Technology & Biotechnology, 72,* 289-302.

Van der Bruggen, V.B., Daems, B., Wilms, D. & Vandecasteele, P. (2001). Mechanisms of Retention and flux decline for the nanofiltration of dye baths from the textile industry. *Separation & Purification Technology, 22,* 519-528.

Walker, G.M. & Weatherly, L.R. (1997). Adsorption of acid dyes onto granular activated carbon in fixed beds. *J. Water Res., 31,* 2093-2101.

Wang, C.-J., Thiele, S. & Bollag, J.-M. (2005). Interaction of 2,4,6-trinitrotoluene (TNT) and 4-amino-2,6-dinitrotoluene with humic monomers in the presence of oxidative enzymes. *Archives Environ. Contamination & Toxicology, 42,* 1-8.

Waranusantigul, P., Pokethtitiyook, P., Kruatrachue, M. & Upatham, E.S. (2003). Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spiraodela polyrrhiza*). *Environ. Pollution, 125,* 385-392.

Watters, J.C., Biagtan, E. & Senler, O. (1991). Ultrafiltration of a textile plant effluent. *Separation Science & Technology, 26,* 1295-1313.

Weber, E.J. & Stickney, V.C. (1993). Hydrolysis kinetics of Reactive Blue 19-vinyl sulfone. *Water Research, 27,* 63-37.

Wu, Z., Joo, H., Ahn, I.-S., Haam, S., Kim, J.-H. & Lee, K. (2004). Organic dye adsorption on mesoporous hybrid gels. *Chemical Engineering J., 102,* 277-282.

Xu, Y., Lebrun, R.E., Gallo, P.-J. & Blond, P. (1999). Treatment of textile dye plant effluent by nanofiltration membrane. *Separation & Purification Technology, 34,* 2501-2519.

Zouboulis, A.I., Chai, X.-L. & Katsoyiannis, I.A. (2004). The application of bioflocculant for the removal of humic acids from stabilized landfill leachates. *J. Environ. Management, 70,* 35-41.

✉ **Mr. Bizuneh Adinew**
Department of Chemistry,
Mizan-Tepi University
P.O. Box No. 121,
Tepi, Ethiopia
E-mail: buzeadinew@gmail.com