Textile Wastewater Treatment Options: A Critical Review

Khadija Siddique, Muhammad Rizwan, Munazzam Jawad Shahid, Shafaqat Ali, Rehan Ahmad, and Hina Rizvi

Abstract Textile industry is one of the largest water-consuming industries in the world, and its wastewater contains many pollutants such as dyes, degradable organics, detergents, stabilizing agents, desizers, inorganic salts, and heavy metals. In Pakistan, most of the textile industries discharge untreated wastewater into water bodies without any treatment, which percolates into the groundwater posing a threat to the health and socioeconomic life of the people. Pretreatment, dyeing, printing, and finishing are the main steps in dyeing and printing process of textile industries. A large amount of wastewater is being generated by all these processes, which contains many pollutants like reactive dyes, chemicals, high chemical oxygen demand (COD), biological oxygen demand (BOD), and organic compounds. Research has been conducted since long to treat textile wastewater in an economical and efficient way. There are many processes for removal of polluted compounds from water that include physicochemical, biological, combined treatment processes, and other technologies. All over the world, ecological standards are gaining importance in every step of textile unit. Due to the strict implementation of environmental standards, it is important to adopt an eco-friendly model of textile industry that overcomes all flaws from its start to end product. The main challenge is to develop a design that can be considered as cost-effective and to substitute chemicals that are less harmful or can be easily treated. On the basis of wastewater characteristics and literature review, appropriate scheme of treatment processes was proposed.

Keywords Textile wastewater • Treatment • Toxicity • Chemicals • Pollution

Textile Industry Wastewater: Challenges

The increasing population in Pakistan is requiring economic growth so the industrial progress has been stirred up to meet the demands of growing population. On the other hand, the regulatory measures are being neglected from the very

K. Siddique • M. Rizwan • M.J. Shahid • S. Ali (✉) • R. Ahmad • H. Rizvi
Department of Environmental Sciences and Engineering, Government College University, Allama Iqbal Road, Faisalabad 38000, Pakistan
e-mail: shafaqataligill@yahoo.com

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first, and the situation is getting worse as the implementation policy for control measures is being neglected (Husain and Hussain 2012). The textile sector is playing an important role in Pakistan's economy as it is providing employment to 38% of people; along with, it is an important source of foreign exchange. Out of the total export, 65% of country export is provided by the textile sector alone (Bauer 2001). In all over the country, many industries are working and strengthening the economy by their production; out of this total production, textile industry accounts for 46%. Some of the industrial products are also exported to foreign countries; textile products are also exported and provide 9% of gross national product (GNP) (Sudipta et al. 2005). Keeping in view, all these facts, we can say that textile industry is the backbone of Pakistan economy. The textile sector is based on 670 industries that are working in all over the country. Out of this 670, 300 are situated in Karachi alone, and the remaining 370 are working in different areas of Punjab (Ara 1998).

It has been published in the yearbook of China that 390 million tons of sewage water is producing each year in China. Out of these 390 million tons, 51% is produced by industrial sector, and this rate is increased by 1% each year (Ho and McKay 2003). According to a rough estimate, the textile sector has a major contribution toward 51% of the sewage wastewater as 70 billion tons per year of wastewater is coming out of dyeing industries alone. This wastewater has heavy pollution load, and it is ridiculous to discharge this water without any prior treatment. As compared to agricultural use, the industrial use of water is very little. The heavy pollution load in wastewater makes water resources unfit for other uses. In water-scarce countries like Pakistan, the reuse of water is a constant demand because an extensive amount of water is needed for agricultural activities. Therefore, water management is a challenge for us as freshwater resources are decreasing rapidly and water is getting polluted with industrial activities (Anindya et al. 2005).

Textile industry is one of the biggest industries in the world, and a large amount of water is consumed in its processing. Different stages of textile industry are named as singeing, desizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing. All textile industries use these processes according to their requirement (El-Gohary and Tawfik 2009). The environmental problems created by textile industry wastewater are due to increased oxygen demand, high color, and large amount of suspended solids. Wastewater of textile unit contains many pollutants, like inorganic compounds, dye waste, color residues, catalytic chemicals, and cleaning solvents (USEPA 1997). It has been studied that in all over the world, overall production of dyes is 700,000 tons each year (Riera-Torres et al. 2010). There are different combinations of dyes that are being used to color different stuffs. Some of these dyes are degraded naturally, but some need special treatment, as they can't be degraded naturally. There are different types of dyes that are chemically different from each other. These dyes include azo dyes, xanthene dyes, nitro dyes, phthalocyanine dyes, etc. (Gupta and Suhas 2009). Dyes can be further classified as acid dyes, basic dyes, and reactive dyes. The combination of different dyes used to achieve different shades makes the treatment process more difficult as each dye has different chemical natures (Andre et al. 2005). It is believed that all over the world, more than one million tons of dyes are manufactured each year and out of this, 0.28 million tons are discharged into wastewater (Robert and Sanjeev 2005). Textile industry wastewater especially from dyeing and printing industries needs proper treatment before its discharge in water bodies as major contribution of the largest amount of textile wastewater is from the developing countries. In textile processing industry, wastewater contains many pollutants and needs to be treated as they can cause serious health impacts to aquatic life as well as human beings (Lau and Ismail 2009). Therefore, it is an utmost need to treat textile wastewater so that problems related to pollution caused by it can be avoided.

Pretreatment, dyeing, printing, and finishing are the main steps in dyeing and printing process of textile industries. A large amount of wastewater is being generated by all these processes, which contains many pollutants like reactive dyes, chemicals, high chemical oxygen demand (COD), biological oxygen demand (BOD), and organic compounds (El-Gohary and Tawfik 2009). Research has been conducted since long to treat textile wastewater in an economical and efficient way. There are many processes for removal of polluted compounds from water that include physicochemical, biological, and combined treatment processes and other technologies (Phan et al. 2000). There are many sulfide compounds used in textile industry that are environmental concerns because of their hazardous nature. So, a combination of biological and chemical methods is being reviewed for sulfur treatment (Nguyen and Juang 2013). All over the world, ecological standards are gaining importance in every step of textile unit. Due to the strict implementation of environmental standards, it is important to adopt an eco-friendly model of textile industry that overcomes all flaws from its start to end product (Robinson et al. 1997).

The main challenge is to develop a design that can be considered as cost-effective and to substitute chemicals that are less harmful or can be easily treated. Recycling can be a preferred option in this regard as it can solve two problems. First of all, recycling means less generation of waste. Secondly, it is economically beneficial to develop techniques to use recycled products. Control techniques can be divided into three types: (1) an efficient design using less polluting agents and minimizing waste generation; (2) after generation of waste, an effective treatment option for this wastewater; and (3) finding suitable steps where recycled products can be applied (Sule and Bardhan 1999). Dyeing and finishing processes in textile industry are major threats as they are using large quantities of chemicals and dyeing agents that cannot be treated easily (Mustafa and Delia 2006). Organic nature of these chemicals makes the problem serious as they have complex structure. Heavy metals are another concern.

Main Steps in Textile Processing Industry

The main processes of a textile industry include singeing, desizing, scouring bleaching, mercerizing, dyeing, printing, finishing, and marketing. Textile wastewater includes (a) suspended solids, (b) mineral oils, (c) nonrecyclable or low recyclable surfactants, (d) wet-finishing process that produces phenols (e.g., dyeing), (e) halogenated organics produced in bleaching that is using solvents, and (f) textile effluents that are usually hot and highly colored and may have heavy metals (e.g., chromium, copper, zinc).

Treatment Options

Textile wastewater handling is a blend of different methods. The principal phase comprises typically of physical steps. Physicochemical methods have been extensively used in textile treatment plants, which give good removal efficiency of suspended materials, but it is not as much effective to remove COD. Various textile wastewater approaches are given below.

Physical Methods of Decoloration

Equalization and Homogenization

Textile dyeing wastewater usually needs pre-handling to ensure uniform flow of water for steady operation. Generally, the flexible container is fixed to handle the wastewater. Meanwhile, to avoid the cotton fur and the slurry settle in depth, air is used in the container for mixing. Eight hours of retention time is usually required.

Floatation

Floatation is a triple-phase combination of water, gas, and solid. In this process, air under pressure is introduced that combines with particles in the form of bubbles. This mixture settled down due to its lower density, and the heavy material separated out due to higher density. It can successfully eliminate the fibers from textile wastewater.

Adsorption

Some organic dyes are not easily biodegradable because of their structure. They have long chain of carbon, which causes a limitation, and they are resistant to degrade in normal biotic conditions. Treatment of such organic dyes is important, and it demands best knowledge of abiotic conditions to degrade such compounds. Adsorption is the greatest applied technique in wastewater management that can mix the wastewater and the spongy material powder or granules, such as carbon and clay, or allows the wastewater to pass through the sieve bed made up of granular matter. Through this technique, contaminants in the wastewater are adsorbed on the surface of the spongy material or sieve.

Adsorption is said to be a feasible abiotic condition to treat such organic waste. It is important to have an idea about the conditions affecting adsorption capabilities of such compounds, which may depend on water hardness, time of treatment, and many other factors. Sludge of adsorption process is an important component so it is necessary to develop better understanding about the treatment process and sludge quality (Ozcan et al. 2004). It has been suggested that there should be 3 g per liter of sludge, and minimum time of reaction should be 24 h and 6 days for maximum. The maximum time limit is rarely needed because most of the dyes require 1-day treatment only. Hardness of water should be 80 mg per liter, which gives best removal. The removal efficiency of dyes from this process is considered to be 1 g per liter to 30 mg per liter. The concept of activated sludge treatment gives tremendous improvement in treatment process. There are various materials used as adsorbents in sludge treatment such as charcoals, activated carbons, clays, soils, and coagulants (Silva et al. 2004). Some information about molecule size and charge on dye, its pH, and salt complex is important because adsorption process is not that simple but it's a combination of adsorption and ion exchange process. Although there is a vast variety of adsorbent available in the market, not all are appropriate for commercial use. Price, ease to handle the adsorbent, and binding capacity are parameters which should be kept in mind while applying them in treatment processes for commercial use. Lignocellulose is one of the effective adsorbents, which is used on a large scale because it is not costly and effective against acid dyes (Pignon et al. 2000). Adsorption is a time-consuming process, and sludge produced by this process may not be easy to handle which is the main drawback of this process.

Low-Cost Adsorbents

The nonconventional low-cost adsorbent should have some specific properties in order to be used as dye adsorption. Those properties can be (a) efficient to remove an extensive variety of dyes, (b) high rate of adsorption and capacity, (c) high ability to tolerate extensive range of wastewater parameters, and (d) highly selective for different concentrations.

Natural Materials

Clays

Natural clay minerals have grabbed the attention of mankind since the civilization time. Clay materials are famous as adsorbents due to their low cost, ease of availability in most of the world continents, high potential for ion exchange, and sorption properties. The clay materials have a layered structure and mostly favorable as host materials. The classification of clay materials is based on the differences in the layered structures such as mica (illite), smectites (saponite, montmorillonite), serpentine, pyrophyllite (talc), kaolinite, vermiculite, and sepiolite (Shichi and Takagi 2000). The natural clay shows adsorption capabilities due to a net negative charge on the mineral structure. The negative charge of clay minerals attracts the positive-charged species, and so adsorption takes place. The sorption properties depend on the high porosity and high surface area (Alkan et al. 2004). Montmorillonite clay possesses the largest surface area and highest capacity for cation exchange. The current market price of montmorillonite clay is about US$ 0.04–0.12/kg and is considered as 20 times cheaper than the activated carbon (Babel and Kurniawan 2003). The clay minerals such as kaolinite, bentonite, diatomite, and Fuller's earth are now becoming popular to be used in recent years due to their unique adsorption capacity for organic and inorganic molecules. Different scholars have extensively studied the interactions between the dyes and clay particles reported in articles (Alkan et al. 2005, 2004; Gu¨rses et al. 2004; Wang et al. 2004; Al-Bastaki and Banat 2004; Ozcan et al. 2004; Ozdemir et al. 2004; Al-Ghouti et al. 2003; Atun et al. 2003).

Siliceous Materials

Natural siliceous sorbents such as glasses, alunite, silica beads, perlite, and dolomite are becoming popular to be used for wastewater due to their abundance, low price, and availability. The most prominent in inorganic materials are the silica beads (Crini and Morcellet 2002; Woolard et al. 2002; Harris et al. 2001; Phan et al. 2000), having silanol groups on the hydrophilic surface responsible for the chemical reactivity. Their porous texture, mechanical stability, and high surface area are the key factors, which make them suitable as sorbents in decontamination applications. The presence of acidic silanol on the siliceous material surface causes an irreversible and strong nonspecific adsorption. So the negative features of sorbents should be eliminated. The interaction of siliceous materials with dyes can be promoted by modifying the silica surface using silane-coupling agents having amino functional group (Krysztafkiewicz et al. 2002). Another important sorbent from siliceous materials is alunite (Dill 2001). Alunite mineral comes from the jarosite group and consists of approximately 50% SiO_2. The characteristics of alunite are discussed in the review by Dill in 2001. The untreated alunite does not show good adsorbent properties (Ozacar and Sengil 2003). In order to use alunite as good adsorbent for removing colors, a suitable process is done to obtain alunite-type layered structure (Ozacar and Sengil 2002).

Zeolites

Zeolites are the highly porous aluminosilicates having different cavity structures. Zeolites are extensively used as substitute materials in particular areas such as sorptive applications. Zeolites are useful in removing the trace amounts of pollutants, e.g., phenols and heavy metal ions due to their cage-like structures appropriate for ion exchange. A lot of the literature is available on sorbent behavior of the neutral zeolites (Ozdemir et al. 2004; Armagan et al. 2004; Meshko et al. 2001). The zeolite efficiency to remove dyes may not be better than clay materials, but the easy access, availability and low cost make them suitable for many applications (Calzaferri et al. 2000).

Biosorbents

Chitin and Chitosan

The emerging biosorption method uses biopolymers such as chitin and chitosan for sorption of dyes. Chitin and chitosan are renewable, abundant, and biodegradable resources. Several studies on chitin and chitosan revealed that chitosan-based biosorbents are competent materials and have tremendously high attraction for many categories of dye years (Chiou and Li 2002, 2002; Chao et al. 2004; Chiou et al. 2004). They are versatile materials and can be used as sorbents in different forms, from flake types to bead types, gels, or fibers (Wu et al. 2000, 2001a, b). Wong et al. (2004) demonstrated the chitosan performance to remove acid dyes as an adsorbent in detail. According to his research, the adsorption capacities of chitosan for acid red 18, acid red 73, acid orange 10, and acid orange 12 were 693.2, 728.2, 922.9, and 973.3 mg/g, respectively.

Peat

Peat possesses porosity and is a complex soil material having organic matter in several stages of decomposition. The classification of peat is based on nature of parent materials. Peats are identified into four groups such as moss peat, woody peat, herbaceous peat, and sedimentary peat. The peat is plentiful, inexpensive, and available as biosorbent for a variety of pollutants. The polar property of peat makes them suitable for removal of dyes from solution (Allen et al. 2004; Ho and McKay 2003). The raw peat has some limitations such as low mechanic strength; poor chemical stability, to leach fulvic acid; a high affinity for water; and a tendency to shrink or/and swell (Sun and Yang 2003).

Biomass

Bioadsorption and/or decolorization of dye wastewater by white-rot fungi, (dead or living) biomass, and other microbial cultures was the subject of much research as reviewed in several recent papers (McMullan et al. 2001; Robinson et al. 2001; Stolz 2001; Pearce et al. 2003; Aksu 2005). In fungal decolorization, fungi can be categorized into two classes based on their life state: living cells to biosorb and biodegrade dyes and dead cells to adsorb dye (Fu and Viraraghavan 2001a). The recent studies have focused on the removal of dyes with strains of *Aspergillus niger* (Fu and Viraraghavan 2002a, b) and *Rhizopus arrhizus* (Aksu and Tezer 2000). Fu and Viraraghavan (2001b, 2002a, b) confirmed that *Aspergillus niger* as biosorbent shows remarkable properties for dye removal.

Miscellaneous Sorbents

Starch has been studied as low-cost sorbent (Delval et al. 2001, 2002, 2003) and cyclodextrins (Crini and Morcellet 2002; Crini et al. 2002a, b; Crini 2003). Starch belongs to carbohydrate class and is present as an energy storage material in living plants. It has also been demonstrated that cross-linked cyclodextrin gels can be used for efficient extraction of dyes. The sorption properties are enhanced due to existence of CD molecules in the polymer network (Crini and Morcellet 2002; Crini et al. 2002a, b; Crini 2003).

Chemical Methods

Oxidative Process

Oxidative procedures are characterized as an extensively applied chemical technique for the handling of textile discharge, where decolorization is the purpose. The key chemical is hydrogen peroxide (H_2O_2) that forms hydroxyl radicals, which are strong oxidizing agents and are capable to decolorize a variety of dyes (Entezari and Pe´trier 2004). Oxidation process is being used from so long, and it is found to be an easy to handle process that has been extensively used on commercial basis. Hydrogen peroxide is highly stable, and there are various methods of its activation, which are named accordingly.

Fenton Treatment

It is a very useful technique for wastewater treatment. It has its own specification which is found to be very effective to treat COD and gives the best removal against many dyes. In the first technique, hydroxyl radical is produced from H_2O_2 during Fenton reaction, where hydrogen peroxide is added to an acidic mixture (pH = 2–3) having Fe^{2+} ions. The reaction is exothermic and must be performed at temperature greater than ambient (Hassan and Hawkyard 2002). Besides many advantages, this process also has a limitation. Sludge produced by this process contains many impurities, and it requires proper land disposal that is not easy to handle. Fenton sludge recycling is a proposed technique to get rid of harmful impacts that makes it easy to handle this sludge (Joseph et al. 2000). Mechanical handling of this sludge is a possible option. The sludge contains phosphate that can be removed, that makes this sludge less harmful, and it may be treated through biotic processes.

Ozonation

Ozone is being used for the wastewater treatment since 1970. It is highly instable which makes it a strong oxidizer. When compared to chlorine having oxidizing potential of 1.36, it was found to be a better oxidizing agent with an oxidizing potential of 2.07 (Koch et al. 2002). It was mainly used against drinking water, and the main purpose was to make it clean, but its other properties against toxic compounds of wastewater make it a favorable option in textile wastewater treatment. It was found to be effective against many aromatic hydrocarbons, phenols, pesticides, etc. It is a very active and rapid decolorization handling method. Ozonation can tackle with the double bonds in dyes, and COD can be lowered by this method. Many of the nonbiodegradable products can be easily decomposed. 18.5 and 9.1 mg/l concentrations of ozone are enough to remove 50 and 60% COD after 60 and 90 min, respectively (Selcuk 2005). In this process, the usual application is the use of sodium hypochlorite that has the ability to break azo bond. The shortcoming of this process is that it releases amine compounds and these can cause cancer. It also has a limitation that it is readily decomposed in water having a life span of just 20 min. This is the main drawback of this treatment, and the time may get shortened enough when the wastewater having dyes is projected toward this treatment (El-Din and Smith (2002)). Other factors may influence its stability in water such as pH, temperature, etc. Ozone stability is highly affected by the presence of alkaline salts. It may get reduced when alkaline water is treated against it, while natural salts have a positive impact and enhance its stability (Arslan 2001). Temperature has a negative impact on ozone solubility. With increasing temperature, it becomes less soluble in water (Ma and Graham 2000).

Several options are keeping concern regarding the reduction in the parameter like COD, BOD, and TOC. Ince and Tezcanli (2001) stated that ozone treatment doesn't reflect any changes in COD. Ikehata (1975) conveyed a decrease in COD and BOD standards, while Koch et al. (2002) found that the use of ozone treatment will increase in the value of two parameters. Practices with TOC decline are constant, viz., treatment with ozone does not effect it. Meanwhile, addition in oxygen in soluble composites with ozone is not successful at an initial stage.

Carriere et al. (1991) advocate ozone treatment as a tertiary treatment, succeeding as an activated sludge process. The ratio of other substances present in dye wastewater is lesser than the present in the pure solution (up to 20% of dye leftover in the water after ozone treatment). At the very first step, eradication of foaming and reducing agents increases color removal efficiency by ozone treatment (Andreozzi et al. 2001a).

H_2O_2 UV Radiation

All the above-stated complications (sludge evolution and renewal increase the intensity of polluted wastewater caused by ozonation) can be stated away by oxygen addition with hydrogen peroxide, initiated with UV light. The single element used in the treatment is H_2O_2, and due to its final breakdown into oxygen, it is not problematic. Peroxide is activated by UV light. Aspects persuading H_2O_2/UV processes are concentration of hydrogen peroxide, the strength of UV radiation, pH, dye composition, and dyebath structure. Overall, discoloration is utmost successful at pH = 7, at greater UV irradiant concentrations (1600 W rather than 800 W), with an ideal concentration of H_2O_2, which varies for diverse dye sessions, and through a dyebath that does not cover oxidizing agents having an oxidizing capacity advanced than that of peroxide (Andreozzi et al. 2001a). According to Andreozzi et al. (2001b), the easiest decomposable dyes are acid dyes, and with an accumulative number of azo groups, the discoloration efficiency declines. Arslan et al. (2000) reported prolonged decoloration required by the yellow and green dyes, while on the other hand, quick decoloration is showed by the direct, metal-complex, and disperse dyes. In the collection of blue dyes eliminated, only blue dyes were not vat decolorized, yet their composition alters with the procedure in such a way that they can be simply filtrated. The filtrate is colorless. For pigments, H_2O_2/UV method is not appropriate, since they form a filmlike covering which is tough to eliminate.

Hydrogen Peroxide

The efficiency of method relies on the peroxidase usage, its strength, pH, and the temperature of the medium. Fukushima and Tatsumi (2001) studied the discoloration of acid dye by three kinds of peroxidases [horseradish (HRP), soybean (SPO), and *Arthromyces ramosus* (ARP)] as peroxide activator. By calculating the absorbance capacity, they found that the persistency was the highest via ARP. The discoloration rate augmented with higher peroxidase accumulation and temperature of medium and was the highest at pH 9.5.

NaOCl

Cl compounds are useful in the chemical oxidation of colored wastewaters. Electrophilic breakdown occurs at the amino group by Cl+pledgees and speeds up the consequent azo bond cleavage. Namboodri et al. (1994) reported the adequate discoloration of acid and direct dyes. Treatment of reactive dyes prerequisite longer times, while solutions of metal-complex dyes persisted partially colored (Manu and Chaudhari 2003). Disband dyes do not decolorize with NaOCl. Decoloration rate rises with increase in chlorine intensity and declining pH of medium. According to Omura (1994), dyes encompassing amino or exchanged amino groups on the naphthalene ring, i.e., dyes derivative from aminonaphthol- and naphthylamine-sulfonic acids, are the greatest subject for chlorine decoloration. One feature which has come to the front in current years, and which is related to chlorine-centered decoloration practices, is that, for atmosphere causes, the upcoming use of chemicals comprising chlorine should be controlled. Since 5 and 60% of European chemical manufacture openly or ultimately rest on chlorine, the influence of such a prohibition could be huge, mainly for organic colorant production. However, it must be illustrated that even though about 40% of worldwide used pigments comprise chlorine, this corresponds to less than 0.02% of the total chlorine production (Clarke and Steinle 1995).

Ion Exchange

It's a treatment process that has been used to treat wastewater excluding dye-containing wastewater. The main reason of avoidance was a misconception, and it was thought that this method is not effective against dye-containing wastewater and its effectiveness slows down further when wastewater is loaded with other additives in consort with dyes. This flaw was removed with an excellent work of Baouab et al. (2001) who proved in his experiment that sulfur-containing dyes and those with acidic nature could better be treated with a combination of anion exchange column that is packed in series and a nonpolar resin. This was a great turning point in treatment of textile wastewater because it added another positive option against dye treatment and it could be further explored within time. The ion exchange resins needed to be regenerated after one-time removal, and this task was completed with the help of organic solvents. The organic solvents are not that much cheap, and their use increased the operational cost that was the major drawback of ion exchange method.

The research on the highlighted above method provided wise choices and the use of quaternized cellulose. The sulfonate group of dye makes an association with the amine group of resin through columbic forces, or other bonding forces may be developed between them such as van der Waals forces or hydrogen bonding (Glover 1993). The efficiency of a resin to remove dye from wastewater can be judged through these bonding. If there is a strong bonding present between dye and resin, there will be effective removal of dye. There are many theories about the effectiveness of this method. According to Laszlo (1994), chloride concentration has a negative impact of dye removal efficiency. With the increased concentration of chlorine, there will be less bonding between dye and resin, while sulfate and carbonate have a null impact on this bonding so their concentration does not affect the dye removal efficiency. In the same way, with the addition of sodium hydroxide, the binding process completely gets stopped. This can be positively used in treatment process, and using sodium hydroxide can regenerate the resin. The main reason of this poor bonding is that, when pH is increased, the proton may be removed from quaternary amine and makes conjugate base which may increase the hydroxyl group that may result in a repulsion force between dye and resin.

Coagulation and Sedimentation

This technique is one of the most used techniques in the past. In this process, some of the chemicals are added in the water that assists the charged particles to make some compound that can be coagulated in water. Usually, the colloids carry negative charges so the coagulants are normally inorganic or organic cationic coagulants (with positive charge in water). Some of the organic polymers cause coagulation to an extent that these coagulants combine to give groups and form sediments that is easy to extract (Ciardelli and Ranieri 2001). The most commonly used chemicals are $FeCI_3$, AI_2 $(SO_4)_3$, $FeSO_4$, and lime (Verma et al. 2012).

Electrocoagulation

In this technique, effluents are treated in a chamber in which metal electrodes are used to treat wastewater. Electrode plates are suspended in effluent solution, and it can remove metal oxide at a specific pH. Metal oxides are coagulated and can be easily removed from the solution. This method is effective and has been reviewed in many articles (Khandegar and Saroha 2013). This technique uses direct current source between metal electrodes immersed in the effluent, which causes the dissolution of electrode plates into the effluent. The metal ions, at an appropriate pH, can form wide range of coagulated species and metal hydroxides that destabilize and aggregate particles or precipitate and adsorb the dissolved contaminants. Therefore, the objective of the present manuscript is to review the potential of electrocoagulation for the treatment of industrial effluents, mainly removal of dyes from textile effluent.

Reverse Osmosis

Reverse osmosis membranes have a holding degree of 90% or greater for most kinds of ionic complexes. Decolorization and removal of chemical auxiliaries in dyehouse wastewater can be done in a single step by reverse osmosis. Reverse osmosis causes the elimination of all mineral salts, hydrolyzed responsive dyes, and chemical auxiliaries. This process needs a very high energy since a very high pressure is required herein (Babu et al. 2007).

Nanofiltration

Nanofiltration has been used for the management of color discharges from the textile industry. Nanofiltration membranes hold low molecular weight organic complexes, divalent ions, big monovalent ions, hydrolyzed responsive dyes, and dyeing auxiliaries (Ellouze et al. 2012). In most available studies regarding dyehouse discharges, the amount of mineral salts does not surpass 20 g/L, and the amount of dyestuff does not surpass 1.5 g/L (Babu et al. 2007).

Biological Treatment

As compared to physiochemical and photochemical methods, biological methods can be categorized as cost-effective substitutes of textile wastewater treatment. All the other methods are costly and have major drawbacks when applied to textile industry. All the possibilities of biological methods have been studied, and they are being applied in textile industries using different microorganisms (Sarayu and Sandhya 2012). It has been studied that a single strain of bacteria or fungi is effective to remove a dye, but it cannot be applied to remove another dye. Therefore, this method can't be adopted at commercial scale (Mendez-Paz et al. 2005). Recently, a natural colonized algae and duckweed plants were found to be very effective to treat textile wastewater in a pond experiment (Sekomo et al. 2014). Biological methods can be categorized as aerobic and anaerobic processes, and they give the best results when applied to remove organic pollutants from textile wastewater (Frank et al. 2001). In field applications, aerobic methods did not give the best results in color removal. Many of the dyes, especially azo dyes, are found to be resistant in aerobic application (Mustafa and Delia 2006). Urban anaerobic sludge blanket reactor has been introduced in textile wastewater treatment, and it gives the best results in treatment of xenobiotic compounds. It has the ability to handle very resistant compounds also (Jantsch et al. 2002).

Aerobic Biodegradation

There is a natural process in the aquatic ecosystem named as aerobic biodegradation that is necessary to treat the wastewater of rivers and streams and makes them clean from pollution loads. The biodegradability of many compounds can be judged by many parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved oxygen (DO), and the evaluation of carbon dioxide

(Dos Santos et al. 2003). The main factor of the whole procedure is the assessment of the chemicals that can be easily biodegraded. There are OECD 301 guidelines available that must be adopted, and by using this method, there should be 70% DOC removal (OECD 1993).

If the compound is assessed as biodegradable and conditions are favorable, there is a possibility that the compound will be biodegraded in wastewater plant same like it can be degraded in natural environment (Cruz and Buitron 2000). Strotmann et al. (1995) made a research and developed COz/DOC scheme for effective removal of DOC. In this design, the compound was mineralized and DOC was eliminated. There were remarkable results of this procedure, and when it was compared with Zahn-Wellens test, it provided better information of biodegradability of compounds. On the basis of these results, the behavior of many compounds can be explored in natural environment and in wastewater treatment plants as well.

Anaerobic Biodegradation

Anaerobic degradation is degradation when there is an absence of oxygen or very low oxygen present in the medium. This kind of degradation usually occurs in lower sediments in natural aqueous environment because that is poor oxygen medium. Some kind of sewage waste is also degraded by this procedure. So it can be predicted that a compound having low solubility in water and can be adsorbed on solids can be subjected to anaerobic degradation. Anaerobic bacteria or microorganisms achieve this task. This is a complete sequence step process in which bacteria that act in acidic medium act on organics such as carbohydrates and fats. These organics may be converted in alcohols and other simple compounds with the action of acidic bacteria. These products then stimulate the acetogenic bacteria, which further convert them in carbon dioxide and molecular hydrogen. Then, after reduction of these products, methane is generated, and methanogen bacteria perform this task. Biogas is an important parameter in anaerobic treatment that gives an assessment about the rate of experiment. There are many researches available which can explore the aerobic and anaerobic treatment, but a comparative study of both procedures is missing. There was an effort to assess the volume of biogas, but there are no set standards to make predictions on the basis of this research (Cruz and Buitron 2000; Dos Santos et al. 2004).

Complexometric Methods (Refining with Cucurbituril)

It's a tough choice to use the effective method to treat wastewater because each process has its own merits and demerits. When we used activated carbon treatment, this can be effective against organic dye removal, but the other impurities can't be handled by using this process in the same way; each process has its own limitation. It was not until 1905, when there was a little noise about an organic compound introduced with the name of cucurbituril. But a remarkable research was not conducted on this compound. Freeman et al. (1981) explored its chemical properties. Cucurbituril is a polymer that is made up of glycoluril and formaldehyde. Studies have revealed that the complex has fairly good sorption capability for various types of textile dyes. Cucurbituril is recognized to make a complex with aromatic dyes, and it is reflected that this method is effective for the absorbance of reactive dyes (Robinson et al. 2001). Cucurbituril was not found to be soluble in aqueous medium, and its macrocyclic property made it more appropriate against dye treatment. It makes insoluble complexes that can be easily removed from wastewater. Later, Buschmann et al. (1996) did an extensive research on this compound. This was an effective method and can be used in solid state as well. The removal efficiency of cucurbituril was checked against many dyes such as acid, base, reactive, and direct dyes, and it provided excellent results against all of them. The rate of removal depends on many factors such as there may be high solubility of the complex formed, or there may be poor bonding between dye and cucurbituril. One of the plus points of this method is that it can never be disturbed by the presence of organic compounds in wastewater.

Comparison of Different Treatment Methods

There are different methods and technologies that are being applied to treat the textile wastewater. Different methods provide different efficiencies to remove color and organic waste. For example, advanced oxidation process is found to be most effective and gives the best result in color removal. Fenton's reagents (H_2O_2 and Fe^{2+}) and ozonation are the termed as advanced oxidation technologies that can be applied to textile wastewater to achieve the best results, but they have some limitations as well. They are costly, and a large amount of waste in the form of sludge is produced by these methods. The sludge produced by this method is difficult to manage (Marco and Jose 2007). Some of the physical methods such as coagulation flocculation are also found to be effective, but lime, alum, and polyelectrolytes used in this process cause an enormous amount of sludge that is difficult to manage and treat, as it can't be disposed easily. Therefore, this method can't be applied alone in textile wastewater treatment. Adsorption process is an expensive process as it uses activated carbon that is very costly. Other adsorbents used in adsorption of dyes have high cost, and the textile industry can't adopt this method due to high operational cost. Reverse osmosis technique in textile wastewater treatment is found to be very useful, but its operational cost is also very high, as it requires very high pressure, and a large amount of energy is consumed in this process. The budget of textile industries adopting membrane filtration techniques can be disturbed as nanofiltration and ultrafiltration processes require high energy, and sludge produced by this process is not easy to handle (Allegre et al. 2006). Another method uses ultraviolet light, and oxidation compounds such as H_2O_2 are also being used to treat textile waste, but different catalysts used in this process produce by-products that are very harmful (Muruganandham and Swaminathan 2004). There are some methods having high color removal efficiencies. Electrochemical oxidation is one of them as it has the ability to remove color, and by-products produced by this method are nontoxic and easy to handle. But it has its own limitation as its operational cost is also very high and it can disturb the budget of textile industry (Mohan et al. 2007).

Generally, a combination of two or more advanced oxidation processes such as UV/ozone, UV/H_2O_2, ultrasound/ozone, sonophotochemical/sonophotocatalytic oxidation, etc. leads to an enhanced generation of the hydroxyl radicals, which eventually results in higher oxidation rates. The efficacy of the process and the extent of synergism depend not only on the enhancement in the number of free radicals but also on the alteration of the reactor conditions or configuration leading to a better contact of the generated free radicals with the pollutant molecules and also better utilization of the oxidants and catalytic activity (Gogate and Pandit 2000a).

Combining ozone and hydrogen peroxide with ultrasound leads to a better utilization of both the oxidant, hence higher degradation rates due to the dissociation of ozone and hydrogen peroxide under the action of ultrasound. The mass transfer resistance, which is a major limiting factor for the application of ozone or hydrogen peroxide alone, is also eliminated due to the enhanced turbulence generated by ultrasound. The operating frequency is a crucial factor in deciding the synergism and should not be increased beyond 500 kHz (Gogate and Pandit 2000b). The problems of high-frequency operation and existence of optima beyond which the rates of degradation decrease have been discussed in detail in the earlier work (Gogate et al. 2002). Ozone/hydrogen peroxide hybrid technique gives better results as compared to the use of ozone or hydrogen peroxide especially for the treatment of pollutants, refractory toward ozone, e.g., organophosphoric acid tri-esters. As the synergism is strongly dependent on the efficient use of hydroxyl radicals, concentration of radical scavenging agents plays a crucial role in deciding the overall efficacy of the process (Gogate and Pandit 2004).

In the case of sonophotochemical/sonophotocatalytic reactors, it is important to have simultaneous irradiation of ultrasound and UV light rather than sequential operation. Addition of hydrogen peroxide or ozone to this hybrid system until an optimum value as an additional source of the free radicals also increases the extent of destruction (Fung et al. 2001) The major factor controlling the overall efficiency of destruction is, however, the stability of the photocatalyst under the effect of ultrasound, and efforts are required in terms of new designs, which will protect the catalyst but at the same time will give enhanced effects (Fung et al. 2001). Photo-Fenton processes offer additional advantages in terms of possibility in the use of sunlight instead of UV light with a minor decrease in the rate of degradation, which is a very important factor for the scale-up and commercial use as the costs of treatments will be substantially lower for the sunlight irradiation.

All the processes discussed above have their own merits and demerits. Indeed, the selection of the process that gives the best outcome with less polluting by-products and low cost is a difficult task (Rajkumar and Kim 2006) (Table 1).

Table 1 Representative studies on the applications of combined treatment systems on textile effluent

Treatment processes	First stage	Second stage	Outcome	References
Physical/ membrane treatment	Coagulation	Ultrafiltration	Achieved substantial colloidal particle removal (>97%) of turbidity removal) regardless of type and dosage of coagulants used, but degree of membrane fouling was highly dependent on type of coagulants used. Study has proven that inorganic coagulants were more efficient to reduce fouling compared to polymeric coagulants	Choo et al. (2007)
Membrane treatment	Ultrafiltration	Nanofiltration	Authors claimed that UF was an appropriate pretreatment of an NR/RO process for textile wastewater reuse. To deal with the wastewater with high variability values of COD and conductivity, they observed that flux decline was significant at the lowest cross flow velocity studied due to the solid deposition onto the membrane surface	Barredo-Damas et al. (2006)
Physical/ membrane treatment	Coagulation/ flocculation	Nanofiltration	Study reported that the quality of permeate after coagulation/ flocculation did not match the requirement of reuse on the site. However, this method could act as pretreatment of NF to limit membrane fouling. By using this integrated approach, high-quality permeate could be obtained	Suksaroj et al. (2005)

(continued)

Table 1 (continued)

Treatment processes	First stage	Second stage	Outcome	References
Chemical/ membrane treatment (2005)	Electrochemical oxidation	Membrane filtration	Study indicated the feasibility of combined processes for treatment of textile wastewater. Membrane prior to electro-chemical oxidation process showed promising results in terms of COD, turbidity, and color removal (*R*COD = 89.2%, *R*turbidity = 98.3%, *R*color = 91.1%) compared to electrochemical oxidation prior to membrane process (*R*COD = 86.2%, *R*turbidity = 95.1%, *R*color = 85.2%). This is due to lower color concentration remaining in wastewater after the electrochemical oxidation process	Chen et al. (2005)
Chemical/ biological treatment (2003)	Ozonation	Aerobic	The use of ozonation as pretreatment was able to increase the bioavailability of the dye before it was treated with the aerobic process. To achieve higher color (99.8%) and DOC (85%) removal, higher doses of ozone were required. This would make it less economically favorable	Libra and Sosath (2003)
Physical/ membrane treatment	Sand filtration and membrane filtration	Nanofiltration	Sand filtration and MF in a pilot plant were fundamental in reduction of suspended solids (100%) and turbidity (78%). To completely remove COD, conductivity, and color, NF was responsible for removal	Marcucci et al. (2002)

A combination of physical, chemical, and biological method can be cost-effective and efficient treatment option for textile wastewater treatment. In a recent study, a combination of Fenton and anaerobic oxidation (F + SBR) reactor was found to be very effective in removing *E. coli* and toxic organic compounds (Blanco et al. 2012). A best strategy toward the textile industry pollution reduction is adoption of cleaner production technologies.

There are three strategies that can be implemented in textile industry designs. These strategies are briefly summarized hereunder.

Less Polluting Raw Material

Selection of less polluting raw material is a prescreening process, and by adopting this strategy, textile companies can reduce waste generation from the very first step such as, instead of azo dyes, use vat dyes when possible, and reuse dye and wash wastewater for preceding process (Tsai and Chou 2004).

Substituted Products

The less polluting and easily degradable chemicals can substitute highly polluted chemicals that cannot be easily degraded. In the same way, textile companies can select the treatment designs that cause less pollution like substitution of chemical treatment with the mechanical one (Fitzpatrick et al. 2010).

Process Modification

Industries should adopt the process that is cost-effective, is energy efficient, and according to local conditions provides the best degradation. Usually a hybrid model can be used to achieve the best removal (Van der Bruggen et al. 2004). The objective of this study was to provide the best treatment options according to Pakistan situation. The combination of two processes enhances the ability to degrade the pollutants. The best design should have unique characteristics such as (a) the capacity to provide high biodegradation and maximum removal rate that cannot be achieved by the single process, (b) retention time which does not exceed the time of single process, and (c) its cost-effectiveness.

Conclusions and Perspectives

It must be said that the advanced oxidation processes or even the hybrid methods may not be useful in degrading large quantum of the effluent with economic efficiency and hence it is advisable to use these methods for reducing the toxicity of the pollutant stream to a certain level beyond which biological oxidation can take care of the complete mineralization of the biodegradable products. An optimized pretreatment stage (in terms of the oxidant dose and the reduction in the toxicity level) will substantially decrease the total treatment time and hence the size of the reactor using the combination technique. It is recommended that the added oxidants, e.g., hydrogen peroxides, are completely utilized in the pretreatment stage alone, as its continued presence may hamper the activity of the microorganisms. It is also important to analyze the constituents of the effluent stream after the pretreatment stage as it may happen that some of the intermediates formed as a result of the oxidation are biorefractory or more toxic than the parent compound.

It is also important to develop realistic and generalized kinetic and yet mechanistic models for predicting the rates of the degradation process as a function of different operating parameters. The developed kinetic model should consider the effect of all the constituents of effluent stream even if the concentrations are in traces, e.g., radical scavengers and also the different reactions taking place in the chain of radical reactions. In Pakistan, most of the textile industries discharge untreated wastewater into water bodies without any treatment, which percolates into the groundwater posing a threat to the health and socioeconomic life of the people. Characterization of wastewater is necessary to determine the type and scheme of treatment required. This chapter proposes the treatment options to control textile wastewater pollution. It is clear that textile wastewater can be treated through different processes including Fenton treatment, ozonation, adsorption, nanofilteration, aerobic biological treatment, and anaerobic treatment such as upflow anaerobic sludge blanket reactor, etc. After comparing the advantages and disadvantages of these processes, the best strategy is to use aerobic and anaerobic biological treatment in combination for textile industry wastewater treatment (Manu and Sanjeev 2003). Moreover, instead of focusing on end-of-pipe treatment, the adoption of cleaner production technologies is necessary to reduce pollution at source. This can be done through selection of less polluting alternate raw materials, reuse of wash water, and conservation of water, chemicals, and energy by following cleaner production practices in textile industries.

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