

Treatment and Reuse of Dye Wastewater from the Textile Industry: A Review of Advanced Treatment Technologies

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ABSTRACT:

Water pollution due to color from textile dyeing and finishing industries is a topic of major concern of today's researchers. Dye effluents are highly toxic as they contain a large number of metal complex dyes. Large amount of unfixed dyes remain in effluent after completion of dyeing process, which leads to pollution of water if discharged in water body and this effluent cannot be reused as process water because they contain complex chemicals. Such dye effluent causes many water born diseases and increase the BOD and COD level of water bodies. Textile industry dye effluents are difficult to treat by conventional and biological processes, as most of dyes are toxic and non-biodegradable. The dye molecules are complex structure, and are difficult to breakdown biologically and can not be treated efficiently by only conventional methods. Advanced Oxidation Processes (AOPs) are widely used for the decolorization of textile industry dye effluent and also the removal of recalcitrant organic constituents from industrial waste water. Such water can be reused as process water more than once and re-circulating of process water in the same use for a number of times for textile industry. Advanced Oxidation Processes (AOPs) hold great promise to provide alternative for better treatment and protection of environment, thus are reviewed in this paper. This study focuses on the Advanced Treatment technologies and the goal of these treatment processes is to enable the textile industry to reuse the wastewater in textile processes through effective methodologies.

1. INTRODUCTION

The textile industry produce large amount of dye effluents, which are highly toxic as they contain a large number of metal complex dyes. In addition to dyes, textile wastewater also contains solids, oil, many complex organics and high quantities of chemical residue from process such as bleaching and dyeing. Strong colour of the textile wastewater is the most serious problem of the textile industrial effluents. Textile industry generates highly polluting wastewater and their treatment is a very serious problem due to high Total Dissolved Solids (TDS), presence of toxic heavy metals and non-biodegradable nature of the dyestuffs present in the effluent (Eswaramoorthi et al. 2008). Many operations of textile process are water intensive in textile production. Therefore, a purification treatment to recycle water must have much better performances than for simple discharge according to the limits imposed by legislation. There are many processes available for the removal of dyes by conventional treatment technologies including biological and chemical oxidation, coagulation and adsorption but they can not be effectively used individually. For example, the coagulation process effectively decolorized insoluble dyes, such as disperse dyes, but does not work well for soluble dyes. The activated carbon absorbent is not suitable for insoluble dyes and the biological process does not effectively decolorize because most dyes are toxic to organisms used in the process. Most of the dye molecules are complex, particularly reactive azo dyes cause special environmental concern due to their degradation products, such as aromatic amines which are highly carcinogenic (Arslan and Seremet, 2004). The use of a variety of dyes and auxiliary chemicals result in the discharge of toxic waste into natural water bodies. More than 8000 chemically different types of dyes are currently manufactured and the biggest consumers of these dyes are the textile industries (Rajgopalan, 1995).

Textile industries are probably the most potential contributors as far as color pollution are concerned. Among the above, dyes are difficult to be decolorized due to their complex structure, synthetic origin and recalcitrant nature, which makes it obligatory to remove them from industrial effluent before being disposed into hydrological system (Brown, 1987). The industries are thus facing problems in maintaining a profitable level of production while reducing the intake of fresh water. Another problem is the disposal of large volumes of effluents which abides by environmental standards. These are generally not amenable to conventional biological, physical and chemical treatment processes due to their recalcitrant and complex nature (Arslan et al., 1999; Azbar et al., 2004). These dyes are difficult to breakdown biologically and can not be treated efficiently by only conventional methods using aerobic or anaerobic processes, especially acid and reactive dye treatment has been most problematic, as they tend to pass through conventional treatment system unaffected. Advanced oxidation processes (O_3 , O_3/H_2O_2 , O_3/UV , UV/H_2O_2 , $O_3/UV/H_2O_2$ and Fe^{2+}/H_2O_2) for the degradation of nonbiodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods. AOPs include hydrogen peroxide (H_2O_2), ozone (O_3) and UV irradiations, which have proved to be much efficient treatment processes (Lidia. Stanislaw et al. 2001). AOPs based on the generation of very reactive and oxidizing free radicals have been used with increasing interest due to their high oxidant power.

This paper reviews different Advanced oxidation processes (O_3 , O_3/H_2O_2 , O_3/UV , UV/H_2O_2 , $O_3/UV/H_2O_2$ and Fe^{2+}/H_2O_2) and their combination for remediation of textile industry dye effluents. This review also focuses on Advanced Oxidation Processes (AOPs) methods and tools for analyzing water savings and reuse of such process water more than once and re-circulating of process water in the same use for a number of times for textile industry.

2. CHARECTARISTICS OF DYE WASTEWATER

The textile industry generates wastewater mainly from the wet-processing originates from bleaching and washing and these processes generates wastewater of great chemical complexity and diversity. Textile industry effluents are known to present extreme variations of pH, high temperature, and high concentration of dissolved solids (both Total Dissolved Solids and Total Suspended Solid) and dissolved salts. Textile dye wastewater can be classified in 3 classes according to Chemical Oxygen Demand (COD) content and color density; high, average and low intense wastewater. High intense wastewater has COD concentration over 1500mg/l and very low light permeability. Average intense wastewater has 800-1500mg/l COD whereas lower intense wastewater has under 800mg/l COD content. In general, most of the wastewater are place in average or lower intense wastewater class (Lin and Peng, 1994). Table 1 shows characteristics of textile wastewater. The degree of difficulty in refining the wastewater is related with the degree of relative pollution. Major water pollution problems in Textile Industry are discussed below:

2.1 Color

Presence of color in the waste is one of the main problems in textile industry. Color is easily visible to human eyes, even at very low concentration. Hence, color from textile wastes carries significant esthetic importance. Most of the dyes are stable. They are also not easily degradable by the conventional treatment methods. Removal of dyes from the effluent is major problem in most of textile industries.

2.2. Dissolved Solids

Dissolved solids contained in the industry effluents are also a critical parameter. Use of common salt and glauber salt etc. in the processes, directly increase total dissolve solids (TDS) level in the effluent. TDS are difficult to be treated with conventional treatment systems. Disposal of high TDS bearing effluents can lead to increase in TDS of ground water and surface water. Dissolved solids in effluent may also be harmful to vegetation and restrict its use for agricultural purpose.

2.3. Toxic metals

Wastewater of textiles is not free from metal contents. There are mainly two sources of metals. Firstly, the metals may come as impurity with the chemicals used during processing such as caustic soda, sodium carbonate and salts. For instance, caustic soda may contain mercury if produced using mercury cell processes. Secondly, the source of metal could be dye stuffs like metalised mordent dyes. The metal complex dyes are mostly based on chromium.

2.4. Residual chlorine

The use of chlorine compounds in textile processing result in residual chlorine in the waste stream. The wastewater (if disposed without treatment) depletes dissolved oxygen in the receiving water body and as such aquatic life gets affected. Residual chlorine may also react with other compounds in the wastewater stream to form chlorine derivatives.

2.5. Organic pollutants

Organic pollutants originating from organic compounds of dyestuffs, acids, sizing materials, enzymes, tallow etc. are also found in textile effluent. Such impurities are reflected in the analysis of biochemical oxygen demand (BOD) and COD. In many textile units, particularly engaged in synthetic processing, low BOD/COD ratio of effluent is observed which makes even biological treatment not a ready proposition.

Table 1. Characteristics of Textile Wastewater (Lin and Peng, 1994).

Type	BOD(mg/L)	COD(mg/L)	pH	Temperature (°C)
High Strength	500	1500	10	28
Average Strength	270	970	9	28
Low Strength	100	460	10	31

3. METHODS FOR TREATMENT OF DYE EFFLUENTS

During the past two decades, several decolorization techniques have been reported, few of which have been accepted by industries. There is a need to find alternative treatments that are effective in removing dyes and colorants from large volume of effluents. The color of effluent is as indication of pollution if it discharges into water bodies. The color of water, polluted with organic colorants, reduces when the cleavage of the $-C=C-$ bond the $-N=N-$ bond and heterocyclic and aromatic ring occurs.

There are various methods which are formed by the physical, chemical and biological methods for treatment of textile industry wastewater are follows:

3.1 Physical method

Some physical methods like adsorption, irradiation and ion-exchange are effective and proven technology having potential application in wastewater treatment. Some absorbents like chitin, which contain amino nitrogen, tend to have a significantly larger adsorption capacity in acid dyes. Many adsorbents made from waste materials, for removal of dye and colored organic matters from aqueous media are of low cost (Bousher et al.1997). The activated carbon having a high adsorption capacity for both acid and basic dyes, is most common method of dye removal by adsorption (Nassar et al. 1991).The adsorption method has difficulties in the treatment of insoluble dyestuffs wastewater and it is difficult to find the desorption process (W. G. Kuo.et al.1992, S.H. Kim et al.2002). Irradiation process is effective for removal of a wide range of colorants at low volume, but in this treatment dissolved oxygen requirement is very high. Ion exchange cannot accommodate a wide range of dyes and further perform poorly in the presence of other additives in wastewater.

3.2 Chemical method

Chemical methods like coagulation and flocculation are generally used in order to eliminate organic materials. Coagulant materials are usually effective on decomposed dyeing substance. Coagulation is effective for treatment of insoluble dyestuff wastewater but not so effective for soluble dyestuff wastewater (S.F. Kang et al., 2000, W. G. Kuo. et al., 1992). The disadvantages of the method are excessive cost, excessive mud and cost for removing that mud (Gaehr et al., 1994). The high cost of chemicals for precipitation as well as for pH adjustment, problem associated with dewatering and disposing of generated sludge and high concentration of residual action levels which remains in the supernatant is some of the limitations of this method.

3.3 Biological method

Most of the biological processes are effective in removing chemical oxygen demand (COD) and turbidity whereas they are not effective in removing color (Lin et al., 1997). An anaerobic step followed by an aerobic step may represent a significant advancement in biological treatment and decolourization in future (Bahorsky 1998, Ong et al., 2005).

4. ADVANCED OXIDATION PROCESSES (AOPs)

Advanced oxidation processes is an advanced method characterized by production of ($\bullet\text{OH}$) radical intermediates (Glaze et al. 1987). Table 2 shows the relative oxidation potentials of several chemical oxidizers (Carey, 1992; Techcommentary, 1996; Zhou and Smith 2002; Metcalf and Eddy, 2003). Generation of hydroxyl radicals ($\bullet\text{OH}$) is commonly accelerated by combining O_3 , H_2O_2 , TiO_2 , UV radiation, electron-beam irradiation and ultrasound. Of these, $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV and $\text{H}_2\text{O}_2/\text{UV}$ hold the greatest promise to oxidize textile wastewater. Combination of these oxidizing agents showed great promise to treat textile industry wastewater (Arslan et al., 2000, Adel et al., 2004). Once generated the hydroxyl radicals can attack organic chemicals by radical addition (Eq. 1), hydrogen abstraction (Eq. 2) and electron transfer (Eq. 3) (SES, 1994). In the following reactions, R is used to describe the reacting organic compound.



Table 2. Oxidizing potential for conventional oxidizing agents

Oxidizing agent	Electrochemical oxidation potential EOP), V	EOP relative to Chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

5. TEXTILE EFFLUENTS: TREATMENT AND REUSE

The textile industry is very water intensive. Water is used for cleaning the raw material and for many flushing steps during the whole production. The cleaning process depends on the kind of wastewater and also on the amount of used water. A comparison of the textile effluent and the standard for discharge of textile wastewater into receiving waters shows that the wastewaters have to be treated in order to meet the acceptable range of the effluent discharge standards. If untreated wastewater would be discharged in aquatic environment, some effects could take place, for example:

Effect of BOD:

Depletes dissolved oxygen from streams, lakes and oceans; may cause death of aerobic organisms (fish kills etc.); increases anaerobic properties of water.

Effect of TSS:

Increases turbidity (less light - reduced photosynthesis, causes fish's gills to get plugged up); increases silting (reduces lifetime of lakes, changes benthic ecology).

Effect of pH:

Organisms are very susceptible to acids and bases.

The textile wastewater treatment methods are broadly classified into four main stages such as preliminary, primary, secondary and tertiary treatments to treat the textile effluents. The preliminary treatment processes involve mixing and equalization. Figure 1 shows the preliminary treatment processes. The primary treatment involves screening, sedimentation, chemical coagulation and flocculation. Secondary treatment involves the removal of colloidal particles. Tertiary treatments are very important because they serve as polishing of effluent treatment (Ajibola, V. O. et al., 2001).

It is worthwhile to mention that the textile wastewater contains significant quantities of chemical substances and dyestuffs. The conventional treatment methods are not very effective in removal of pollutants such as color, dissolved solids, trace metals etc., so there is the need for efficient treatment methods or advanced treatment methods.

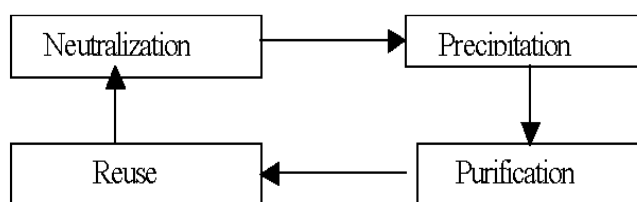


Figure 1. Preliminary Treatment Processes

5.1 Treatment of Textile Dye Effluents by Advanced Oxidation Processes

Textile effluents require advanced treatment methods to remove particular contaminants like various types of dyes, dissolved solids, heavy metals and organic substances and prepare the treated effluent for reuse. The prime mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals ($\cdot\text{OH}$) are effective in destroying organic chemicals because they are reactive electrophiles that react rapidly and nonselectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions compared to conventional oxidants such as H_2O_2 or KMnO_4 (Gogate and Pandit, 2004). AOPs are capable of achieving desired color destruction of wastewater and it can completely oxidize organic pollutants to CO_2 , water and salts (De et al. 1999). Kang et al. (2000) reported the removal of color from textile waters by $\cdot\text{OH}$ radical oxidation, markedly related with the amount of $\cdot\text{OH}$ formed at pH 3–5. Up to 96% of color was removed within 30 min. All oxidation processes were capable of completely decolourizing the wastewater within 30 min. Decolourization proceeded fastest by the $\text{O}_3/\text{Mn(II)}$ process, whereas the $\text{O}_3/\text{H}_2\text{O}_2$ combination was more efficient in the removal of dissolved organic carbon. Oxidation by ozone is capable of degrading chlorinated hydrocarbon, phenols, pesticides and aromatic hydrocarbon (Xu et al., 1999). Arslan & Balcioglu (2001) observed enhanced biodegradability in terms of BOD_5/COD ratio achieved by the Fe(II) ion catalysed ozonation of pretreated wastewater with two fold increase for the optimized oxidation technologies. (Botau et al. (2001) reported the disappearance of color due to the azo bond breaking and partial oxidation of the aromatic rings during the ozonation of aqueous solutions of MG 150 orange and FFN (B15) blue dye. Perez et al. (2002a) investigated the combination of Fenton and photo-Fenton reaction in the treatment of textile effluents and reported the effectiveness of these methods in the decolouration of coloured wastewater upto

90%. Oxidization of the textile wastewater with hydrogen peroxide alone has been found ineffective at both acid and alkali values (Olçay et al., 1996), while under UV irradiation, H_2O_2 are photolyzed to form two hydroxyl radicals ($2\text{OH}^\bullet$) that react with organic contaminants (Crittenden et al., 1999). At acidic pH, H_2O_2 reacts very slowly with O_3 whereas at high pH the dissociation of H_2O_2 into $\text{HO}_2^\bullet$ is very high which in turn initiates ozone decomposition more effectively than $\text{OH}^\bullet$ (J. Staehlin and J. Hoigne (1982).

5.2 Process Water Re-Use

The impacts on the environment by textile industry have been recognized for some time, both in terms of the discharge of pollutants and the consumption of water and energy. The textile sector has a high water demand. Its biggest impact on the environment is related to primary water consumption (annual 839.8 million m^3 of finished textile) and waste water discharge annual 637.3 million m^3 (CSE 2004). Therefore, reuse of the effluents represents an economical and ecological challenge for the overall sector. The cleaning process depends on the kind of wastewater (not every plant applies the same production process) and also on the amount of used water. Water savings in textile processing industries can be made by recovering and re-using of water at processes itself. There are few areas where reuses options can be examined by the units listed hereunder:

- Recycling of final wash water after bleaching as a wash water for second scouring step or for earlier bleaching steps
- Reusing bleaching wash water to start another bleaching batch
- Re-use of hot bleach water for starting optical brightening batch
- Re-use of optical brightening wash water to start another batch of optical brightening batch
- Final wash water of cone scouring and bleaching can be used as wash water for scouring and bleaching

6. CONCLUSIONS

Water use in textile industry is very high due to a combination of factors including obsolete process technology, poor recycling and reuse practices and poor wastewater treatment. Advanced oxidation processes for the treatment of textile effluents are promising methods for purification aimed at reuse of textile wastewaters, resulting in direct environmental and economic benefits. These methods provide complete removal of color and reduce recalcitrant wastewater loads from textile dyeing and finishing effluents and treated waters can be reused satisfactorily in dyeing process. It is quite difficult to define a general quality standard for textile water reuse because of the different requirements of each fiber (silk, cotton, polyester etc.), of the textile process (e.g., scouring, desizing, dyeing, washing, etc.) and the different quality required for the finalized fabric.

It appears that advanced oxidation processes are preferable option compared to other wastewater treatment techniques because of the constant quality of effluent that is almost completely softened and free of color and surfactants.

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