



Study of environmental issues in textile industries and recent wastewater treatment technology

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ABSTRACT

Textile industries are the major source of environmental pollution In terms of quality as well as quantity. The textile industries consume large quantities of water (200 m³/ton of product) out of which around 90% is appeared as wastewater. Textile wastewater contains dye as the major pollutant which is not only recalcitrant but also imparts intense color to the waste effluent. Improper disposal of textile wastewater causes serious environmental problems affecting the aquatic organism adversely. The present study deals with the detailed study of environmental issues and treatment options. The industry generates huge amount of wastewater contains toxic pollutants. Several treatment technologies are using now days with high efficiency and from the present study it was found that advanced oxidation process is very effective in terms of pollutants removal efficiency as well as cost requirement.

Keywords: Wet processing, Water pollution, Advanced Oxidation

1. INTRODUCTION

In India, textile industry is one of the most important industries. The total industrial production of 14% generates from this industry, and it accounts for 3% of total Gross Domestic Product (GDP) in the country. The textile industries consume large quantities of

water (200 m³/ton of product) and generate significant volumes of wastewater (~90% of consumed water) (Verma *et al.*, 2012). The wastewater contains intense color and high amount of contaminants, thus proper treatment is required before final disposal to the receiving water body. In the textile wastewater, dye is considered the color imparting component which is difficult to treat by conventional processes. The dyes are washed off during the dyeing process, thus, the residual dyes always present in the dye bath effluent and may be as much as 50% (reactive dyes) of the initial dye load (Parsons, 2004; Wilas *et al.* 2016; Beata, 2015). A well-known and widely used treatment method for the industrial effluent is activated sludge process with modifications. However, the conventional treatment methods are not suitable for the treatment of colored waste stream (Uygun and Kok, 1999). Physico-chemical treatment technologies such as, membrane processes, ion exchange and activated carbon adsorption can only transfer pollutants from one phase to another rather than eliminating the pollutants (Erswell *et al.*, 2002). Different combinations of activated sludge process with physical and chemical treatment processes have also been used for textile wastewater treatment.

Advanced oxidation process (AOP) can cause complete or partial destruction of organics from textile wastewater. Thus this process can be used as a pretreatment method before biological degradation. AOPs are based on the generation of reactive and oxidation of free radicals, particularly hydroxyl radicals (HO[•]) which have high oxidation potential (Yonar *et al.*, 2005). The conventional Fenton process using Fe²⁺ and H₂O₂ requires a continuous supply of active metal specie, to make up for the metal lost by precipitation. Recently, Fenton's process is considered as one of the preferred alternative for the treatment of industrial effluents but this process is suffered with the problem of sludge disposal (Bokare and Choi, 2010). A relatively new process, known as chromium induced advanced oxidation process, is in development stage and also has great potential of the degradation of pollutants. In this process, the continuous supply of metal specie is not required, because it is regenerated by redox cycle of the metal specie (Bokare and Choi, 2011).

2. WET PROCESSING STEPS IN A TEXTILE INDUSTRY

Wet processing usually covers pretreatment, dyeing, printing and finishing. All the processes are carried out in an aqueous medium. The flow diagram for various steps involved in textile processing is shown in Figure 1. The various wet processing steps are briefly discussed in the following paragraph (Amin *et al.*, 2008).

Sizing is carried out for the purpose of removing the loose hairy fibers from the surface of the cloth, thereby giving it a smooth, even and clean looking face. Sizing is an essential process for the textile material which has to be subjected to mercerizing, dyeing and printing in the downstream processes.

Desizing is the process of removing sizing materials from the fabric, which is applied in order to increase the strength of the yarn. Fabric which has not been desized, is very stiff and causes difficulty in its treatment in subsequent processes.

Scouring is a chemical washing process carried out on cotton fabric to remove natural wax and non-fibrous impurities (e.g. the remains of seed fragments) from the fibers and any added soiling or dirt. The fabric is boiled in an alkali solution which forms soap with free fatty acids.

Bleaching improves whiteness by removing natural coloration and the remaining trace impurities from the cotton. The desired degree of bleaching is determined by the required whiteness and absorbency. Cotton being a vegetable fiber is bleached using an oxidizing agent, such as dilute sodium hypochlorite or dilute hydrogen peroxide. If the fabric is to be dyed in a deep shade, then lower level of bleaching is acceptable. However, for white bed sheets and medical applications, the highest level of whiteness and absorbency is essential.

Mercerizing is a treatment for cotton fabric and thread that gives fabric or yarn a lustrous appearance and strength. The process is applied to cellulosic materials like cotton. During mercerizing, the fabric is treated with sodium hydroxide solution to cause swelling of the fibers. This results in improved strength and dye affinity. Cotton is mercerized under tension, and all alkali must be washed out before the tension is released otherwise the fabric may shrink.

Dyeing is the process of adding color to textile products like fibers and yarns. Dyeing is normally done in a special solution containing dyes and particular chemical. After dyeing, the dye molecules have un-dissociated chemical bond with fiber molecules. The temperature and time are the two key controlling factors in this process.

Finishing is a series of processes to which all bleached, dyed, printed and certain grey fabrics are subjected before sending to the market. The object of textile finishing is to render the goods fit for their purpose or end-use and/or improves serviceability of the fabric. Fabric may receive considerable added value by applying one or more finishing processes.

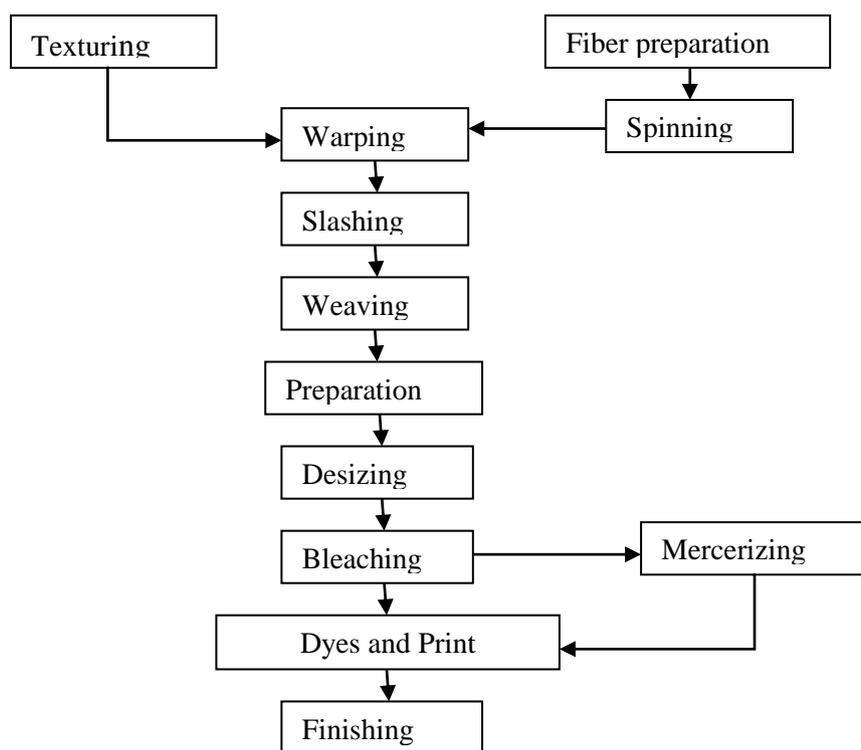


Figure 1. Flow diagram of highlighting steps in textile processing (Babu et al., 2007)

3. MAJOR POLLUTANTS IN TEXTILE EFFLUENT

There are three major pollutants found in textile effluent which include color, dissolved solids and toxic metals.

Color: The presence of color in the wastewater is one of the main problems in textile industry which is easily visible to human eyes even at very low dye concentration. Most of the dyes are stable, not easily degradable and are unaffected by light.

Solids: The use of inorganic sodium salts (NaCl and Na₂SO₄) in the above processes directly increase total dissolved solids (TDS) level in the effluent which forms the major fraction of total solids (TS) and are not removable using conventional treatment.

Toxic metals: The presence of toxic metals in the textile wastewater is another major problem. The metals may come as impurity with the chemicals (such as caustic soda, sodium carbonate and salts) used during processing or may be present in dye stuffs (like metalized mordent dyes).

4. CHARACTERISTICS OF TEXTILE EFFLUENT

The waste materials generated at each level of cotton textile processing are presented in Table 1. The unused materials from the textile processes are discharged with the wastewater which has high color and considerable biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The typical characteristics of effluents from textile plants are shown in Table 2. The discharge standards for the safe disposal of textile effluent prescribed by Central Pollution Control Board are presented in Table 3

Table 1. Waste generation from textile processing (Babu *et al.*, 2007)

Process	Wastewater
Fiber preparation	Little or no wastewater generated.
Yarn spinning	Little or no wastewater generated.
Slashing/sizing	BOD, COD, metals, cleaning waste.
Weaving	Little or no wastewater generated.
Tufting	Little or no wastewater generated.
Desizing	Biological Oxygen Demand from water sizes, synthetic size, lubricants, biocides, anti-static substances.
Scouring	Disinfectants and insecticide residues; NaOH, detergents, fats, oils; pectin, wax, knitting lubricants; spin finishes, solvents.
Bleaching	Sodium silicate, H ₂ O ₂ , organic stabilizer; high pH.
Singeing	Little or no wastewater generated.

Mercerizing	High pH, Sodium hydroxide.
Dyeing	Metals; salt; surfactants; toxics; organic processing assistance; cationic materials; color; BOD; sulfide; acidity/alkalinity; spent solvents.
Printing	Suspended solids, urea, solvents, color, metals, heat, BOD, foam.
Finishing	BOD, COD, suspended solids, toxics, used up solvents.
Product fabrication	Minimum or nil wastewater generated.

Table 2. Typical characteristics of textile effluent (Korbhati *et al.*, 2008)

Parameters	Value
pH	5.1-12
TSS	18-270 mg/L
TDS	2100-12260 mg/L
COD	200-3505 mg/L
Conductivity	15.78 mS/cm
Chlorides	1240-3761 mg/L

Table 3. Standards for cotton textile industries (CPCB, 1986)

Parameters	Value
pH	5.5-9.0
TSS (mg/L)	100
TDS (mg/L)	500
BOD (mg/L)	30
COD (mg/L)	250
Total residual chlorine, mg/L	1

Oil and grease, mg/L	10
Total chromium as Cr, mg/L	2
Sulphide as S, mg/L	2

Table 4. Summary of research studies on degradation of dyes using AOPs

Textile dye	Results	Major conclusion	Reference
H_2O_2/UV			
Reactive black 5	Color removal 100%, TOC reduction = 90% and COD reduction = 74%	Color removal efficiency very good but the COD removal efficiency was comparatively low.	Ince and Gonenc (1997)
C.I. Reactive Red 243	At pH 11, color removal = 99.3%	Combined use of hydrogen peroxide and ultraviolet radiation was effective to treat synthetic solutions of C.I. Reactive Red 243.	Yokoyama <i>et al.</i> (2007)
Blue-N-RM-2114	At pH = 7.29, decolorization efficiency = 100%, TOC removal = 93%	TOC removal was incomplete while the color was completely disappeared.	Amin <i>et al.</i> (2008)
Basic Violet (B. V.) 16	At pH 4.5, Color, TOC and color removals = 99%, 81% and 53%, respectively	UV/ H_2O_2 process was found to be a suitable treatment method for complete decolorization for BV16. The rate of color decay followed pseudo-first order kinetics with respect to the UV-visible absorption of the test dye during reaction. The partial reduction of COD represents the production of small organic molecular fragments and incomplete mineralization of dye by UV/ H_2O_2 process.	Zahra <i>et al.</i> (2012)
TiO_2/UV			
Real dyeing effluent	With 3 g/L TiO_2 , decoloration = 100%.	The process was found capable of 100% decolorizing the real textile wastewater. The extent of conversion was dependent on type and concentration of TiO_2 .	Pantelis <i>et al.</i> (2006)

Fenton's process			
Degradation of 6 types of 20 dyes (acidic, reactive, direct, cationic, disperse and vat dyes)	Color removal from acidic, reactive, direct, cationic dyes was 87-100% and for disperse, and vat dyes it was 56 - 79%.	The process showed lower preference for disperse and vat dyes but for other dyes, it was very good as the removal efficiency reach to 100%.	Xu <i>et al.</i> (2004)
Reactive black 5	At pH = 3, COD removal = 71-84% and color removal = 99%	71% COD and 99% color removal were observed with a dye concentration of 100 mg/L and 84% COD and 99% COD & color reduction was observed with dye concentration of 200 mg/L. Toxicity of the wastewater was also reduced after the treatment.	Meric <i>et al.</i> (2004)
Reactive blue 19	At pH = 3, 85% COD removal was observed after 40 min and 85% was observed after 120 min.	For textile wastewater containing reactive dye is well treatable by this process, COD removal obtain much better than the other processes.	Emami <i>et al.</i> (2010)

5. ADVANCED OXIDATION PROCESS

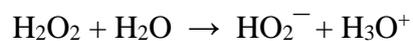
The main mechanism of AOPs is the generation of highly reactive free radicals (Metcalf & Eddy, 2003). The reactive free radicals are responsible for oxidizing the complex organic constituents to the simpler intermediates and end products. There are several ways in which degradation of organics can happen during the oxidation (Metcalf & Eddy, 2003): (i) a structural change in the parent compound with same molecular formula, (ii) structural change in the parent compound to produce other compounds which may be less or more toxic and (c) mineralization of organic carbon in to CO₂. Some selected AOPs using H₂O₂ as oxidant are discussed in the following paragraphs.

Hydrogen peroxide/ozone (H₂O₂/O₃) based AOP

The addition of O₃ into wastewater may cause the complex chain of reactions that may result in the formation of radicals such as HO[•] and the superoxide radical (O₂^{•-}) (Hoigne, 1998). HO[•] is very powerful oxidant, even more powerful than O₃. Direct oxidation by O₃ occurs very slowly (Hoigne, 1998).

Hydrogen peroxide can be combined with ozone to enhance the transformation of O₃ to HO[•] in solution. H₂O₂ itself being a weak acid partially dissociates into the hydro-peroxide ion

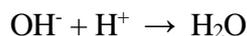
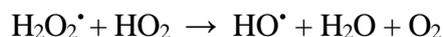
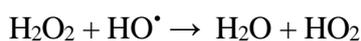
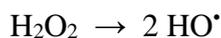
(HO₂⁻) in water. H₂O₂ reacts slowly with O₃, whereas the HO₂⁻ can have a rapid reaction with O₃ to form HO[•] (Hoigne, 1998).



H₂O₂ acts as a catalyst and accelerates the decomposition of ozone to form hydroxyl radical when a mixture of hydrogen peroxide and ozone is used to treat wastewater. At acidic pH, H₂O₂ reacts very slowly with O₃ whereas at high pH, the dissociation of H₂O₂ into HO₂⁻ is very high which initiates ozone decomposition more effectively than HO[•]. The inhibitory performance of H₂O₂/O₃ process depends on the H₂O₂ to O₃ mass ratio. Ratio ranging from 0.3-0.6 for different type of dyes as some studies suggest (Rein, 2001).

Hydrogen peroxide/UV (H₂O₂/UV) based AOP

The effectiveness of H₂O₂/UV process relies on the several synergistic oxidation mechanisms for the destruction of organics. The oxidation of organics can happen by either coordinate photolysis or responses with hydroxyl radicals. Hydroxyl radicals are delivered from the photolytic separation of H₂O₂ in water by UV light (Wagler and Malley, 1994). The following reactions may occur in the process:

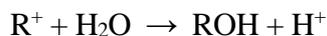
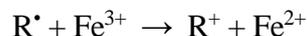
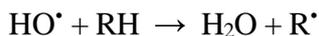


Wang et al. (2002) reported that H₂O₂/UV treatment was capable of destroying the chromophore structure of azo dyes. UV irradiation in the presence of H₂O₂ resulted in the complete decolorization of sulphonated azo and anthraquinone dyes.

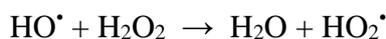
Kdasi *et al.* (2004) found 99.9% decolorization of Remazol Brilliant blue dye with an H₂O₂ concentration of 12.5 ml L⁻¹. The temperature did not show any significant role in the removal of color.

Fenton's process

Fenton's oxidation using H₂O₂/Fe²⁺ system is one of the potential methods for treating textile - dyeing wastewater. The Fenton's treatment has two distinct stages: (i) the formation of hydroxyl radicals and (ii) ferric coagulation (Gulkaya *et al.*, 2006). If H₂O₂ and ferrous ions are added to an aqueous system containing an organic substrate in a strong acid medium, some complex redox reactions are expected to occur. The hydroxyl radical generated from Fe²⁺ and H₂O₂ reaction will attack the organic substrate (RH). The following reactions are expected to occur (Gulkaya *et al.*, 2006):



Additionally, many other reactions such as the radical–radical reaction or the reaction of the HO[•] with H₂O₂ are also possible (Gulkaya *et al.*, 2006).



The peroxy radicals (HO₂[•]) also contribute in the oxidation reaction. The rapid depletion of H₂O₂ is often observed with Fenton's reagent. Another possibility is the auto-generation of Fe²⁺ in the system according to the following reaction.



Cr³⁺/H₂O₂ based AOP

AOPs utilizing H₂O₂ as a forerunner of hydroxyl radical (HO[•]) have developed as effective advancements for the fast decimation of obstinate natural mixes. The achievement of H₂O₂-construct oxidation forms depends fundamentally with respect to the decision of reagent used to upgrade the arrangement of HO[•] from H₂O₂ decay. The dynamic metal specie is devoured as a reagent and lost through precipitation extremely confines the procedure productivity. Thus, the persistent supply of metal reagent is expected to support the enactment of H₂O₂ which causes the issue of metal sludge.

Hence, the metal initiated deterioration of H₂O₂ ought to require the era of the dynamic metal specie through a redox cycle. To accomplish this target, the redox condition of metal species ought to be steady over an extensive variety of pH. Chromium exists in more extensive scope of oxidation states (from -2 to +6), with the trivalent [Cr³⁺] and hexavalent [Cr⁶⁺ or chromate] species ordinarily found in water (Bokare and Choi, 2010).

Cr⁶⁺ is a strong oxidant [E⁰ (HCrO₄ /Cr³⁺) = 1.35 V] and rapid reaction occurs with several reducing agents (such as Fe⁰, Fe²⁺, S²⁻, and natural organic based material) to form Cr³⁺. However, Cr³⁺ is thermodynamically stable under reduction process and is readily oxidized to Cr⁶⁺ by FeOH²⁺. H₂O₂ alone can interconvert Cr³⁺ and Cr⁶⁺ into each other because of its capacity to behave as both an oxidizing agent [E⁰ (H₂O₂/H₂O) = 1.77 V] and a reducing agent [E⁰ (O₂/H₂O₂) = 0.68 V] (Bokare and Choi (2010). The reducing strength of H₂O₂ strongly increases with decrease in pH. The H₂O₂-induced reduction of Cr⁶⁺ to Cr³⁺ is used for removal of chromate from the wastewaters.

Bokare and Choi (2011) investigated the oxidative degradation of organic pollutants which are water soluble, using 4-chlorophenol (4-CP) as the primary substrate. This was achieved with the concurrent H₂O₂ mediated transformation of Cr³⁺ to Cr⁶⁺. As a result, generation of HO[•] using Cr³⁺/H₂O₂ and Cr⁶⁺/H₂O₂ reactions is possible, either concurrently or sequentially. They reported 90% degradation of 4-CP at pH 7.

The reaction between Cr^{3+} and H_2O_2 system generates hydroxyl radical (HO^\bullet) like Fenton's reaction with simultaneous formation of process intermediate Cr^{4+} species and Cr^{4+} immediately generates another HO^\bullet from H_2O_2 and generate Cr^{5+} species and so on.



6. SUMMARY AND CONCLUSION

Quality and quantity wise textile effluent water playing a big role of industrial pollution in Environment. Organics, color (dye), COD, heavy metals present in wastewater is far higher than the standard recommended by CPCB. Proper treatment technology needs to establish to reduce the level of pollution.

Textile industry wastes can be treated with or without isolation of emanating streams. Treatment of gushing streams on the whole can give recuperation of water however the parsonage of salt may not be attainable. Isolation of emanating streams on other hand makes it conceivable to recuperate both water and salts. The exceptionally dirtying emanating streams, for example, spent color shower have low volume, which are typically 10 for each penny of the aggregate gushing release. The rest of the 90 for every penny of gushing is contributed by low dirtying streams like wash water. Partition of these streams could be managed to the point that low contaminating stream contains ostensible broke down solids with the goal that it meets quality necessity for its reuse or transfer after treatment. Propel treatment strategies can be properly connected to oversee both the effluent streams. The advance treatment techniques, while decreasing the contamination issues likewise give scope for recuperation and reuse of water and salts.

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