Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater:
A Review

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Abstract—Textile wastewater containing dyes are difficult to treat by conventional biological processes as most of the dyes are non-biodegradable and are toxic to the microorganisms. These dyes can be easily treated if the conventional treatment methods are incorporated with the advanced oxidation process which can break the complex structure of the dye and make it more amenable to bio-degradation. This paper reviews different Advanced Oxidation Processes (AOPs) like ozonation, hydrogen peroxide, UV radiation and their combination for comparison of treatment efficiencies for remediation of textile wastewater. The paper reveals that the treatment efficiencies of various options depends on the characteristics of the wastewater to be treated.

Keywords—Textile Wastewater; Dyes; Advanced Oxidation Processes

I. INTRODUCTION

The textile wastewater is characterized by high content of dyestuff, salts, high COD derived from additives, suspended solid (SS) and fluctuating pH. The textile industry uses approximately 21-377 m³ of water per ton of textile produced and thus generates large quantities of wastewater from different steps of dyeing and finishing process [1]. The textile wastewater treatment is a very serious problem due to several reasons viz., a) high Total Dissolved Solids (TDS) content of the waste water, b) presence of toxic heavy metals such as Cr, As, Cu, Zn, etc., c) non-biodegradable nature of organic dye stuffs present in the effluent, and d) presence of free-chlorine and dissolved silica [2]. The major environmental concern is the removal of colour from textile and dyestuff manufacturing wastewater. [3] reported that out of 87 dyestuff only 47% are biodegradable.

Conventional process used to treat wastewater from textile industry includes chemical precipitation with alum or ferrous sulphate which suffers from drawbacks such as generation of a large volume of sludge leading to the disposal problem, the contamination of chemical substances in the treated wastewater, etc. Moreover these processes are inefficient in completely oxidizing dyestuffs and organic compounds of complex structure. To overcome these problems advanced oxidation processes (AOPs) have been developed to generate hydroxyl free radicals by different techniques. AOPs include hydrogen peroxide (H₂O₂), Ozone (O₃) and UV irradiation, which have proved to be much efficient in treatment process [4], [5].

This paper reviews different advanced oxidation processes (O₃, O₃/UV, H₂O₂/UV, O₃/H₂O₂/UV, Fe²⁺/H₂O₂) used for treating the textile wastewater. It highlights the efficacy and limitations of all the processes involved in the oxidation and treatment of textile wastewater.

II. CHARACTERISTICS

Characteristics of textile wastewater vary from plant to plant depending upon the processes used. The main parameters that characterize the textile wastewater are Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS), Dissolved Solids (DS), pH, Chloride, Sodium, etc. Typical wastewater characteristics are shown in Table 1. Textile wastewater exhibit low BOD to COD ratio (0.1) reflecting large amount of non-biodegradable organic matter. [3], [6]. COD values are extremely high as compared to other parameters. Though low Bio-Chemical Oxygen Demand, the effluent may be toxic to aquatic life and can’t be disposed off without treatment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.0– 10.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>35-45 C</td>
</tr>
<tr>
<td>Biochemical Oxygen Demand (mg/L)</td>
<td>100 – 4,000</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (mg/L)</td>
<td>150 – 10,000</td>
</tr>
<tr>
<td>Total Suspended Solids (mg/L)</td>
<td>100 – 5,000</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg/L)</td>
<td>1,800 – 6,000</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>1,000 – 6,000</td>
</tr>
<tr>
<td>Total Alkalinity (mg/l)</td>
<td>500 - 800</td>
</tr>
<tr>
<td>Sodium (mg/l)</td>
<td>610 – 2,175</td>
</tr>
<tr>
<td>Total Kjeldahl Nitrogen (mg/L)</td>
<td>70 – 80</td>
</tr>
<tr>
<td>Colour (Pt-Co)</td>
<td>50-2500</td>
</tr>
</tbody>
</table>

* Source [1, 2, 11, 17, 19, 30, 45]

III. ADVANCED OXIDATION PROCESSES (AOPs)

The aim of AOP is the generation of free hydroxyl radical (OH·), a highly reactive, non-selective oxidizing agent (Eₒ=2.8 V), which can destroy even the recalcitrant pollutants. The generation oh hydroxyl is highly accelerated by combining ozone (O₃), hydrogen peroxide (H₂O₂),
titanium dioxide (TiO₂), heterogeneous photo-catalysis, UV radiation or high electron beam radiation. Various types of AOPs include Ozone/H₂O₂, Ozone/UV/H₂O₂, Ozone/TiO₂/H₂O₂, Ozone/TiO₂/UV, H₂O₂/Fe²⁺, H₂O₂/UV/Fe²⁺, Ozone/UV [7].

IV. OZONE (O₃)

Ozone can be artificially produced by the action of high voltage discharge in air or oxygen. There are various types of ozone generators like corona discharge tube ozone generator, UV ozone generators, vacuum-ultraviolet (VUV) ozone generators, Plasma fire Glass Tube and Cold Plasma Ozone Generator. Ozone is highly unstable and must be generated on site. Its oxidation potential (-2.07V) is greater than that of hypochlorite acid (-1.49V) or chlorine (-1.36V). The free radicals (HO₂⁺ and HO⁺) produced due to the decomposition of ozone, react with a variety of impurities such as metal salts, organic matter including micro organisms, hydrogen and hydroxide ions. They are more potent germicides than hypochlorite acid by factors of 10 to 100 fold and disinfect 3,125 times faster than chlorine.

There are three fundamental mechanisms which apply to the oxidation of organic compounds reacting with ozone i.e. (a) the addition mechanism which occurs with organic compounds containing aliphatic unsaturated compounds, such as olefin; (b) the ozonide Mechanism in which ozone can add across a double bond to form an ozonide. This reaction occurs readily in non aqueous solvents, but as soon as water is added, the ozone hydrolyzes to other products, with cleavage of the former double bond; and (c) the substitution mechanism involves replacement of one atom or functional group with another. This specific reaction also can be viewed as an insertion reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydrogen group on the ring: oxidation also can involve cleavage of carbon-carbon bonds to produce fragmented organic compounds [8].

Ozone application can be generalized into two; a powerful disinfection and a strong oxidant to remove colour and odour, eliminating trace toxic synthetic organic compounds and assisting in coagulation [9]. The biodegradability index (BOD₅/COD) of textile waste water tend to increase due to ozone. However, this increase depends on the type and concentration of dye [10] for example 1.6 times [11], 11-66 times in waste water containing azo dyes and upto 80 times in water containing reactive yellow 84 dye [12]. Ozone treatment of textile waste water also removes its colour depending on concentration of the dye [11, 13, 14]. more is its concentration, higher is the consumption of ozone which can be explained in two ways a) more and more injection of ozone, enhances mass transfer and hence, its concentration in liquid phase, b) more is the concentration of die more are the intermediates present to consume ozone for their oxidation [10]. Bio treated textile wastewater on 40-60 min ozonation yielded 99% of decolourisation efficiency [15].

Different factors like pH, COD and temperature effect ozonation. Reference [8] documented that ozone, at low pH levels (less than 7), reacts primarily as the O₃ molecule by selective and sometimes relatively slow reactions. Ozone at elevated pH (above 8) rapidly decomposes into hydroxyl free radicals, which react very quickly and hence, pH ranging from 8 to 10 is most suitable for oxidation of organic molecules. According to [12] ozonation of the hydrolyzed dye (Reactive Yellow 84) decreased as solution pH decreased from 6.1 to 3.2 when ozone concentration was 18.5 mg/L. [14] documented 32% reduction in the dye decolourisation time when the pH values changed from 2 to 12. Hydroxyl radical produced due to decomposition of ozone explains the increased dissociation of ozone with increasing alkalinity [16]. Previous researchers documented that pH also effects the COD and TOC removals using ozone [10]. Low COD removal of disperse dyes (10%) at pH 8 and 0.5g dm⁻³ of ozone concentration were discovered by [4] while, [17] documented high TOC removal for simulated reactive dye bath effluent at pH 7 and 2,970 mg/L of ozone concentration. Higher TOC and COD removals are because of the fact that at pH 7, the radical type reaction becomes effective and also the simultaneous inhibiting effect of carbonate ions is very less [10].

Temperature and COD also affect ozonation. Reference [18] documented that colour removal of bio-treated textile wastewater depends on initial COD of textile wastewater. About, 99% and 95% of colour removal was achieved when initial COD was 160 and 203 mg/L, respectively. In addition, colour removal efficiency increased with increasing the temperature from 25°C to 50°C. Reference [13] documented COD removal depended on strength of dye waste, where slight COD reduction occurred from the medium and high dye waste. The low COD reduction is attributable to the fact that the structured polymer dye molecules are oxidized by ozonation to small molecules, such as acetic acid, aldehyde, ketones, etc., instead of CO₂ and water. According to [10] high colour removal can be achieved on wastewater, which contains high initial dye concentration and low initial COD. There are several catalysts used in conjunction with Ozone such as semi-precious and precious metals, ultrasonic agitation, H₂O₂, electro-coagulation. The O₃/UV process is much more effective relative to simple treatment using ozone as this process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals [10]. Maximum radiation output of 254 nm from the UV lamp must be used for an efficient ozone photolysis. This fact has also been proved by [19] who found O₃/UV treatment of biologically treated textile wastewater reduced COD from 200-400 mg/L to 50 mg/L in 30 minutes, while, using ozone alone COD reduced to 286 mg/L in same duration. Reference [20] documented that using O₃/UV process high COD removal would be achieved under basic conditions (pH=9).

V. PEROXONE (H₂O₂/O₃)

When a mixture of hydrogen peroxide and ozone is used to treat wastewater, H₂O₂ acts as a catalyst and accelerates the decomposition of ozone to hydroxyl radical. At acidic pH, H₂O₂ reacts very slowly with O₃ whereas at high pH the dissociation of H₂O₂ into HO₂⁺ is very high which in turn initiates ozone decomposition more effectively than OH⁺.
Reactive Yellow 15 using 
complete decolourization of C.I. Reactive Blue 220 and C.I. the type of dye decolorized. Reference [25] achieved 
flow rate) and at this condition, the mass ratio of removed 
discoloration of the dyes.

Temperature does not have any significant effect on 
decreases resulting in the decrease in efficiency. 
Hence the instantaneous concentration of hydroxyl radicals 
scavenging effect of carbonate at higher pH values [10]. 
Moreover, the H2O2 alone is quite ineffective in the treatment of textile wastewater at both alkaline and acidic pH [26], while under 
UV irradiation, H2O2 are photolysed to form two hydroxyl radicals (2OH*) which react with organic contaminants [10]. 
Hydroxyl free radicals have a higher oxidation potential (2.8 
V) than hydrogen peroxide (1.78 V). Reference [27] has 
demonstrated that UV-H2O2 process is able to destroy totally 
the chromophoric structure of dyes with the varying reaction rates for different dyes. H2O2/UV offers several advantages 
on other AOPs viz., (i) no sludge generation during any stage of treatment (ii) can be carried out under ambient conditions (iii) oxygen formed can be utilized for aerobic biological decay process.
pH plays a significant role in the discoloration of dyes by 
H2O2/UV process. The process has been found to be more effective in an acid medium in context to discoloration [27]. Reference [28] demonstrated that increasing the pH from the 7.29 to 11.11 led to a decrease in the removal efficiency from 100% to 86.96%. This decrease in efficiency at alkaline pH can be attributed to the fact that a part of H2O2 is used for the oxidation of alkalai forming dioxygen and water rather than producing hydroxyl radicals under UV radiation. Moreover, the H2O2/UV process is more sensitive to the scavenging effect of carbonate at higher pH values [10]. Hence the instantaneous concentration of hydroxyl radicals decreases resulting in the decrease in efficiency. Temperature does not have any significant effect on discoloration of the dyes.

Dose of H2O2 also plays a vital role in discoloration process. Removal efficiency increases as the doses of H2O2 is increased up to a certain critical value after which the efficiency starts to decrease [16, 22, 27, 28]. Keeping other factors stabilized, the decolorization efficiency decreased 
from 90.69% to 82.3% when the dose was increased from 
10cm² to 12cm² [28]. High level of H2O2 acts as a scavenger for hydroxyl radicals [29]. At high concentration H2O2 starts to compete with the dye for reaction with hydroxyl radicals since H2O is less reactive than OH* radical. In addition, the OH* radicals generated at high concentration will readily dimerise to H2O [30]. Hence the dose of H2O2 needs to be optimized so as to maximize the efficiency.

Contact time also affects the decolorization process. The reaction time required for dye removal using H2O2 varies 
according to the type of dyes. Complete destruction of reactive dyes and azo dyes have been recorded in 30-90 minutes [31, 32]. It has been documented that depending upon the initial atrazine concentration, more than 99% of the atrazine can be degraded in less than 15 minutes [7]. Higher reaction time enhances the colour removal process.

Initial dye concentration and H2O2/UV removal efficiency are inversely related. The increase in dye concentration 
simply increases the number of dye molecules and not the hydroxyl radical concentration. Moreover it induces a rise in internal optical density and the solution becomes more and more impermeable to UV radiation. Consequently the rate of photolysis of hydrogen peroxide which depends directly on the incident intensity decreases. So when initial dye concentration in increased, the production of hydroxyl radicals decreases [28] and thus the removal efficiency decreases.

It was found that although the decolorization efficiency reaches 100%, the total organic carbon (TOC) removal did not reach that percentage. Reference [28] found that the final TOC of a dye containing initial TOC concentration of 62 mg/dm² and undergoing 100% decolorization to be 4.34 mg/dm² (93% removal efficiency). Reference [31] also demonstrated 80-82% of TOC removal in 1-2 hrs for reactive dyes by H2O2/UV process. This can be attributed to the destruction of dye into intermediates that are no longer visible and need smaller amounts of oxygen to completely oxidize while at the same time causing high TOC values [33]. The decomposition rate of dye increases with the increase in UV light intensity [34]. Under optimal conditions, the removal efficiency increased from 90.69% to 100% by increasing the UV power from 18 to 54 W. This increase in decolorization is due to the increased production of hydroxyl radical [35].

VII. FENTON’S REAGENT (H2O2:Fe²⁺)
The Fenton’s process generates great amount of 
radicals with powerful oxidizing potential (2.8 eV) which has a very short life, but is reactive and attacks dyes by either abstracting a hydrogen atom or adding itself to double bonds
The Fenton process can be defined as the oxidation of organic compounds in an aqueous solution. Initially an 
increase in colour removal was observed with the increase in ferrous sulphate amount for all concentrations of green cationic dyes. The fact that the rate of decolourization increases with an increase in the concentration of ferrous ions was shown in the study performed by [36] on green cationic dyes in textile wastewater. The pH of the solution,
amount of ferrous ions, concentration of \( \text{H}_2\text{O}_2 \), initial concentration of the pollutant and presence of other ions considerably affects the Fenton process [37]. Fenton’s reagent can be electro-produced with abundant and cheap feedstock: oxygen saturated wastewater and solar energy [38]. Fenton’s oxidation (FO) was used to degrade Remazol Black 5, Remazol Red, Remazol Blue, Remazol Yellow and was found highly effective in their decolourisation (>99%) [39]. The optimal values of hydrogen peroxide and ferrous ion concentrations were found to be 3 and 0.3 M, respectively which resulted in a COD reduction of 56.4% with temperature having a mild effect [40]. It was also discovered that in the first 10 min of the Fenton’s reaction, more than 90% of COD removal can be achieved. Fenton’s oxidation process is not only effective for decolourisation of dyes but degradation of aromatic Amines is also possible at pH 3. More than 95% of colour was removed with Fenton’s oxidation process for RB5, RB13, and AO7 azo dyes [41]. [42] obtained 100% colour removal and more than 90% decrease in COD with the Fenton process conducted at pH 3, \( \text{Fe}^{2+} \) dose = 400 mg/L and \( \text{H}_2\text{O}_2 \) = 550 mg/L on industrial waste water.

VIII. TiO\(_2\)/UV

The mechanism lies in the production of OH free radical by induction of electron transformation using UV illumination. Although its mechanism is similar to that of \( \text{H}_2\text{O}_2/\text{UV} \), \( \text{O}_3/\text{UV} \), etc, TiO\(_2\) is preferred over other due to its stability under various conditions, its high potential to produce radicals and its easy availability and low price [43]. TiO\(_2\) is introduced with the help of reactors for example Thin Film Fixed Bed Reactor (TFFBR) or Aerated Cascade Photoreactor (APC). However APC have shown 3-13 times higher degradation efficiency than TFFBR. A study on effect of TiO\(_2\)/UV on acid blue 9 has shown the degradation efficiency to be 97%. The kinetics of the degradation was found to be of zeroth order with the initial concentration of dye and catalyst affecting the kinetics and the order of reaction. Several studies are still on way to optimize the performance of this method [44].

IX. CONCLUSIONS

Advanced oxidation processes are better treatment options than the conventional treatment methods commonly adopted in wastewater treatment plants. These methods provide complete removal of refractory organics like dyes and reduce the toxicity of the effluent discharged into the streams and rivers. Various combinations of AOP processes like ozone, UV, \( \text{H}_2\text{O}_2 \) etc. may provide efficient treatment of textile wastewater depending upon the characteristics of wastewater to be treated. Further, the economic optimization of these processes must be worked out for treating voluminous amount of wastewater by AOPs.

REFERENCES


“Oxidation of acid red 151 solutions by peroxxone (O3/H2O2) process”- A thesis submitted to the Graduate School of Natural and Applied Sciences of Middle East Technical University by Ebru Acar in partial fulfillment of the requirements for the degree of master of science in chemical engineering, September 2004, link- etd.lib.metu.edu.tr/upload/12605527/index.pdf


