Effectiveness of Photocatalytic Decolourization of Reactive Red 120 Dye in Textile Effluent Using UV/H$_2$O$_2$

Rishi Ananthashankar and Abdel Ghaly

Department of Process Engineering and Applied Science,
Faculty of Engineering, Dalhousie University, Halifax, Canada

ABSTRACT

The effectiveness of Advanced Oxidation Process (AOP) for degradation of reactive red 120 dye in aqueous solutions was tested in this present study. Ten different concentrations of the reactive red 120 dye were exposed to UV alone and a combination of UV with two different concentrations (10 ml/L and 20 ml/L) of H$_2$O$_2$ for 10 different retention times at the pH of textile effluent (pH = 10-11). The effect of acidifying the dye solution on the removal efficiency was also investigated. The COD removal efficiency was determined for the most efficient treatment. The dye degradation efficiency obtained after 60 min exposure to UV alone was 27.01% for 50 mg/L dye concentration and 0.33% for 500 mg/L dye concentration. The degradation efficiency obtained after exposure to UV/10 ml/L H$_2$O$_2$ was 99.83% after 25.4 min for the 50 mg/L dye concentration and 99.70% after 60 min for the 500 mg/L dye concentration. Exposure to UV/ 20 ml/L H$_2$O$_2$ resulted in a degradation efficiency of 99.96% after 20 min for the 50 mg/L dye concentration and 99.95% after 60 min for the 500 mg/L dye concentration. Increasing the H$_2$O$_2$ from 10 ml/L to 20 ml/L (UV/20 ml/L H$_2$O$_2$) improved the oxidation efficiency and reduced the treatment time. The Chemical Oxygen Demand (COD) analysis performed on the effluent obtained from the UV/20 ml/L H$_2$O$_2$ treatment showed a COD removal efficiency of 99.96% (from 704 mg/L to 416 mg/L) after 20 min for the 50 mg/L dye concentration and 99.95% (from 1184 mg/L to 256 mg/L) after 60 min for the 500 mg/L dye concentrations. However the final COD concentrations were higher than the COD discharge limit of 80 mg/L. The COD discharge limit of 80 mg/L could be achieved with UV/ 20 ml/L H$_2$O$_2$ treatment by increasing the exposure time (longer than 60 min). The pH of the treated effluent is within the accepted discharge limit of 6-9. Treatment of the dye effluent under acidic condition was slightly faster but the time reduction does not justify the cost of chemicals addition to adjust the pH to 3 before treatment and then to 7 and the further treatment to remove these chemicals before disposal.

Keywords: Textiles, Waste Waters, Dyes, Reactive Red 120, UV, H$_2$O$_2$, UV/ H$_2$O$_2$, Exposure Time

1. INTRODUCTION

The textile industry is one of the oldest and largest industries in the world. It contributes significantly towards the economic growth of textile producing countries by providing employment with no skills thereby increasing the Gross Domestic Product (GDP) of these countries (Gereffi, 2002; Keane and Velde, 2008). China, India, Hong Kong, USA and Mexico are the top five textile producers with world shares of 50, 15, 6, 5 and 3%, respectively (Fashion Products, 2012). Textile industries uses large amount of water for processing textile products Atif (2002) reported that a typical textile industry in Pakistan manufactures 12-20 tonnes of textiles per day and uses 1,000-3,000 m^3 of water/day (60-80 m^3/t). This amount may vary depending on the type of textile produce and the size of production facility.

The textile industries also use significant amounts of dyes and chemicals. Kant (2012) stated that a normal sized textile industry uses about 0.51-0.58 kg of

chemicals per m^3 of water per day. Significant portions of the textile dyes are found in a high concentration in textile effluents due to the large amount of unfixed dyes on the fabrics that gets washed away during the textile finishing processes. According to Dyes and Pigments (2010), approximately 2-40% of dyes are washed away depending on the type of fabric manufactured. Eswaramoorthi *et al*. (2008) reported that textile effluents have a pH in the range of 6-10, a BOD in the range 80-6,000 mg/L and a COD in the range of 150-12,000 mg/L. The characteristics of the effluents may differ according to the type of textile manufactured. Because of the high concentration of chemicals, textile effluents can cause environmental problems if not treated properly.

The high concentrations of chemicals in textile effluents are capable of harming the environment and human health. Laxman (2009) reported that textile effluents are capable of preventing photosynthesis of aquatic plants by blocking the penetration of sunlight into water. Nese *et al*. (2007) stated that textile effluents could prevent the growth of aquatic organisms by increasing the COD/BOD content of the receiving and depleting dissolved oxygen. Prolonged exposure to textile dyes can cause dermatitis, ulceration of skin, irritation of lungs and skin, headaches, nausea and even cancer in some of the cases have been reported (Mathur *et al*., 2005; Jain *et al*., 2003; Nese *et al*., 2007)

Several treatments are employed to remove contaminant from textile effluents. Suspended solids in textile effluents are removed by primary treatments such as coagulation, sedimentation and screening (EPA, 2003). The BOD, COD and organic substances in the effluent are removed by secondary treatment mechanisms including activated sludge, aerated lagoons and trickling filters (Lafond, 2008; Das, 2000). Dissolved salts and metal ions are removed using tertiary treatment processes such as electrodialysis or reverse osmosis (Babu *et al*., 2007; Das, 2000). However, these primary, secondary and tertiary treatment processes were found to be ineffective as some of the textile dyes are complexly structured and are nearly impossible to be degraded by these methods (Ghoreishi and Haghighi, 2003).

The Advanced Oxidation Process (AOPs) is a new and an efficient treatment for the removal of almost all solid components in textile effluents. A maximum of 42% COD removal from textile effluents can be achieved by biological treatment while upto 72% COD removal form effluent can be achieved with AOP (Montano, 2007; Rodriguez, 2003). AOP has the ability to take place under any temperature or pressure without the production of secondary components or sludge.

AOPs make use of oxidants like UV, O_3, H_2O_2, Fe^{2+}, TiO_2, ultra sound and electron beam irradiation to generate OH° radicals, which have the potential to oxidize the organics in the effluents (Stasinakis, 2008; Gogate and Pandit, 2004). These OH° radicals: (a) have an oxidizing potential of 2.33 V (Kdasi *et al*., 2004), (b) have an affinity towards electrons in the system and hence are called electrophiles and (c) have one unpaired electron on its outer shell which makes them unstable and as such try to attain a more stable configuration by reacting with the organics (Munter, 2001).

2. OBJECTIVE

The aim of the study was to investigate the degradation efficiency of the reactive red 120 (HE3B) dye by an Advanced Oxidation Process (AOP). The specific objectives were to: (a) to study the effect of UV alone on the degradation of varying dye concentrations (50-500 mg/L) at a pH of 10.5 (b) to study the effect of UV/H_2O_2 (using 10 and 20 ml/L H_2O_2) on the degradation of varying dye concentrations (50-500 mg/L) at pH 10.5, (c) study the effect of acidifying the dye solution to pH 3 on the degradation efficiency and (d) determine the Chemical Oxygen Demand (COD) removal efficiency for the best treatment process.

3. MATERIALS AND METHODS

3.1. Experimental Apparatus

A custom build photooxidation system (Figure 1) was used in the experiments. The system consists of a photoreactor, an influent feeding tank, a peristaltic pump and an effluent collection tank. The photoreactor was made up of stainless steel with an inner and an outer diameter of 55 and 61 mm, respectively. The total working volume of the photoreactor was 840 ml (Figure 2). A 448 mm long and 0.85 mm thick stainless steel coil (Figure 3) was placed inside the photoreactor to ensure uniform mixing and exposure of the effluent to UV by creating turbulence. A low pressure mercury lamp (Trojan UV, 3020, Ontario, Canada) enclosed in a 21 mm diameter quartz tube and emitting UV light (380 nm) was inserted into the center of the reactor.

The feeding tank was a 20 cm in diameter cylinder made of Poly Vinyl Chloride (PVC) with a working volume of 12 L. The container had 4 mm thick Plexiglas ^{TM} (Poly Methyl Methacrylate) detachable top which had a 4 mm diameter opening to equalize the pressure difference inside the container caused by pumping the dye solution into the photoreactor.
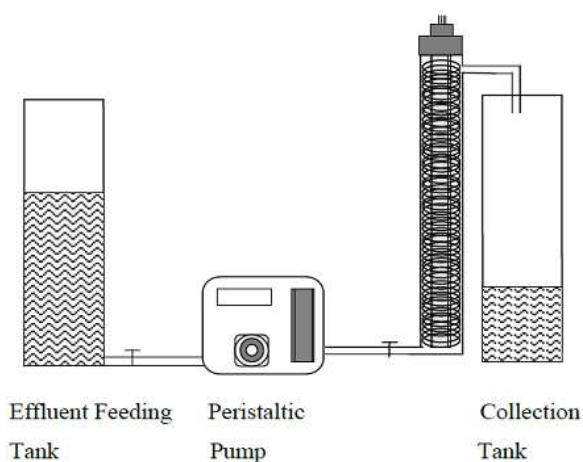
Fig. 1. The photooxidation system

The feeding tank had a fixed bottom made of Plexiglas [TM] and a small outlet port (4 mm diameter) near the bottom to connect the feeding tank to the feeding pump. An identical container was used at the other end of the system to collect the effluent after treatment.

A peristaltic pump (Digi-Staltic, Masterflex Model No: 7523-60, Head Model 77200-50. Barnant Company, Division of Cole Parmer Instrument Co., Barrington, IL, USA.) was used to control the flow rate of the dye solution into the reactor. The pump was connected to the feeding tank and the photoreactor by means of Masterflex precision tubing (06409-14 TYGON, Cole-Parmer Canada Inc., 210-5101, Montreal, Canada.).

3.2. Chemicals

The chemicals used in this study were reactive red 120 dye, hydrogen peroxide, sodium hydroxide and hydrochloric acid. The reactive red 120 (HE3B) dye used in this study was obtained from Sigma Aldrich (R0378-50G, CAS# 61951-82-4, Sigma-Aldrich Inc., St-Louis, MO, USA), 30% Hydrogen peroxide was obtained from Fisher Scientific (Ca #H-325-500, Fisher scientific, Montreal, Quebec, Canada). The sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH to 10.5 (within the pH range of textile effluents of 10-11) and/or to 3. The properties of the reactive red 120 dye are as shown in Table 1.

3.3. Dye Preparation

Reactive red 120 dye concentrations ranging from 50 to 500 mg/L were prepared by dissolving the desired amount of dye in 12 L of water. A digital balance (Model No: PI 314, Denver Instruments, Bohemia, New York, USA) was used to weigh the required amount of dye powder.

Fig. 2. Photo reactor
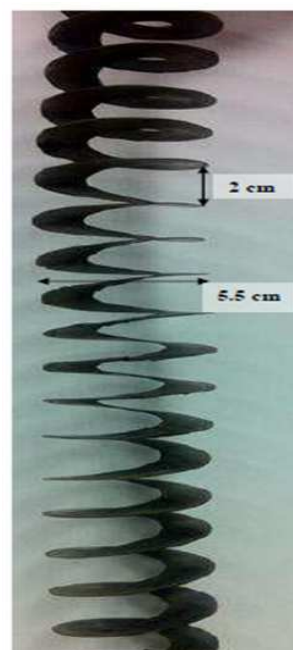
Fig. 3. Stainless steel coil

The dye was then stirred in the water using a magnetic stirrer (Model No: 120S, Fisher Scientific, Ottawa, Ontario, Canada). The resulting solution had a neutral pH of 7. The pH of the solution was adjusted to 10.5 using NaOH. HCl was used to adjust the pH of another batch of

the dye solution to 3. The pH was read using a pH meter (UB-10 Denver Instruments, Bohemia, New York, USA).

3.4. Experimental Procedure

The degradation efficiency of reactive red 120 dye under exposure to UV alone and UV/H_2O_2 was investigated in this study. Ten reactive red 120 dye concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mg/L) were tested under 12 different residence times (5.25, 10, 15, 20, 25.45, 30, 46.66, 49.41, 56 and 60 min) using UV and UV/H_2O_2. Two H_2O_2.concentration (10 and 20 ml/L H_2O_2) were investigated. The flow rate of the peristaltic pump was calculated by dividing the reactor volume by the retention time. The flow rates and the corresponding retention times used in this study are listed in Table 2.
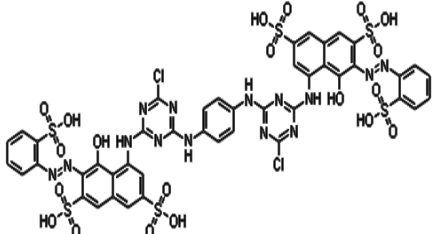
The first set of experiments was carried out using UV alone. The alkaline (pH = 10.5) least concentrated dye solution (50 mg/L) was placed inside the feeding tank and the optical density (OD) was determined. The solution was fed into the photoreactor at the shortest retention time determination. The same procedure was carried out for all dye concentrations and retention times.

The second set of experiments was carried out using UV with 10 ml/L H_2O_2. The alkaline (pH = 10.5) least concentrated dye solution (50 mg/L) was mixed with 10 ml/L H_2O_2 and placed inside the feeding tank. The optical density (OD) was determined and the solution was fed into the photoreactor at the shortest retention time of 5.2 min. Samples were collected from the effluent after reaching steady state and the OD was determined. The same procedure was carried out with all dye concentrations and flow rates.

The third set of experiments was carried out using UV with 20 ml/L H_2O_2. The alkaline (pH = 10.5) least concentrated dye solution (50 mg/L) was mixed with 20 ml/L H_2O_2 and placed inside the feeding tank. The optical density (OD) and chemical oxygen demand (COD) of the dye solution were determined. The dye solution was then fed into the photoreactor at the shortest retention time of 5.2 min. Samples were collected from the effluent after reaching steady state and the OD and COD were determined. The same procedure was carried out with all dye concentrations and flow rates.

The fourth set of experiments was carried out using the best treatment (UV/20 ml/L H_2O_2) with the acidic (pH = 3) dye solutions. The least concentrated acidic (pH= 3) dye solution (50 mg/L) was mixed with 20ml/L H_2O_2 and placed inside the feeding tank. The optical density (OD) and the chemical oxygen demand (COD) of the dye solution were determined. The dye solution was then fed into the photoreactor at the shortest retention time of 5.2 min. Samples were collected from the effluent after reaching steady state and the OD and COD

Table 1. Properties of reactive dye 120 (Red HE3B) (Vinitnantharat *et al.*, 2003).

Properties	Value
Chemical formula	$C_{44}H_{24}Cl_{2}N_{14}Na_{6}O_{20}S_{6}$
Molecular weight	1338.09
Molar Mass	1470
Charge	Negative
Functional group	Diazo
Colour	Bright red
λ_{max} (nm)	511
Structure	

Table 2. Flow rate and the corresponding retention time.

Flow rate (ml/min)	Retention Time (min)
160	05.25
84	10.00
56	15.00
42	20.00
33	25.45
28	30.00
24	35.00
21	40.00
18	46.66
17	49.41
15	56.00
14	60.00

were determined. The same procedure was carried out with all dye solutions and flow rates.

3.5. Experimental Analyses

The chemical oxygen demand (COD) was determined according to the procedure described by APHA (1990). The optical density (OD) of the samples was determined using a spectrophotometer (DR/2500 Illuminator Model, HACH Company, Love land, Colorado, U.S.A) at 535 nm. A dye standard curve was prepared by measuring the OD of samples taken from the ten dye concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L) at 535 nm and plotting the OD values against the dye concentrations. The standard curve (Figure 4) was used to determine the dye concentration in the treated solutions.

4. RESULTS

4.1. UV Treatment

The dye degradation efficiencies of the alkaline (pH = 10.5) dye solutions as a result of exposure to UV alone are shown in Figure 5. When the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution was exposed to UV alone, a maximum degradation efficiency of 27.1% was achieved with the longest retention time of 60 min and only a degradation efficiency of 1.14% was achieved with the shortest retention time of 5.2 min. When the alkaline (pH = 10.5) most concentrated (500 mg/L) dye solution was exposed to UV alone, a degradation efficiency of 0.33% was achieved with the longest retention time of 60 min and no degradation was observed with retention times lower than 60 min.

4.2. UV/10 mL/L H_2O_2 Treatment

The degradation efficiencies of the alkaline (pH = 3) dye solutions as a result of exposure to UV/10 ml/L H_2O_2 are shown in Figure 6. For the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution, a maximum degradation efficiency of 93.62% was obtained when the dye solution was exposed to UV/10 ml H_2O_2 for the shortest retention time of 5.2 min and a maximum degradation of 99.83% was obtained when the dye solution was exposed to UV/ 10 ml/L H_2O_2 for 25.4 min. For the alkaline (pH = 10.5) most concentrated (500 mg/L) dye solution, a maximum degradation efficiency of 20.46% was observed with the shortest retention time of 5.2 min and a maximum degradation efficiency of 99.70% was obtained with the longest retention time of 60 min.

4.3. UV/20 mL/L H_2O_2 Treatment

The dye degradation efficiencies of the alkaline (pH = 10.5) dye solutions obtained as a result of exposure to UV/20 ml/L H_2O_2 are shown in Figure 7. When the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution was exposed to UV/20 ml H_2O_2, a maximum degradation efficiency of 94.2% was obtained with the shortest retention time of 5.2 min while a maximum degradation efficiency of 99.96% was obtained when the dye solution was exposed to UV/ 20 ml/L H_2O_2 for 20 min. For the alkaline (pH = 10.5) most concentrated (500 mg/L) dye solution, a maximum degradation efficiency of 23.33% was observed with the shortest retention time of 5.2 min and a maximum 99.95% degradation efficiency was obtained with the longest retention time of 60 min.
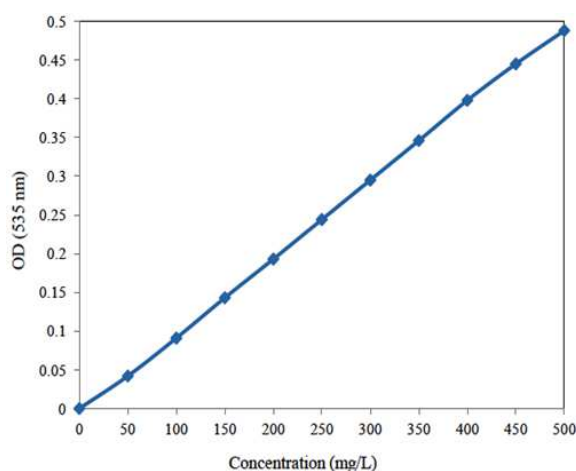

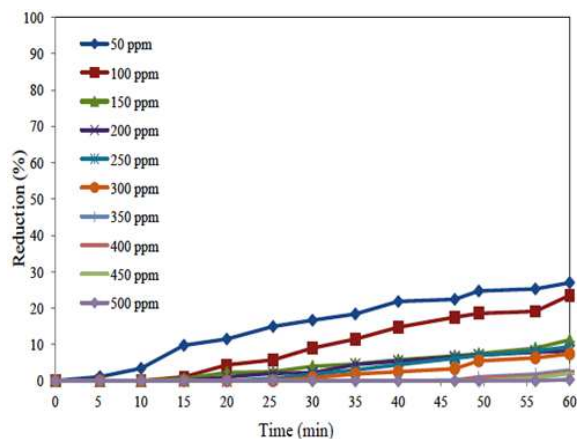Fig. 4. Standard curve for dye concentration

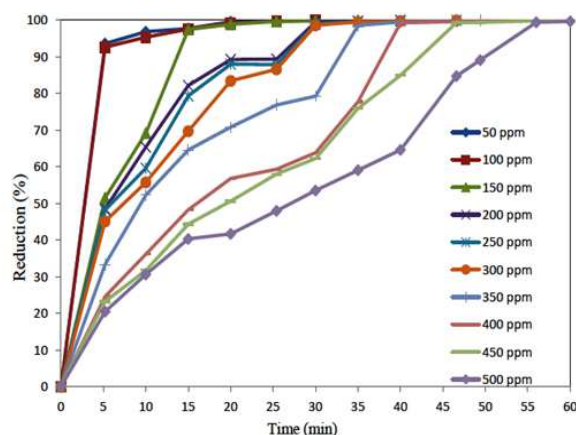Fig. 5. Degradation efficiency of reactive red 120 when treated with UV

Fig. 6. Degradation efficiency of reactive red 120 when treated with UV/10 mL H_2O_2
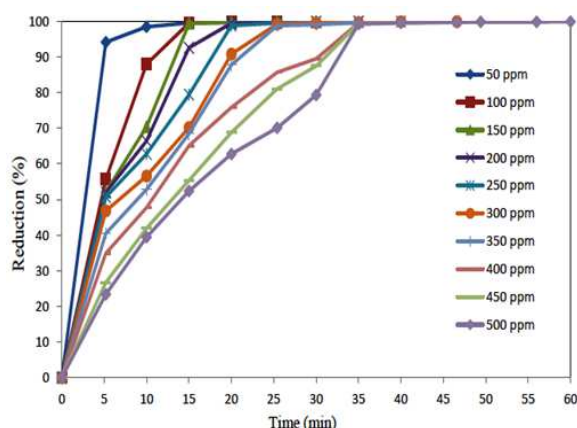
Fig. 7. Degradation efficiency of reactive red 120 when treated with UV/20 mL H_2O_2
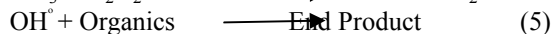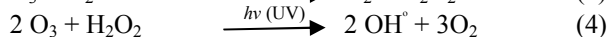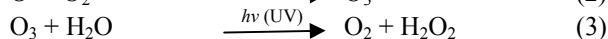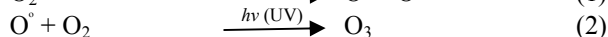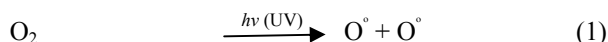
4.4. Chemical Oxygen Demand

The initial results obtained from UV/20 ml/L H_2O_2 provided a better degradation than UV alone and UV/10 ml/L H_2O_2. Therefore, the amount of chemicals in the influent (before treatment) and effluent (after treatment) was determined by performing COD on the samples. The results obtained from the COD analysis are as shown in Figure 8. The highest COD concentration of 704-1184 mg/L (depending on the dye concentration) was observed at 5 minutes from the start of the treatment. The COD then decreased reaching 256-416 mg/L by the end of the experiments, depending on the dye concentration.

5. DISCUSSION

5.1. UV Treatment

The decomposition of textile effluent when exposed to UV could be explained by the following reactions (SET, 2012; EPA US, 2012).

$$O_2 \xrightarrow{\ hv\ (UV)\ } O^\circ + O^\circ \qquad (1)$$

$$O^\circ + O_2 \xrightarrow{\ hv\ (UV)\ } O_3 \qquad (2)$$

$$O_3 + H_2O \xrightarrow{\ hv\ (UV)\ } O_2 + H_2O_2 \qquad (3)$$

$$2\,O_3 + H_2O_2 \xrightarrow{\ hv\ (UV)\ } 2\,OH^\circ + 3O_2 \qquad (4)$$

$$OH^\circ + Organics \longrightarrow End\ Product \qquad (5)$$

Equation 1 shows the production of atomic oxygen radicals as a result of exposure to UV. The oxygen radical (O°) in turn reacts with other oxygen molecules resulting in the production of ozone (O_3) as shown in Equation 2. Equation 3 shows the reaction between ozone and water which results in the production of hydrogen peroxide (H_2O_2). Ozone then interacts with hydrogen peroxide to form hydroxyl radicals (OH°) as shown in Equation 4.
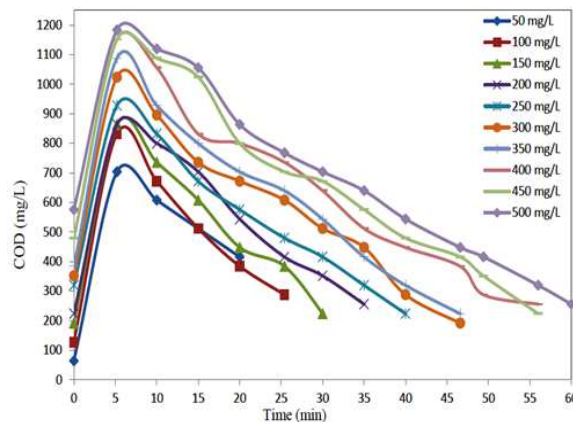

Fig. 8. Chemical oxygen demand of the alkaline solution after treatment with UV/20 mL H_2O_2.

Finally, the produced hydroxyl radicals interact with the dye molecules causing the destruction of the dye.
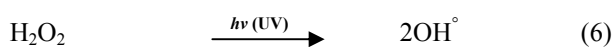
The maximum degradations achieved when the alkaline (pH = 10.5) least concentrated (50 mg/L) and most concentrated (500 mg/L) dye solutions were exposed to UV alone for 60 min were 27.01% and 0.33%, respectively. The results showed that as the dye concentration was increased the dye removal efficiency decreased. No reduction in the dye concentration was witnessed when the alkaline (pH = 10.5) most concentrated (500 mg/L) dye solution was exposed to the UV alone for less than 56 minutes. The low removal efficiency observed in this study was due to the low quantity of hydroxyl radicals produced in the photoreactor and/or the very short life span of ozone and hydrogen peroxide as reported by Kesselman *et al*. (1996).

Several researchers indicated that the use of UV alone as photooxidant was not very effective in destroying textile dyes. Georgiou *et al*. (2002) observed no colour reduction when remazol black B dye solutions were treated with UV alone. Ince and Gonenc (1997) treated an azo dye solution having a concentration of 40 mg/L with UV alone in a photoreactor and observed no significant decomposition of the dye. Ozkan *et al*. (2004) treated azo dyes with UV alone and noted no colour reduction at pH 7 - 11. Galindo and Kalt (1999) stated that the disappearance of dye molecules when used with UV in the absence of other oxidants was negligible. Verma and Ghaly (2008) stated that degradation of textile dyes with UV alone was not effective unless it was accompanied with other photocatalysts. However, in this study, upto 27% removal of the dye was achieved under alkaline condition when the 60 min retention time was used. Therefore, it would be possible to achieve higher removal efficiencies with UV alone using longer retention times.
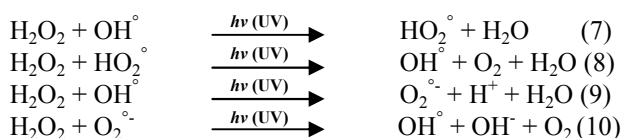
5.2. UV/H$_2$O$_2$ Treatment

UV and H$_2$O$_2$ with different concentrations were used to treat the reactive red 120 dye solution (with different concentrations) under alkaline condition in this study. El-Dein *et al*. (2003) and Daneshvar *et al*. (2005) proposed the following mechanism for the decolourization of organics with the H$_2$O$_2$/UV process. The mechanism includes three steps: initiation, hydroxyl radical propagation and termination.
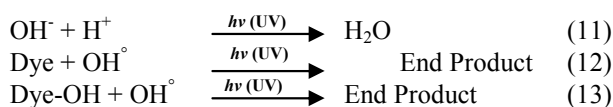
Initiation

$$H_2O_2 \xrightarrow{\;hv\;(UV)\;} 2OH^{\circ} \qquad (6)$$

Hydroxyl radical propagation

$$H_2O_2 + OH^{\circ} \xrightarrow{\;hv\;(UV)\;} HO_2^{\circ} + H_2O \qquad (7)$$
$$H_2O_2 + HO_2^{\circ} \xrightarrow{\;hv\;(UV)\;} OH^{\circ} + O_2 + H_2O \qquad (8)$$
$$H_2O_2 + OH^{\circ} \xrightarrow{\;hv\;(UV)\;} O_2^{\circ -} + H^+ + H_2O \qquad (9)$$
$$H_2O_2 + O_2^{\circ -} \xrightarrow{\;hv\;(UV)\;} OH^{\circ} + OH^- + O_2 \qquad (10)$$

Hydroxyl radical termination

$$OH^- + H^+ \xrightarrow{\;hv\;(UV)\;} H_2O \qquad (11)$$
$$Dye + OH^{\circ} \xrightarrow{\;hv\;(UV)\;} End\ Product \qquad (12)$$
$$Dye\text{-}OH + OH^{\circ} \xrightarrow{\;hv\;(UV)\;} End\ Product \qquad (13)$$

Equation 6 shows the initiation reaction between UV and H$_2$O$_2$ leading to the production of hydroxyl radicals (OH$^{\circ}$). Equations 7, 8, 9 and 10 show the propagation of the reaction involving the production of hydroxyl radicals which helps in the reduction of dye molecules. Equations 11, 12 and 13 show the termination of the reactions which result in the formation of end Product.

When the alkaline (pH = 10.5) reactive red 120 dye solutions of different concentrations (50-500 mg/L) were treated with UV/10ml/L H$_2$O$_2$, near complete degradation (99.70 - 99.96%) was observed for all the concentrations. However, the time required for complete degradation depended on the initial dye concentration. The results showed that 99.83% degradation efficiency was achieved for the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution after 25.4 min when the solution was exposed to UV/10 ml/L H$_2$O$_2$. However, when UV/20 ml/L H$_2$O$_2$ was used with the same dye concentration, 99.96% degradation efficiency was achieved after 20 min. When the alkaline (pH = 10.5) most concentrated dye solution (500 mg/L) was treated with UV/10 ml/L H$_2$O$_2$, a degradation efficiency of 99.70% was obtained after 60 min but when UV/20 ml/L H$_2$O$_2$ was used with the same dye concentration, 99.95% degradation efficiency was obtained after 60 min.

Kdasi *et al*. (2004) stated that treatment of textile dyes with UV/H$_2$O$_2$ was more effective than the treatment with H$_2$O$_2$ alone. Kurbus *et al*. (2003) noted that the decolourisation time required for H$_2$O$_2$/UV process was less than the time required for H$_2$O$_2$/O$_3$. Shu and Chang (2005) compared the decolourization effects of six different azo dyes and found that more than 95% degradation efficiency was achieved when the dye solution was treated with UV/H$_2$O$_2$ in less than 11.5 min, which was higher than the degradation rate achieved with UV/O$_3$ for the same time period. Galindo *et al*. (1999) noted that the actions of UV alone or H$_2$O$_2$ alone on the azo dyes were found to be ineffective (as more than 99% of dye remained in the system after treatment for 120 min) but when the same sample was treated with a combination of UV/H$_2$O$_2$, a dramatic increase in the degradation efficiency of the dye was observed. Verma and Ghaly (2008) reported a 99.9% degradation of 300 mg/L ramazol dye when treated with UV/H$_2$O$_2$ at a retention time of 42 min, which was a much greater degradation than those obtained with just UV or H$_2$O$_2$. Georgiou *et al*. (2002) reported that more than 50% degradation of 100 mg/L reactive dyes was obtained within 20 min under UV/H$_2$O$_2$. Perkowski and Kos (2003) reported that 99% degradation efficiency of the effluents from a dye house was achieved after 2 hours with UV/H$_2$O$_2$. Yang *et al*. (1998) reported that a 95% colour removal was achieved on some reactive, acid, direct and basic dyes when used with UV/H$_2$O$_2$.

Crittenden *et al*. (1999) stated that when H$_2$O$_2$ is exposed to UV, it splits to two hydroxyl radicals which in turn react with the organics in the solution. Georgiou *et al*. (2002) noted that even a small amount of H$_2$O$_2$ (0.1 ml/L) was found to completely destruct colour in less than an hour and if the peroxide amount was increased the destruction time was found to decrease. Modirshahla *et al*. (2007) reported that the improvement in decolourisation was not found to be significant above certain amount of H$_2$O$_2$ due to the recombination of hydroxyl radicals in the solution or the reaction between hydroxyl radicals and H$_2$O$_2$ creating hydroxyl radical scavenging capacity. White (2011) stated that excess amount of H$_2$O$_2$ added to the effluent for treatment might not cause an environmental hazard due to its capacity to degrade under sunlight as shown in Equation 14.

$$2H_2O_2 \xrightarrow{\;Sunlight\;} 2\ H_2O + O_2 \qquad (14)$$
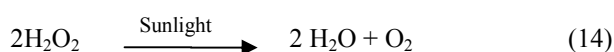
5.3. Acidic Treatment

The 50 mg/L and 500 mg/L dye concentrations were treated with the most efficient treatment (UV with 20 ml/L H_2O_2) at a pH of 3 in order to investigate the effect of pH on removal efficiency. The decolourisation of reactive red 120 dye was found to be faster when treated under acidic pH. A 99.97% degradation efficiency was achieved after 15 min for the acidic (pH = 3) least concentrated (50 mg/L) dye solution and 99.95% degradation efficiency was achieved after at 46.6 min for the acidic (pH = 3) most concentrated (500 mg/L) dye solution compared to 99.96% after 20 min for the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution and 99.95% after 60 min for the alkaline (pH = 10.5) most concentrated (500 mg/L) dye solution as shown in Table 3. It was also observed that the pH of the dye solution was reduced further after the acidic treatment to 2.8 after 15 min exposure time for the least concentrated (50 mg/L) dye solution and to 2.5 after 46.6 min exposure time for the most concentrated (500 mg/L) dye solution.

Several researchers indicated that photooxidation is more efficient under acidic conditions than alkaline conditions. Galindo and Kalt (1999) reported that H_2O_2/UV oxidation was far more efficient when used under an acidic pH. They stated that when H_2O_2 was used with UV under an alkaline condition, it undergoes decomposition forming dioxygen and water which is believed to be the reason for the less initial concentration of $OH^°$. Ganesan and Thanasekaran (2011) reported that the effect of UV/H_2O_2 degradation decreases as the pH increases. They have also noted that the decolourisation efficiency increased as the concentration of H_2O_2 was increased due to the additional production of hydroxyl radicals. Kavitha and Palanisamy (2011) stated that the photocatalytic activity was maximum under acidic condition and was found to decrease when the pH range was increased above 6. Neamtu *et al*. (2003) examined the colour removal efficiency at different pH levels (2, 3, 6.5 and 9.7) and found the best colour removal efficiency (99%) of the reactive red 120 was achieved at a pH of 2 within 15 min. Azbar *et al*. (2004) reported that the best reductions of COD and colour were obtained when the treatment was performed under an acidic pH rather than an alkaline pH.

In this study, the pH was adjusted to 10.5 which is the range of pH for textile effluent. After treatments, the pH decreased and the final pH of the treated effluent was however within the effluent pH discharge limits of 6-9.

Table 3. Maximum removal efficiency for various treatments.

Treatment	Dye Concen-tration (mg/L)	pH	Time (min)	Maximum Removal Efficiency (%)
UV	50	10.5	60.0	27.01
	500	10.5	60.0	0.33
UV/10 ml H_2O_2	50	10.5	25.4	99.83
	500	10.5	60.0	99.70
UV/20 ml H_2O_2	50	10.5	20.0	99.96
	500	10.5	60.0	99.95
UV/20 ml H_2O_2	50	3.0	15.0	99.97
	500	3.0	60.0	99.95

Although, treatment of textile dyes under acidic condition (pH = 3) provided faster decolourisation (16-25%) than those recorded under alkaline conditions, the decrease in decolourization time does not justify the disposal problems associated with lower pH and the cost of chemical addition to the influent to bring the pH to 3 before treatment and then to the effluent to bring the pH to the neutral value before final disposal.

5.4. Chemical Oxygen Demand

When the H_2O_2 was increased to 20 ml/L (UV/ 20 ml/L H_2O_2), the dye degradation was much better (99.96% after 20 min for 50 mg/L dye concentration and 99.95% after 60 min for 500 mg/L dye concentration). Since the UV/20 ml/L H_2O_2 was the most efficient treatment for the dye at all concentrations, the Chemical Oxygen Demand (COD) analysis was performed on the samples obtained from the UV/20 ml/L H_2O_2 treatment to determine the amount of chemicals present in the solution after treatment. From the COD results it was evident that the longer the exposure time, the more the reduction in COD values (416 mg/L for 50 mg/L dye concentration after 20 min and 256 mg/L for 500 mg/L dye concentration after 60 min). Hence textile effluents could be exposed to UV/ 20 ml/L H_2O_2 for more than 60 min to lower the COD to the disposal limit of 80 mg/L (CCME, 2012).

Soutsas *et al*. (2010) stated that, the COD reduction was a function of the dye concentration, the higher the dye concentration, the lower the reduction. They attained complete dye degradation when a dye concentration of 100 mg/L was exposed to UV/H_2O_2, while only an 86% reduction was found when the solution was exposed to UV without H_2O_2. Azbar *et al*. (2004) reported COD reduction of 90% when polyester and acetate dyes were treated with UV/H_2O_2 for a retention time of 90 min, but they attained a higher COD and colour removal when they performed the experiments under an acidic

condition (a pH of 3). Kurbus *et al.* (2003) reported a higher COD reduction with H_2O_2/UV compared to H_2O_2/Fe^{2+}. Shu and Hsieh (2006) experimented with azo, acid and reactive dyes and noted 41.2% COD reduction after being exposed to UV alone for 180 min, 20% COD reduction after being exposed to H_2O_2 alone for 72 hours and 99.5% COD reduction after being exposed to a combination of UV and H_2O_2 for 120 min. Bedoul *et al.* (2008) reported that the COD reduction rate was increased as the amount of H_2O_2 was increased from 1.8 ml/L to 2.75 ml/L.

The results obtained in this study showed that the increase in COD under acidic condition (618 mg/L for 50 mg/L concentration and to 454 mg/L for 500 mg/L) compared to that under alkaline condition (416 mg/L for 50 mg/L concentration and 256 mg/L for 500 mg/L) will require additional costly treatment.

5.5. Effect of Temperature

The current study was carried out at the ambient temperature ($25^{\circ}C$). Muruganandham and Swaminathan (2004) stated that the low pressure UV lamps were found to emit low energy and the rise in the temperature of the dye solution had no effect on the removal efficiency of reactive orange 4. The authors stated that when textile dyes of various concentrations (78-390 mg/L) were exposed to low pressure UV lamps, the photons produced were not able to penetrate the organics and as a result the production of hydroxyl radicals (OH°) are decreased (Equations 1-4). They also suggested the use of additional oxidants for effective removal efficiency.

Chaudhuri and Sur. (2000) reported to have no change in the degradation value of brilliant red 4BLI, orange 3RLI, scarlet PRI, Turquoise PBI and Yellow 4GI when treated with UV/H_2O_2 at temperatures ranging from $29^{\circ}C$ to $59^{\circ}C$. Galindo and Kalt (1999) and Kdasi *et al.* (2004) reported no change in degradation values when the dyes acid orange 5, 6, 7, 20 and 52 were treated with UV/H_2O_2 at temperatures ranging from $22^{\circ}C$ to $45^{\circ}C$. Mahmoud *et al.* (2007) observed decreases in decolourization efficiency of remazol brilliant blue dyes when the temperature was increased from 25 to 100 $^{\circ}C$.

However, some reports in the literature indicated the influence of temperature on the dye degradation when UV is combined with other oxidants. Saien and Soleymani (2007) treated direct blue 71 and reported 7% enhancement in dye degradation as the temperature was increased from 15 $^{\circ}C$ – 45 $^{\circ}C$. The authors suggested that the increase in temperature decreased the solubility of oxygen in water with the consequent reduction in the production of radicals (O°, O_3° and H_2O_2) by UV

(Equations 1, 2 and 3). They concluded a temperature higher than $45^{\circ}C$ should not be used as it will result in low degradation efficiency.

6. CONCLUSION

Ten different concentrations of reactive red 120 dye were exposed to a low pressure UV lamp (380 nm intensity UV) alone and in a combination with 30% H_2O_2 (10 and 20 ml/L) at twelve different retention times. The dye degradation efficiency obtained after 60 min exposure to UV alone was 27.01% for 50 mg/L dye concentration and 0.33% for 500 mg/L dye concentration. The degradation efficiency obtained after exposure to UV/10 ml/L H_2O_2 was 99.83% after 25.4 min for the 50 mg/L dye concentration and 99.70% after 60 min for the 500 mg/L dye concentration. Exposure to UV/ 20 ml/L H_2O_2 resulted in a degradation efficiency of 99.96% after 20 min for the 50 mg/L dye concentration and 99.95% after 60 min for the 500 mg/L dye concentration. Increasing the H_2O_2 from 10 ml/L to 20 ml/L (UV/20 ml/L H_2O_2) improved the oxidation efficiency and reduced the treatment time. The Chemical Oxygen Demand (COD) analysis performed on the effluent obtained from the treatment with UV/20 ml/L H_2O_2 showed a COD removal efficiency of 99.96% (from 704 mg/L to 416 mg/L) after 20 min for the 50 mg/L dye concentration and 99.95% (from 1184 mg/L to 256 mg/L) after 60 min for the 500 mg/L dye concentrations. The final COD concentrations were higher than the COD discharge limit of 80 mg/L. The COD discharge limit of 80 mg/L could be achieved with UV/ 20 ml/L H_2O_2 treatments by increasing the exposure time (longer than 60 min). The pH of the treated effluent is within the accepted limit of 6-9. Treatment of the dye effluent under acidic condition was slightly faster but the time reduction does not justify the cost of chemicals addition to adjust the pH to 3 before treatment and then to 7 before discharge and the further treatment to remove the chemicals before disposal.

7. ACKNOWLEDGEMENT

8. REFERENCES

Atif, S.M., 2002. Impact of Environmental Regulations on the Textile Sector of Pakistan, Geneva.

Science Publications

Azbar, N., T. Yonar and K. Kestioqlu, 2004. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. Chemosphere, 55: 35-43. DOI: 10.1016/j.chemosphere.2003.10.046

Babu, R., A. Parande, S. Raghu and T. Kumar, 2007. Textile technology-cotton textile processing: Waste generation and effluent treatment. J. Cotton Sci., 11: 141-153.

Bedoul, A., K. Sindl and N. Bensalah, 2008. treatment of refractory organics contained in actual agro-industrial wastewaters by UV/H$_2$O$_2$. Clean, 36: 373-379.

CCME, 2012. Canadian Environmental Quality Guidelines and Summary Table.

Chaudhuri, S. and B. Sur, 2000. Oxidative decolourization of reactive dye solution using fly ash as catalyst. Environ. Eng., 16: 583-594.

Crittenden, J., S. Hu, D. Hand and S. Green, 1999. A kinetic model for H$_2$O$_2$/UV process in a completely mixed batch reactor. Water Res., 33: 2315-2328. DOI: 10.1016/S0043-1354(98)00448-5

Daneshvar, N., A. Aleboyeh and A. Khataee, 2005. The evaluation of electrical energy per order (E_{E0}) for photooxidative decolorization of four textile dye solutions by the kinetic model. Chemosphere, 59: 761-767. DOI: 10.1016/j.chemosphere.2004.11.012

Das, S., 2000. Textile effluent treatment – A Solution to the environmental pollution.

Dyes and Pigments, 2010. Textile Dyes.

El-Dein, A., J. Libra and U. Wiesmann, 2003. Mechanism and kinetic model for the decolorization of the azo dye Reactive Black 5 by hydrogen peroxide and UV radiation. Chemosphere, 52: 1069-1077. PMID: 12781240

EPA, 2003. Wastewater Technology Fact Sheet Screening and Grit Removal. Environmental Protection Agency,

EPA US, 2012. Environmental Protection Agency United States.

Eswaramoorthi, S., K. Dhanapal and D. Chauhan, 2008. Advanced in Textile Waste Water Treatment: The Case for UV-Ozonation and Membrane Bioreactor for Common Effluent Treatment Plants in Tirupur, Tamil Nadu, India. Environment with People's Involvement and Co-ordination in India. Coimbatore, India.

Fashion Products, 2012. Fashion Apparel Industry Overview.

Galindo, C. and A. Kalt, 1999. UV–H2O2 oxidation of monoazo dyes in aqueous media: A kinetic study. Dyes Pigments, 40: 27-35. DOI: 10.1016/S0143-7208(98)00027-8

Galindo, C., P. Jacques and A. Kalt, 1999. Photodegradation of the aminoazobenzene acid orange 52 by three advanced oxidation processes: UV/H2O2, UV/TiO2 and VIS/TiO2: Comparative mechanistic and kinetic investigations. J. Photochem. Photobiol., 130: 35-47. DOI: 10.1016/S1010-6030(99)00199-9

Ganesan, R. and K. Thanasekaran, 2011. Decolourisation of textile dyeing wastewater by modified solar photo-fenton oxidation. Int. J. Environ. Sci., 1: 1168-1176.

Georgiou, D., P. Melidis, A. Aivasidis and K. Gimouhopouls, 2002. Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigments, 52: 69-78. DOI: 10.1016/S0143-7208(01)00078-X

Gereffi, G., 2002. Outsourcing and changing patterns of international competition in the apparel commodity chain. Uniersity of Colorado Boulder.

Ghoreishi, S. and R. Haghighi, 2003. Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. Chemical. Eng. J., 95: 163-169. DOI: 10.1016/S1385-8947(03)00100-1

Gogate, P. and A. Pandit, 2004. A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions. Adv. Environ., 8: 501-551. DOI: 10.1016/S1093-0191(03)00032-7

Ince, N. and D. Gonenc, 1997. Treatability of a Textile Azo Dye by UV/H$_2$O$_2$. Environ. Tech., 18: 179-185. DOI: 10.1080/09593330.1997.9618484

Jain, R., M. Bhargava and N. Sharma, 2003. Electrochemical studies on a pharmaceutical azo dye: Tartrazine. Ind. Eng. Chem. Res., 42: 243-247. DOI: 10.1021/ie020228q

Kant, R., 2012. Textile dyeing industry an environmental hazard. Univ. Inst. Fashion Tech, 4: 22-26. DOI: 10.4236/ns.2012.41004

Kavitha, S. and P. Palanisamy, 2011. Photocatalytic and sonophotocatalytic degradation of reactive red 120 using dye sensitized TiO$_2$ under visible light. Int. J. Civil Environ. Eng., 3: 73-89.

Kdasi, A., A. Idris, K. Saed and C. Guan, 2004. Treatment of textile wastewater by advanced oxidation processes – a review. Global Nest. Int. J., 6: 222-230.

Keane, J. and D. Velde, 2008. The role of textile and clothing industried in growth and development strategies. Investment and Growth Programme. Overseas Development Institute.

Kesselman, J., O. Weres, N. Lewis and M. Hoffmann, 1996. Electrochemical production of hydroxyl radical at polycrystalline nb-doped TiO_2 electrodes and estimation of the partitioning between hydroxyl radical and direct hole oxidation pathways. J. Phys. Chem. B,101: 2637-2643. DOI: 10.1021/jp962669r

Kurbus, T., A. Marechal and D. Voncina, 2003. Comparison of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes for the decolorisation of vinylsulphone reactive dyes. Dyes Pigments, 58: 245-252. DOI:10.1016/S0143-7208(03)00085-8

Lafond, R., 2008. Moving Bed Biofilm Reactor (MBBR) A Compact Technology for Upgrading Canadian Municipal Aerated Lagoons. VP Business Development and Marketing.

Laxman, M.S., 2009. Pollution and its control in textile industry. San Blue Enterprises Pvt. Ltd.

Mahmoud, A., M. Brooks and A. Ghaly, 2007. decolorization of remazol brilliant blue dye effluent by advanced photo oxidation process (H2O2/UV system). Am. J. Applied Sci., 4: 1054-1062. DOI: 10.3844/ajassp.2007.1054.1062

Mathur, N., P. Bhatnagar, P. Nagar and M. Bijarnia, 2005. Mutagenicity Assessment of Effluents from Textile/Dye Industries of Sanganer, Jaipur (India): A Case Study. Ecotoxicol. Enviro. Safety, 61: 105-113. PMID: 15814316

Modirshahla, N., M. Behnajady and F. Ghanbary, 2007. Decolorization and mineralization of C.I. acid yellow 23 by fenton and photo-fenton processes. Dyes Pigments, 73: 305-310. DOI: 10.1016/j.dyepig.2006.01.002

Montano, J., 2007. Combination of advanced oxidation processes and biological treatments for commercial reactive azo dyes removal. University of Barcelona.

Munter, R., 2001. Advanced oxidation processes – current status and prospects. Proc. Estonian Acad. Sci. Chem., 50: 59-80.

Muruganandham, M. and M. Swaminathan, 2004. Photochemical oxidation of reactive azo dye with UV–H2O2 process. Dyes Pigments, 62: 269-275. DOI: 10.1016/j.dyepig.2003.12.006

Neamtu, M., A. Yediler, L. Siminiceanu and A. Kettrup, 2003. Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. J. Photochem. Photobiol. A:Chem., 161: 87-93. DOI: 10.1016/S1010-6030(03)00270-3

Nese, T., N. Sivri and I. Toroz, 2007. Pollutants of textile industry wastewater and assessment of its discharge limits by water quality standards. Turkish J. Fisheries Aquatic Sci., 7: 97-103.

Ozkan, A., M. Ozkan, R. Gurkan, M. Akcay and M. Sokmenm, 2004. Photocatalytic degradation of a textile azo dye, Sirius Gelb GC on TiO2 or Ag-TiO2 particles in the absence and presence of UV irradiation: the effects of some inorganic anions on the photocatalysis. Photochem. Photobiol. A: Chem., 163: 29-35. DOI: 10.1016/S1010-6030(03)00426-X,

Perkowski, J. and L. Kos, 2003. Decolouration of Model Dye House Wastewater with Advanced Oxidation Processes. Fibres Textiles Eastern Eur., 11: 67-71.

Rodriguez, M., 2003. Fenton and UV-vis Based advanced oxidation processes in wastewater treatment: Degradation, mineralization and biodegradability enhancement. University of Barcelona.

Saien, J. and A. Soleymani, 2007. Degradation and mineralization of direct blue 71 in a circulating upflow reactor by UV/TiO_2 process and employing a new method in kinetic study. Hazardous Materials 144: 506-512. PMID: 17134827

SET, 2012. Advanced Oxidation Ozone UV Processes. Spartan Environmental Technologies.

Shu, H. and M. Chang, 2005. Decolorization effects of six azo dyes by O_3, UV/O_3 and UV/H_2O_2 processes. Dyes Pigments, 65: 25-31. DOI: 10.1016/j.dyepig.2004.06.014

Shu, H. and W. Hsieh, 2006. Treatment of dye manufacturing plant effluent using an annular UV/H2O2 reactor with multi-UV lamps. Separation Purificat. Technol., 51: 379-386. DOI: 10.1016/j.seppur.2006.03.001

Soutsas, K., V. Karayannis, I. Poulios, A. Riga and K. Ntampefliotis et al., 2010. Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes. Desalination, 250: 345-350. DOI: 10.1016/j.desal.2009.09.054

Stasinakis, A., 2008. Use if selected advances oxidation processes (aops) for wastewater treatment – A mini review. Global Nest., 10: 376-385.

Verma, M. and A. Ghaly, 2008. Treatment of remazol brilliant blue dye effluents by advanced photo oxidation process in TiO_2/UV and H_2O_2/UV reactors. Am. J. Eng. Applied Sci., 1: 230-240. DOI: 10.3844/ajeassp.2008.230.240

Vinitnantharat, S., W. Chartthe and A. Pinitwakul, 2003. Toxicity of reactive red 141 and basic 14 to algae and waterflea. Division Enviro. Technol.

White, R., 2011. 6274, Dalhousie University, Coburg Road, Room 212, Chemistry Building.

Yang, Y., D. Wyatt and M. Bahorsky, 1998. Decolorization of dyes using UV/H_2O_2 photochemical oxidation. Textile Chemist Colorist, 30: 27-35.