

Photocatalytic Decolourization of Textile Effluent Containing Reactive Red 120 Dye With UV/TiO₂

Rishi Ananthashankar and Abdel Ghaly

Department of Process Engineering, Faculty of Engineering, Dalhousie University, Halifax, Nova Scotia, Canada

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ABSTRACT

The efficiency of degradation of an aqueous solution of reactive red 120 dye using Advanced Oxidation Process (AOP) was evaluated. A low pressure UV lamp and a combination of UV/TiO₂ were tested using ten different dye concentrations (50 - 500 mg/L) at several retention times (5.2-60 min) a pH of 10.5. The effect of acidic pH (pH = 3) on dye removal efficiency and the Chemical Oxygen Demand (COD) of the treated effluents were also investigated. When the alkaline (pH = 10.5) reactive red 120 dye solutions were treated using a low pressure (380 nm intensity) UV lamp, a maximum degradation efficiency of 27.01% was obtained for the least concentrated dye (50 mg/L) solution and only a degradation efficiency of 0.33% was obtained for the most concentrated (500 mg/L) dye solution. When the alkaline (pH = 10.5) reactive red 120 solutions were exposed to a combination of UV/TiO₂, a maximum degradation efficiency of 46.70% was obtained for the least concentrated (50 mg/L) dye solution after 60 min and only a degradation efficiency of 2.84% was obtained for the most concentrated (500 mg/L) dye solution after 60 min. When the pH of the reactive red 120 dye solution was reduced to 3, a degradation efficiency of 56.45% was obtained for the least concentrated (50 mg/L) dye solution at 60 min and a degradation efficiency of 14.94% was obtained for the most concentrated (500 mg/L) dye solution at 60 min. However, the increase in degradation efficiency obtained in this study does not justify the cost of chemicals added to adjust the pH to 3 before treatment and then to 7 before final disposal. Also, the addition of chemicals (to adjust the pH) increases the COD of the dye solution thereby necessitating a further costly treatment.

Keywords: Textiles, Wastewaters, Dyes, Reactive red 120, UV, TiO₂, UV/TiO₂, Exposure, Time

1. INTRODUCTION

Textile industries are often considered a pillar in the economic growth of developing (and developed) countries (Chen *et al.*, 2007). They are the backbone of employment in poor countries by providing job with no specialised skills (Keane and Velde, 2008). However, Textile industries are known to utilize huge amounts of water and chemicals in the textile production processes. Kant (2012) reported that a normal sized textile industry, which produces about 8000 kg of textiles per day, utilizes 1.6 million liters of water and 815.68-924.06 kg of chemicals per day (about 0.51-0.58 kg/m³).

Textile fibres undergo various processes including sizing, desizing, scouring, bleaching, mercerizing, dyeing and printing. Various treatment processes are carried out depending on the type of textile fibres (cellulose, protein or synthetic fibre) processed. Numerous amounts of chemicals such as dyes, fixing agents, leveling agents and pH regulators are used during these processes (Ntuli *et al.*, 2009). About 70,000 tonnes of pigments and dyes are used by textile industries annually (Azbar *et al.*, 2004). There is always a portion of dyes that is not fixed to the fabrics during the textile dyeing process and is washed out during the finishing process with the textile effluent (Dyes and Pigments, 2010). Because these effluents are rich in dyes and chemicals (COD, dissolved solids, BOD and heavy

Corresponding Author: Abdel Ghaly, Department of Process Engineering, Faculty of Engineering, Dalhousie University, Halifax, Nova Scotia, Canada Email: Abdel.Ghaly@dal.ca

metals), they cause major environmental and health concerns (Meric *et al.*, 2004; Eswaramoorthi *et al.*, 2008). Prolonged exposure to textile effluents causes dermatitis, severe irritation, ulceration and even cancer (Nese *et al.*, 2007; Jain *et al.*, 2003).

Textile effluents undergo primary, secondary and tertiary treatments before getting disposed of into the environment. Primary treatments such as screening, sedimentation and coagulation are helpful in removing the suspended solids from the effluent (EPA, 2003). Secondary treatments like aerated lagoons, trickling filters and activated sludge systems are used for the removal of BOD, COD and organic substances in the effluent (Das, 2000; Lafond, 2008; Tilley *et al.*, 2008). Tertiary treatment processes including reverse osmosis and electrodialysis are used to separate the effluents from dissolved metal ions or dissolved salts (Das, 2000; Babu *et al.*, 2007). However, these treatment methods are not effective against certain textile dyes. Some of the dye stuff have complex structures which are nearly impossible to be broken down by simple treatment processes (Ghoreishi and Haghghi, 2003).

Advanced Oxidation Processes (AOP) is a newly developed field which makes use of OH° radicals to destroy chemical components that are hard to be oxidised (Alfons and Soo-Myung, 2003; Kdasi *et al.*, 2004; Mahmoud *et al.*, 2007). The oxidants used to generate OH° radicals individually or in a combination include H_2O_2 , UV, O_3 , TiO_2 , Fe^{2+} , electron beam irradiation and ultra sound (Kdasi *et al.*, 2004). OH° radicals are found to have an oxidation potential of 2.33 V and are capable of destroying components that are hard to be oxidised. (Stasinakis, 2008; Gogate and Pandit, 2004; Eswaramoorthi *et al.*, 2008). The advantages of advanced oxidation technologies over other tertiary treatments are: they are fast, do not produce secondary components and do not produce sludge and as such there is no sludge disposal problem (Azbar *et al.*, 2004).

2. OBJECTIVE

The main aim of the study was to investigate the degradation of Reactive Red 120 (HE3B) dye solutions of varying concentration (50-500 mg/L) by Advanced Oxidation Processes. The specific objectives were: (a) to study the effect of UV on the degradation of reactive red 120, (b) to study the effect of combined UV and TiO_2 treatment on the degradation of reactive red 120 dye and (c) study the effect of acidifying the dye solution to pH 3 on the degradation efficiency and (d) determine the chemical oxygen demand removal efficiency of the best treatment.

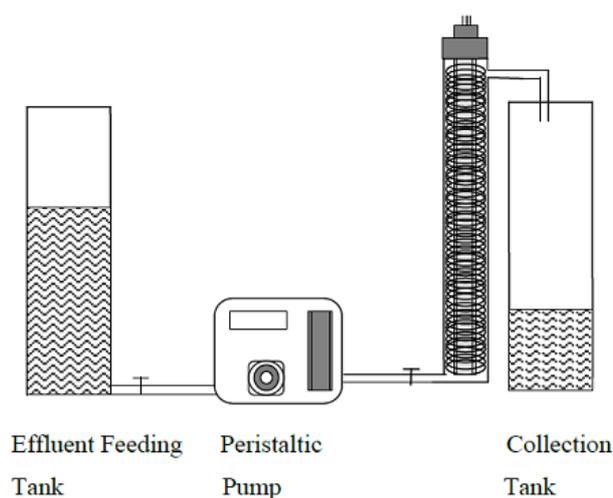


Fig. 1. The photooxidation system

3. MATERIALS AND METHODS

3.1. Experimental Apparatus

The experiments were carried out using a custom built photooxidation system (Fig. 1). The system consisted of a reactive red 120 dye feeding tank, a peristaltic pump, a photoreactor and an effluent collection tank.

The photoreactor (Fig. 2) has an outer and the inner diameters of 61 and 55 mm, respectively. A low pressure mercury lamp (Model UV-3020, Trojan, London, Ontario, Canada), which emits UV light at 380 nm and is enclosed in a 21 mm diameter quartz tube, was used in the photoreactor. The 3 mm stainless steel chamber provides a gap of 17 mm (distance between the quartz sleeve and the inner surface of the reactor casing). A coil (448 mm long and 0.85 mm thick) made out of stainless steel (Fig. 3) with an internal diameter of 21 mm and a pitch of 20 mm was used to create mixing through the spiral motion of the liquid. The working volume of the reactor was 840 mL.

A 12 L dye feeding tank was made of a 20 cm diameter Poly Vinyl Chloride (PVC) container. The PVC container has a detachable top and a fixed bottom made of 4 mm thick Poly Methyl Methacrylate (PMMA or PlexiglasTM) plates. The detachable top has a 4 mm diameter opening to equalize the pressure caused by pumping out the dye from the container by allowing the air flow into the container. A 4 mm outlet port is located in the lower end of the feeding tank and connected to the feeding pump.



Fig. 2. Photo reactor

Masterflex precision tubing (06409-14 TYGON) was used along with a peristaltic pump (Digi-Staltic, Masterflex Model No: 7523-60, Head Model 77200-50. Barnant Company, Division of Cole Parmer Instrument.Co., Barrington, IL) to control the flow (at the required flowrate) of dye solution into the photoreactor. The pump was connected to the feeding tanks and the photoreactor using tygon tubing.

The treated effluent was collected in another 20 mm diameter PVC container with a working volume of 12 L.

The PVC container had a detachable top and a fixed bottom made of 4 mm thick Poly Methyl Methacrylate (PMMA or Plexiglas™).

3.2. Chemicals

The chemicals used in this study were reactive red 120 dye, tetrabutylorthotitanate ($\text{Ti}(\text{OBU})_4$), diethanolamine ($\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$), anhydrous ethyl alcohol, sodium hydroxide (NaOH) and hydrochloric acid (HCl). The reactive red 120 dye was obtained from Sigma Aldrich (R0378-50G, CAS# 61951-82-4, Sigma-Aldrich Inc., St-Louis, MO, USA). Tetrabutylorthotitanate (Titanium (IV) n-butoxide) was obtained from Fisher Scientific (Ca # AC223190010 Fisher scientific, Montreal, Quebec, Canada). The properties of reactive red 120 are shown in **Table 1**.

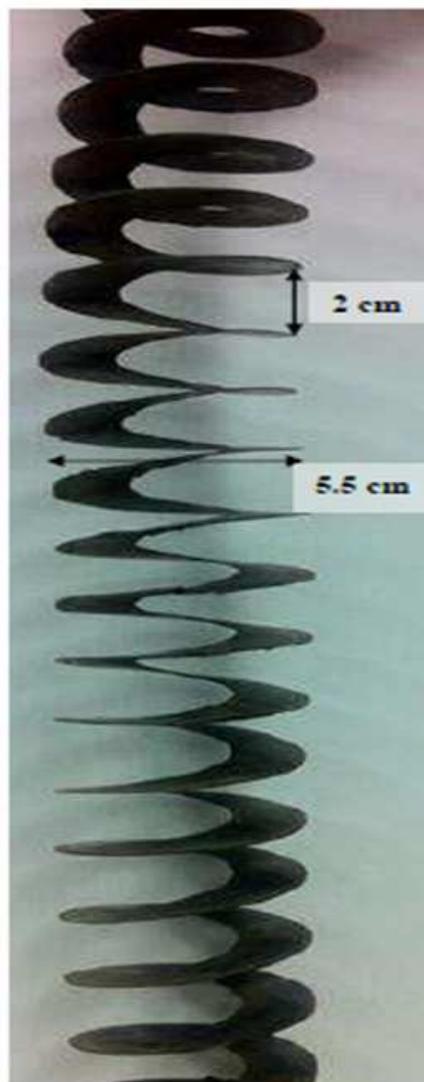


Fig. 3. Stainless steel coil

3.3. Dye Preparation

Ten dye concentrations in the range of 50-500 mg/L of the Reactive red 120 dye were prepared. The desired amounts of the dye to be dissolved in 12 L of water were weighed using a digital balance (Model No: PI 314, Denver Instruments, Bohemia, New York, USA). The solutions were mixed using a magnetic stirrer (Model No: 120S, Fisher Scientific, Ottawa, Ontario, Canada) to ensure that the dye was dissolved completely. The resulting dye solutions had a neutral pH (pH 7). Therefore, the pH of the dye solutions was adjusted to 10.5 which is within the pH range of the textile effluent (10-11) by adding the required amount of NaOH. A pH meter (UB-10 Denver Instruments, Bohemia, New York, USA) was used to measure the pH.

3.4. TiO₂ Preparation

TiO₂ was coated on the coil using the procedure described by Verma and Ghaly (2008). 17.2 mL of Tetrabutylorthotitanate and 4.8 ml of diethanolamine were dissolved in 67.3 ml of anhydrous ethyl alcohol and mixed vigorously for 2 hour. During mixing, 2.7 ml of water and 10 ml of ethanol were mixed together and added to the solution drop wise within 2 hours of mixing. The resulting solution was left to stand for 2 hours in order for the hydrolysis to take place. The stainless steel coil was coated with TiO₂ by immersing the coils into the solution and letting it stand for 15 min. The coil was withdrawn at a rate of 6 mm/sec. The resulting TiO₂ coated coil was calcinated in a furnace (186 A, Fisher Scientific, Montreal, Quebec, Canada) at 100°C for an hour and then at 900°C for 2 hours. The resulting coil was fitted into the UV reactor.

3.5. Experimental Procedure

Experiments were carried out to investigate the degradation efficiency of the photooxidants (UV and UV/TiO₂). Ten different concentrations of the dye solution (50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mg/L) were tested under 12 different retention times (5.25, 10, 15, 20, 25.45, 30, 35, 40, 46.66, 49.41, 56 and 60 min). The retention time of dye solution inside the photoreactor was achieved by controlling the flow rate of the peristaltic pump (Table 2). The flow rate was calculated using the following formula:

$$\text{Flow Rate} = \frac{\text{Reactor Volume}}{\text{Retention Time}} \quad (1)$$

3.5.1. UV Treatment of Alkaline Dye Solutions

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 in the feeding tank. The optical density (OD) of the initial dye solutions was determined. Then, the peristaltic pump was turned on and dye solution was fed into the photoreactor at the lowest retention time of 5.2 min. Samples were collected from the effluent after reaching steady state for OD determination. The same procedure was repeated with all flow rates. The next concentrated alkaline (pH of 10.5) dye solution (100 mg/L) was placed in feeding tank and same procedure was followed with all flow rates. The entire process was repeated with the remaining alkaline dye solutions.

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

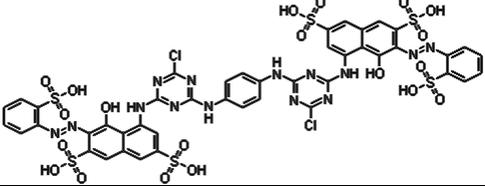
Properties	Value
Chemical formula	C ₄₄ H ₂₄ Cl ₂ N ₁₄ Na ₆ O ₂₀ S ₆
Molecular weight	1338.09
Molar Mass	1470
Charge	Negative
Functional group	Diazo
Colour	Bright red
λ _{max} (nm)	511
Structure	

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

3.5.2. UV/TiO₂ Treatment of Alkaline Dye Solutions

The second set of experiments was carried out using UV/TiO₂. The alkaline (pH = 10.5) least concentrated dye solution (50 mg/L) was placed in the feeding tank. The OD and COD of the initial dye solution were determined. Then, the peristaltic pump was turned on and dye solution was fed into the photoreactor at the retention time of 5.2 min. Samples were collected from the effluent after reaching steady state for OD and COD all flow rates and the remaining alkaline (pH of 10.5) dye solutions (100-500 mg/L).

3.5.3. UV/TiO₂ Treatment of Acid Dye Solutions

The third set of experiments was carried out using UV/TiO₂ with acidic dye solutions (pH = 3). The pH of the dye solution was adjusted to 3 using HCl. The acidic (pH = 3) least concentrated dye solution (50 mg/L) was placed in the feeding tank. The OD and COD of the initial dye solution were determined. The

peristaltic pump was turned on and the dye solution was fed into the reactor at a retention time of 5.2 min. Samples were collected from the effluent after reaching steady state for OD and COD determinations. The same procedure was repeated using the flow rate of 60 min. The procedure was also repeated with the acidic (pH = 3) most concentrated dye solution (500 mg/L) at 5.2 and 60 min retention times.

3.6. Experimental Analysis

The Chemical Oxygen Demand of the samples was determined according to the procedure described by APHA (1980). The optical density 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 taking samples from the ten dye concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L) for optical density measurement. The OD values were plotted against the dye concentrations as shown in Fig. 4. The standard curve was used to determine the concentration of the treated solution.

4. RESULTS

4.1. UV Treatment of Alkaline Dye Solutions

The dye degradation efficiencies for different alkaline dye concentrations as a result of exposure to UV alone are shown in Fig. 5. Increasing the dye concentration and/or reducing the exposure time reduced the dye removal efficiency. When the least concentrated dye solution (50 mg/L) was treated with UV alone, only 27.1% of the dye was removed using the longest retention time of 60 min while only 1.14% of the dye was removed using the shortest retention time of 5.2 min. Also, 0.33% of the most concentrated dye solution (500 mg/L) was removed using the longest retention time of 60 min and no reduction was observed at retention times less than 60 min.

4.2. UV/TiO₂ Treatment of Alkaline Dye Solutions

The dye degradation efficiencies for different alkaline dye concentrations as a result of exposure to UV/TiO₂ are shown in Fig. 6. A removal efficiency of 46.70% was observed for the least concentrated dye solution (50 mg/L) using the longest retention time of 60 min while only 1.64% removal efficiency was achieved using the shortest retention time of 5.2 min.

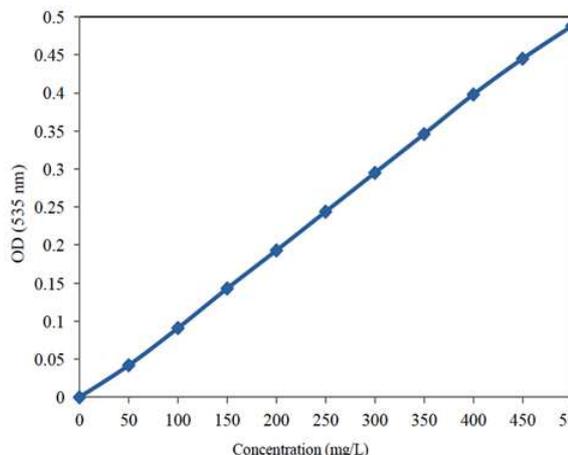


Fig. 4. Reactive 120 dye standard curve

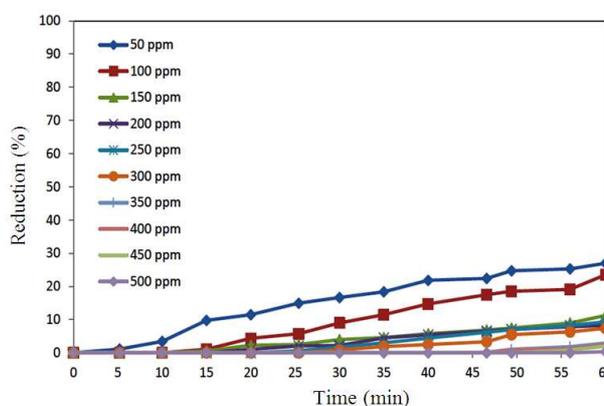


Fig. 5. Reactive 120 dye standard curve

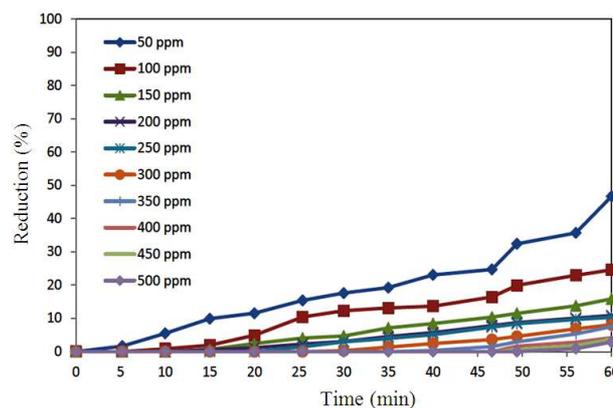


Fig. 6. Degradation efficiency of reactive red 120 dye when treated with UV/TiO₂

When the most concentrated dye solution (500 mg/L) was exposed to UV/TiO₂, only 2.84% of the dye was observed using the longest retention time of 60 min and

no reduction was observed when the shortest retention time of 5.2 min was used.

4.3. UV/TiO₂ Treatment of Acidic Dye Solutions

Several researchers reported increased degradation efficiencies of textile effluent when the pH of the treated dye solution was decreased to 3. In this study, the least concentrated (50 mg/L) and the most concentrated (500 mg/L) dye solutions were treated with UV/TiO₂ after adjusting the pH to 3. The results are as shown in **Table 3**. A degradation efficiency of 86.45% was achieved when the acid dye (pH = 3) of 50 mg/L concentration was exposed to UV/TiO₂ for 60 min compared to a degradation efficiency of 46.70% under the alkaline pH of 10.5. Also, a degradation efficiency of 14.94% was achieved with the most concentrated (500 mg/L) acidic dye solution (pH = 3) after being exposed to UV/TiO₂ for 60 min, compared to a degradation efficiency of 2.84% under alkaline pH of 10.5.

4.4. Chemical Oxygen Demand

Since the UV/TiO₂ treatment was more efficient than UV alone for all dye concentrations, the COD analysis was conducted on the alkaline and acidic dye solution samples obtained after treatments with UV/TiO₂.

The results are as shown in **Table 4**. COD removal efficiencies of 10.42% and 83.43% were achieved for the acidic (pH = 3) least concentrated (50 mg/L) dye solution when exposed to UV/TiO₂ for 5.2 and 60 min compared to a COD removal efficiencies of 5.25% and 41.88% under the alkaline pH of 10.5, respectively. When the acidic (pH = 3) most concentrated (500 mg/L) dye solutions were exposed to UV/TiO₂ for 5.2 and 60 min, COD removal efficiencies of 3.92 and 20.82% were achieved compared to COD removal efficiencies of 2.57 and 7.67% under the alkaline pH of 10.5, respectively.

5. DISCUSSION

5.1. UV Treatment

The decomposition of textile effluent as a result of exposure to UV could be explained by the following reactions (SET, 2012; EPA US, 2012):



Table 3. Degradation efficiency of the reactive red 120 dye treated with UV/TiO₂ at various pH for 5.2 and 60 min as measured by optical density

Concentration (mg/L)	pH	Retention Time (min)	Degradation (%)
50	-3.0	5.2	3.97
		60.0	86.45
		60.0	46.70
500	-3.0	5.2	0.00
		60.0	14.94
		60.0	2.84

Table 4. Chemical oxygen demand of reactive red 120 dye treated with UV/TiO₂ at varying pH and retention times

Concentration (mg/L)	pH	Retention Time (min)	Final COD (mg/L)	Degradation (mg/L)
50	3.0	5.2	43.00	10.42
		60.0	7.95	83.43
		60.0	45.00	6.25
500	10.5	5.2	27.90	41.88
		60.0	462.80	3.98
		60.0	381.64	20.82
500	10.5	5.2	469.60	2.57
		60.0	445.00	7.67

Initial COD of 50 mg/L dye concentration = 48 mg/L

Initial COD of 500 mg/L dye concentration = 482 mg/L

Equation 2 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 (O₃) as shown in Equation 3. Equation 4 shows the reaction between ozone and water which results in the production of hydrogen peroxide (H₂O₂). Also, ozone interacts with hydrogen peroxide to form hydroxyl radicals (OH[°]) as shown in Equation 5. Finally, the produced hydroxyl radicals interact with the dye molecules causing the destruction of the dye (Equation 6).

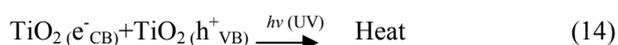
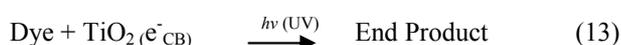
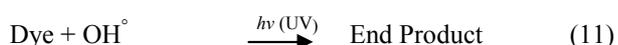
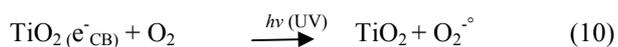
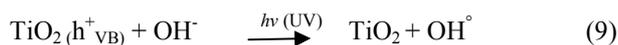
In this study, the maximum degradations achieved when the alkaline (pH = 10.5) least concentrated (50 mg/L) and most concentrated (500 mg/L) dye solutions were exposed to UV for 60 min were 27.01 and 0.33%, respectively. The results showed that as the dye concentration increased the dye removal efficiency decreased and/or the required retention time increased. No reduction in the dye concentration was witnessed when the most concentrated alkaline (pH = 10.5) dye solution (500 mg/L) was exposed to the UV for 56 minutes or less. This very low removal efficiency was due to the low quantity of hydroxyl radicals produced and/or

the very short life span of ozone and hydrogen peroxide produced 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. Galindo and Kalt (1999) stated that the disappearance of dye molecules when used with UV in the absence of other oxidants was negligible. 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) tested the effects of UV on the degradation of azo dyes and noted that when UV was used alone it did not give any colour reduction at a pH in the range of 7-11. Georgiou *et al.* (2002) observed no colour reduction when remazol black B dye solution was treated with UV alone. Verma and Ghaly (2008) stated that degradation of textile dyes with UV was not found effective unless it was accompanied with other oxidants/photocatalysts. However, in this study, upto 27% removal efficiency of alkaline dye with low concentration (50 mg/L) was achieved with UV alone when the 60 min retention time was used. Thus, it may be possible to achieve higher removal efficiencies with UV alone using longer retention times.

5.2. UV/TiO₂ Treatment

Titanium oxide is a naturally occurring compound with oxidizing property. Tang and An (1995) and Tang *et al.* (2010) proposed the following mechanism for the degradation of textile dyes with TiO₂ in the presence of UV:



Where:

TiO₂(h⁺_{VB}) = Valence-band holes

TiO₂(e⁻_{CB}) = Conduction-band electrons

Upon irradiation by UV, the electrons on the surface of the semiconductor (TiO₂) becomes excited forming

positive valance band holes (TiO₂(h⁺_{VB})) and conduction band electrons (TiO₂(e⁻_{CB})) as shown in Equation 7. The valance band holes are good oxidizers and have the potential to oxidise water and OH⁻ into OH[°] radicals as shown in Equations 8 and 9. The conduction band electrons (TiO₂(e⁻_{CB})) on the other hand act as reducers when interacting with O₂ as shown in Equation 10. A chain termination occurs resulting in the destruction of the dye radicals as shown in Equations 11, 12 and 13. Finally, the interaction between the positive valance band holes (TiO₂(h⁺_{VB})) and the conduction band electrons (TiO₂(e⁻_{CB})) results in the production of heat as shown in Equation 14.

In this study, maximum degradations of 46.7% and 2.84% were observed when the alkaline (pH = 10.5) least concentrated (50 mg/L) and the most concentrated (500 mg/L) dye solutions were treated with UV/TiO₂ using the longest retention time of 60 min, respectively. These were about 72.23% and 76.06% increases in the removal efficiency above those obtained with the treatments with UV alone for the 50 and 500 mg/L dye concentrations, respectively. However, the maximum degradation observed for the least concentrated (50 mg/L) and the most concentrated (500 mg/L) dye solutions when the shortest retention time of 5.2 min was used were 1.64% and 0%, respectively. This was about 96.96% increase for the alkaline (pH = 10.5) least concentrated (50 mg/L) dye solution above that obtained with the treatment of UV alone.

Kusvuran *et al.* (2004) reported 40% degradation of 40 mg/L reactive red 120 dye when the dye solution was exposed to UV/TiO₂ for 30 min. Kavitha and Palanisamy (2010) stated that only a slight degradation was observed when azo dyes were exposed to UV/TiO₂ for 30 min and that could be due to the absorption of dye molecules onto the surface of TiO₂. The authors also noted a degradation of 84% when the dye solution was exposed for 120 min. Verma and Ghaly (2008) reported 12.5% degradation of 300 mg/L remazol dye after exposing the dye solution to UV/TiO₂ for 84 min and a higher degradation of 46.70% for low dye concentration (50 mg/L) after exposure for 60 min. Sohrabi and Ghavami (2008) noted 83.58% degradation when the dye solution was exposed to UV/TiO₂ for 140 min. The removal efficiency obtained in this study is higher than those reported in literature for similar concentrations and retention times.

5.3. Effect of Temperature

The current study was carried out at ambient temperature (25°C). Muruganandham and Swaminathan (2004) stated that 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 dye. Mahmoud *et al.* (2007) treated a remazol dye solution in UV reactor at 25 and 100°C and obtained a maximum degradation of 12.3% under both temperatures and indicated that the temperature had no effect on degradation of dye. Galindo and Kalt (1999) stated that there was no significant change in the degradation rate when dye solutions containing acid orange 5, 6, 7, 20 and 52 were treated with UV alone in the temperature range of 22-45°C. Muruganandham and Swaminathan (2004) 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 2-5). The authors suggested the use of additional oxidants for effective dye removal efficiency.

However, reports in the literature indicated the influence of temperature on the dye degradation when UV is combined with other oxidants. Jain and Sikarwar (2008) noted that degradation of erioglaucline dye as a result of exposure to UV/TiO₂ increased as the temperature was increased from 20 to 40°C. Saien and Soleymani (2007) reported 7% increase in dye degradation as the temperature was increased from 15 °C to 45°C. Stasinakis (2008) reported that the dye degradation rate as a result of exposure to UV/TiO₂ was found to decrease when the temperature of the dye solution was increased from 25 to 80°C. Saien and Soleymani (2007) and Jain and Sikarwar (2008) stated that higher temperatures lead to the recombination of the positive (TiO₂ (h^+_{VB})) valance-band holes (which interacts with H₂O to produce OH° radicals) and the negative (TiO₂ (e^-_{CB})) conduction-band electrons (which interact with OH⁻ to produce OH° radicals) as shown in Equations 8 and 9 and as a result the concentration of hydroxide radicals (OH°) was significantly reduced. They also noted that the increase in temperature decreases 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 2-4). They concluded that a temperature higher than 45°C should not be used as it will result in low degradation efficiency.

5.4. Effect of pH

In this study the first two sets of experiments (UV and UV/TiO₂) were carried out after adjusting the pH of the dye solution to 10.5 which is within the range of pH of the textile effluent (10-11). In the third set of experiments, the most concentrated (500 mg/L) and the least concentrated (50 mg/L) dye solutions were treated

with UV/TiO₂ under acidic condition (pH = 3). Adjusting the pH of the dye solution to 3 increased the degradation efficiency from 46.70% (at pH 10.5) to 86.45% (39.75% increase) for the least concentrated (50 mg/L) dye solution and from 2.84% (at pH 10.5) to 14.94% (12.1% increase) for the most concentrated (500 mg/L) dye solution after treatment with UV/TiO₂ for 60 min.

Verma and Ghaly (2008) reported no significant degradation of 50 mg/L remazol brilliant blue dye when the solution was treated with UV alone at a pH of 7 and a temperature of 25°C whereas 27.01% degradation of the dye was achieved after 60 min exposure to UV alone at 25°C after the pH was adjusted to 10.5. Sugiarto *et al.* (2002) reported to have found no significant degradation of the rhodamine B, methyl orange and chicago sky blue dyes when exposed to UV alone after adjusting the pH to 3.5. Malik and Sanyal (2004) noted that the degradation rates of the dye when using UV even under a lower pH was much slower when compared to using UV in a combination with other oxidants.

Several researches reported that the effect of pH on the degradation efficiency of textile dyes as a result of exposure to UV/TiO₂ was significant. Kavitha and Palanisamy (2011) stated that the photocatalytic activity was maximum under acidic condition and was found to decrease when the pH was increased above 6. Kusvuran *et al.* (2004) reported 90% degradation of 40 mg/L reactive red 120 dye as a result of exposure to UV/TiO₂ when the pH was adjusted to 3 and found the degradation efficiency to decrease with increase in pH. Neamtu *et al.* (2003) examined colour removal at different pH levels (2, 3, 6.5 and 9.7) and found the best colour removal efficiency (99%) of reactive red 120 to be achieved at pH of 2 within 15 min. Kusvuran *et al.* (2004) and Saien and Soleymani (2007) stated that textile dyes have sulfonated groups in their structures which are negatively charged. The acidic medium influences the absorption of dye onto the TiO₂ surface and the OH° radicals created aids in the destruction of dye. On the other hand, the alkaline medium does not enhance the absorption of dye onto the surface of TiO₂ resulting in a low degradation efficiency.

In the present study, the increases in degradation efficiency as a result of adjusting the pH to 3 do not justify the cost of chemicals added to adjust the pH of the dye effluent from 10 to 3 before treatment and then from 3 to 7 before the final discharge.

5.5. COD Removal

In this study, the acidic (pH = 3) least concentrated (50 mg/L) and most concentrated (500 mg/L) dye solutions were treated with UV/TiO₂. A COD reduction of 83.43% was observed for the acidic (pH = 3) least

concentrated dye solution (50 mg/L) compared to a COD reduction of 41.88% at the alkaline pH of 10.5. Also, a COD reduction of 20.82% was observed for the acidic (pH = 3) most concentrated dye solution (500 mg/L) compared to a COD reduction of 7.67% at the alkaline pH of 10.5.

Liu *et al.* (2006) achieved a COD removal efficiency of 73.01% (31.5 to 8.5 mg/L) when an acid yellow 17 was exposed to UV/TiO₂ for 9 hours at pH 3. Park *et al.* (2003) reported a COD removal efficiency of 56% (96 to 42.24 mg/L) when a reactive red 120 dye was exposed to UV/TiO₂ for 90 min at pH 5. Sahunin *et al.* (2006) achieved a COD removal efficiency of 52% (27,000 to 14040 mg/L) when a textile effluent (containing acid dye and various chemicals) was treated with UV/TiO₂/Fe²⁺ for 5 min at pH 3. The COD results obtained in the present study showed much higher COD reductions in much shorter retention times.

Photooxidation treatments of textile effluents at acidic pH have proven to be more effective in the degradation of textile dyes than at alkaline pH. However, in the present study, when effluents with an initial pH of 10.5 were treated with UV/TiO₂, the pH was found to decrease to a pH of 9.7 after 60 min, making the pH of the effluent near the permitted discharge limit of 6-9. Also, exposure of acidic (pH = 3) dye solution to UV for 60 min was found to decrease the pH further to 2.4 thus making it more acidic. Although treatment with acidic pH was proven to be faster, the cost of chemicals to be added to the effluent to bring the pH to 3 before treatment and then to bring it to neutral (pH = 7) before the final disposal does not justify the treatment cost.

6. CONCLUSION

The effectiveness of Advanced Oxidation Process (AOP) against the degradation of ten different reactive red 120 dye concentrations were tested using UV and TiO₂ at various retention times. When the alkaline (pH = 10.5) reactive red 120 dye solutions were treated using a low pressure (380 nm intensity) UV lamp, a maximum degradation efficiency of 27.01% was obtained for the least concentrated dye (50 mg/L) solution and only a degradation efficiency of 0.33% was obtained for the most concentrated (500 mg/L) dye solution. When the alkaline (pH = 10.5) reactive red 120 solutions were exposed to a combination of UV/TiO₂, a maximum degradation efficiency of 46.70% was obtained for the least concentrated (50 mg/L) dye solution after 60 min and only a degradation efficiency of 2.84% was obtained for the most concentrated (500 mg/L) dye solution after 60 min. When the pH of the reactive red 120 dye solution was reduced to 3, a degradation efficiency of 56.45% was obtained for the least concentrated (50

mg/L) dye solution at 60 min and a degradation efficiency of 14.94% was obtained for the most concentrated (500 mg/L) dye solution at 60 min. However, the increase in degradation efficiency obtained in this study does not justify the cost of chemicals added to adjust the pH to 3 before treatment and then to 7 before final disposal. Also, the addition of chemicals (to adjust the pH) increase the COD of the dye solution, thereby necessitating a further costly treatment.

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