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TREATMENT OF TEXTILE EFFLUENT CONTAINING REACTIVE BLACK 5 DYE USING ADVANCED OXIDATION

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ABSTRACT

Wastewaters originated from textile industry contain various pollutants including a high content of organic matter and color problem depending on forms of dyes, surface-active materials. Azo dyes are difficult to degrade by the current conventional treatment processes. They are characterized by the presence of the nitrogen-nitrogen bond ($-N=N-$) in the center and hence they are highly electron deficient.

Several biological, chemical methods for degradation of textile effluents are being followed, but real challenge is to find a method that is effective, comparatively fast and cost effective. Advanced oxidation is an emerging field that uses oxidants producing hydroxyl radicals to oxidize toxic compounds into non-harmful by-products.

The effectiveness of photo-oxidation on reactive black 5, a widely used complex structured azo dye, was evaluated. Dye concentrations in the range of 50-500mg/L were treated with UV alone and H_2O_2 /UV under 12 different residence time (5.2-60 min). The best combination was selected for Chemical Oxygen Demand (COD) analysis to determine the amount of chemicals retained in the effluent after treatment. The textile industry produces effluents with a pH of 10-11 and hence, the dye pH was adjusted to 10-11.

The effects of UV radiation, UV/ 10 ml H_2O_2 and UV/ 20 ml H_2O_2 were evaluated and the results were compared to select the best oxidation method. The maximum degradation obtained after 60 min exposure to UV alone was 27.01% and 0.33% for 50 mg/L dye concentration and 500 mg/L dye concentration, respectively.

The degradation obtained after exposure to UV/10 ml/L H_2O_2 was 99.70% after 25.4 min for the 50 mg/L concentration and 99.70% after 60 min for the 500 mg/L concentration. Exposure to UV/ 20 ml/L H_2O_2 resulted in the degradation of 99.96% after 20 min for the 50 mg/L dye concentration and 99.95% degradation after 60 min for the 500 mg/L dye concentration. Increasing the H_2O_2 from 10 mg/L to 20 mg/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 UV/20 ml/L H_2O_2 treated samples showed the COD of the effluent (after treatment) was 416 mg/L after 20 min for the 50 mg/L dye concentration and 256 mg/L after 60 min for the 500 mg/L dye

concentrations which are higher than the COD discharge limit of 250 mg/L. The COD discharge limit of 250 mg/L could be achieved with UV/ 20 ml/L treatment by increasing the exposure time (longer than 60 min). The pH of the treated effluent is within the discharge-accepted limit of 6-9. Treatment of the dye effluent under alkaline condition was slower but it does not justify at the acidic condition due to the cost of chemicals addition to adjust the pH and the further treatment to remove the chemicals before disposal. The temperature after treatment was always found to be increased from 22°C to 41°C after 60 min of exposure to UV.

KEYWORDS

Reactive black 5 dye, Decolourization, Photooxidation, Textile, UV/H₂O₂ technology

1. INTRODUCTION

Wastewaters originated from textile industry contain various pollutants including a high content of organic matter and color problem depending on forms of dyes, surface active materials and textile additives materials used in the process. Textile dyes can be structurally different. Reactive azo dyes are the most commonly applied among more than 10000 dyes applied in textile processing industries.

Discharge of azo dyes is undesirable not only for aesthetic reasons but also because many azo dyes and their intermediate products are toxic to aquatic life and mutagenic to humans.

Azo dyes are resistant to biodegradation under aerobic conditions, although many researchers applied anaerobic Color removal successfully. However, the high quantity and the context of wastewater originated from textile industry are not proper to apply anaerobic process because the decolorization takes place by the breakdown of the azo bonds, which leads to formation of aromatic amines. The formed intermediates are not biodegradable under aerobic condition, and they are toxic than the dye molecules themselves.

Textile and Clothing (T&C) is one of the largest and oldest industries present globally. The T&C industry provides jobs with no required special skills, which in turn plays a major role in providing employment in poor countries like Bangladesh, Vietnam, Sri Lanka and Mauritius and therefore, plays a vital role in the increase of Gross Domestic Product (GDP) value of these countries (Keane and Velde, 2008).

The textile industry is classified into three main categories: cellulose fibres, protein fibres and synthetic fibres. The type of dyes and chemicals used in the textile industry are found to differ depending on the fabrics manufactured. Direct dyes, naphthol dyes and vat dyes are some of the dyes used to dye cellulose fibres (Lorimer et al, 2001;

Burch, 2009 and Robert et al., 2008). Protein fibres are dyed using azo dyes, natural dyes and lanaset dyes (Moody and Needles, 2004, Burch, 2009, Schmidt et al, 2002 and Robert et al., 2008). Other dyes like those that dispersed dyes, basic dyes and direct dyes are used to dye synthetic fibres (Butkinshaw, 1995; Burch, 2009).

Textile industries produce large amounts of liquid wastes. These textile effluents contain organic and inorganic compounds (Elliott et al, 1954). During the dyeing processes, not all dyes that are applied to the fabrics are fixed on them and there is always a portion of these dyes that remains unfixed to the fabrics and are washed out. These unfixed dyes are found to be in high concentrations in textile effluents (Dyes and Pigments, 2010). The amount of water consumed and released varies depending on the type of fabrics produced (Moustafa, 2008). Almost $0.08 - 0.15 \text{ m}^3$ of water is used to produce 1 kg of fabrics. It is estimated that about $1,000 - 3,000 \text{ m}^3$ of water is let out after processing about 12 – 20 tons of textiles per day (Pagga and brown, 1986; Kdasi et al., 2004). These effluents are rich in dyes and chemicals, some of which are non-biodegradable and carcinogenic and pose a major threat to health and the environment. Several primary, secondary and tertiary treatment processes like flocculation, trickling filters and electro dialysis have been used to treat these effluents. However, these 2 treatments are not found effective against the removal of all dyes and chemicals used (Kdasi et al., 2004, Eswaramoorthi et al., 2008). The effluents do not only contain high concentration of dyes used in the industry, but also contain the chemicals used in the various processing stages. Some trace metals such as Cr, As, Cu and Zn are present in these effluent and are capable of causing several health problems including haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis. Textile effluents are also found to contain other organic and microbial impurities (Nese et al., 2007; Laxman, 2009).

Cotton fibers are mainly dyed using azo dyes, which are one of the largest groups of synthetic colorants used in the industry (Mohan et al., 2002). Azo dyes are difficult to degrade by the current conventional treatment processes. They are characterized by the presence of the nitrogen-nitrogen bond ($-N=N-$) in the center and hence they are highly electron deficient (Robert et al., 2008). Due to their poor exhaustion properties, about 40% remain unfixed in the effluents (Manu, 2003). The amount of dyes present in a typical dye bath is about 1000 mg/L (Azbar et al, 2003). A general effluent is characterized by a pH of 9-11, a COD of 1300-2000 mg/L, total dissolved solids of 4900-7000 mg/L, a color of 1500-4500 ADMI and a temperature of $35-45^\circ\text{C}$ (Manu, 2003, Eswaramoorthi et al., 2008).

These azo dyes are found to be complex in nature and have been found to show carcinogenic evidences on reductive cleavage. These dyes are capable of altering the physical and engineering properties of soil, deteriorating water bodies and causing harm to the flora and fauna in the environment (Manu, 2003). Savin and Butnaru (2008) observed that the toxic nature of dyes causes death to the soil microorganisms, which in turn affect the agricultural productivity. Hence, removing the dye contents from effluents before disposal is paramount.

Advanced oxidation processes (AOPs) were developed to generate hydroxyl free radicals using different oxidants under different combinations and these radicals were found to destroy components that are not destroyed under conventional oxidation processes (Kestioglu et al., 2005; Kdasi et al., 2004). AOP using ozone, Ultra Violet, TiO₂, fenton, photo-fenton and hydrogen peroxide can be used to treat dyes. The main advantage of AOPs over the other treatment processes is its pronounced destructive nature, which results in the mineralization of organic contaminants present in wastewater (Kdasi et al., 2004). AOPs are considered as a low or non-waste generation technology, which destroys the complex structures using short-lived chemical species with a high oxidation power. The hydroxyl radical (OH[•]) is the main oxidative power of AOPs (Arslan et al., 1999; Kestioglu et al., 2005). The OH[•] radicals can be generated by chemical, electrical, mechanical or radiation energy. Therefore, AOPs are classified under chemical, catalytic, photochemical, photocatalytic, mechanical and electrical processes.

In this research, the production of hydroxyl radical using H₂O₂ and UV individually and in different combinations and their effectiveness in degrading the azo dye – Reactive Black 5 (RB5) are evaluated.

1.1 OBJECTIVES

The main aim of this study was to evaluate the effectiveness of Advanced Oxidation Process (AOP) for degradation of the textile dye Reactive Black 5 (RB5). The specific objectives of the studies were:

1. To study the effect of UV on the degradation of reactive Black 5 dye of varying concentration (50- 500 mg/L).
2. To study the effect of combined UV and of H₂O₂ treatment on the degradation of reactive black 5 dye of varying concentration (50-500 mg/L).
3. To compare the effectiveness of the two treatments and select the most efficient treatment process.
4. Evaluate the effect of pH on the treatment efficiency and time.
5. Evaluate the pollution reduction potential of the treated effluent using COD, temperature and pH as pollution measurement parameters

2. MATERIALS AND METHODS

2.1 Experimental Apparatus

The experiments were carried out using a custom-built photo oxidation system. The system consists of a reactive black 5 dye feeding tank, a peristaltic pump, a photo reactor and treated effluent collection tank.

The dye-feeding tank was a 20 cm diameter Poly Vinyl Chloride (PVC) container, with a working volume of about 12 L. The PVC container has a detachable top and a fixed bottom made out of 4 mm thick Poly Methyl Methacrylate. 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 airflow into the container. A 4 mm outlet port is located in the lower end of the feeding tank and connected to the feeding pump.

Masterflex precision tubing was used along with a peristaltic pump to control the flow of dye solution into the reactors at required flow rates. The pump was connected to the feeding tanks and the photo reactor using tygon tubing. Masterflex precision tubing was used with pump to provide the required flow rate.

The outer and the inner diameters of the reactor were 61 and 55 mm, respectively. A low-pressure mercury lamp, which emits UV light at 535 nm enclosed in a 21 mm diameter quartz tube, was used. 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). The working volume of the reactor was 840 ml. The treated effluent was collected using 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 out of 4 mm thick Poly Methyl Methacrylate.

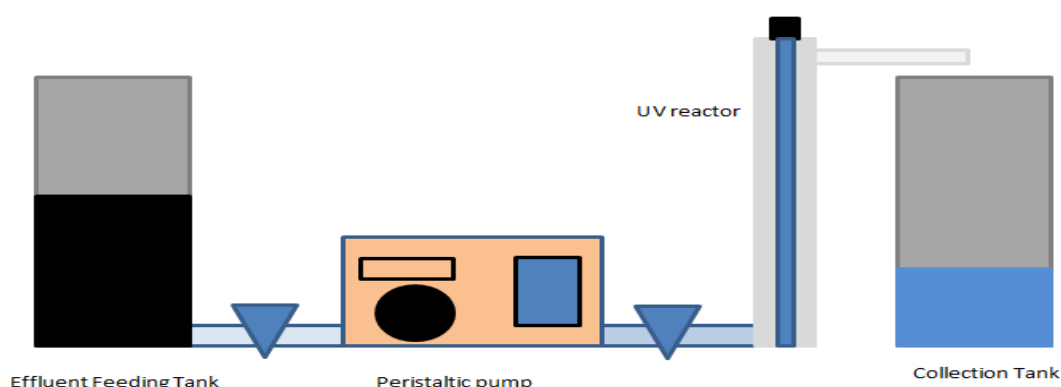


Figure 2.1: Diagram of experimental apparatus

2.2 Experimental Design

Experiments were carried out to investigate the degradation efficiency of the oxidants UV, H₂O₂ in different combinations of UV, UV/ H₂O₂. Different concentrations of the dye solution (50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mg/L) were tested with the different combinations of the oxidants under 12 different retention times. The retention time of the dye inside the reactor is based on the flow rate set on the peristaltic pump. The flow rate is calculated using the following formula.

$$\frac{\text{Volume of the reactor}}{\text{Retention time required}} = \text{Flow rate} \quad (4.1)$$

2.3 Experimental Protocol

The first set of experiments was carried out using UV alone. The desired amount of dye was mixed in water and the pH was adjusted, the optical density of the raw feed was determined using spectrophotometer at 535 nm. Then, the raw dye was fed into the reactor at a flow rate of 5.2 ml/min. The OD of the samples collected at the other end after reacting steady state was determined. The same procedure was repeated with other flow rates.

The second set of experiments was carried out using both UV and H₂O₂. The reactive dye was weighed and mixed in water. Then, H₂O₂ (10 ml/L) was mixed along with the dye in the desired amount of water and stirred. The optical density of the raw dye was measured. The pH was adjusted and the resulting solution was fed to the reactor at a flow rate of 5.2 ml/L. The optical density of the sample at the other end was measured. The same procedure was repeated with other flow rates. The third set of experiments was similar to the second set except that the amount of H₂O₂ added to the dye solution was 20 ml/L. The sample procedure was followed till all flow rates have been tested. The Chemical Oxygen Demand analysis was performed on the effluent according to the procedure described by APHA (1980). The percentage reduction of dye after the treatment was calculated as follows.

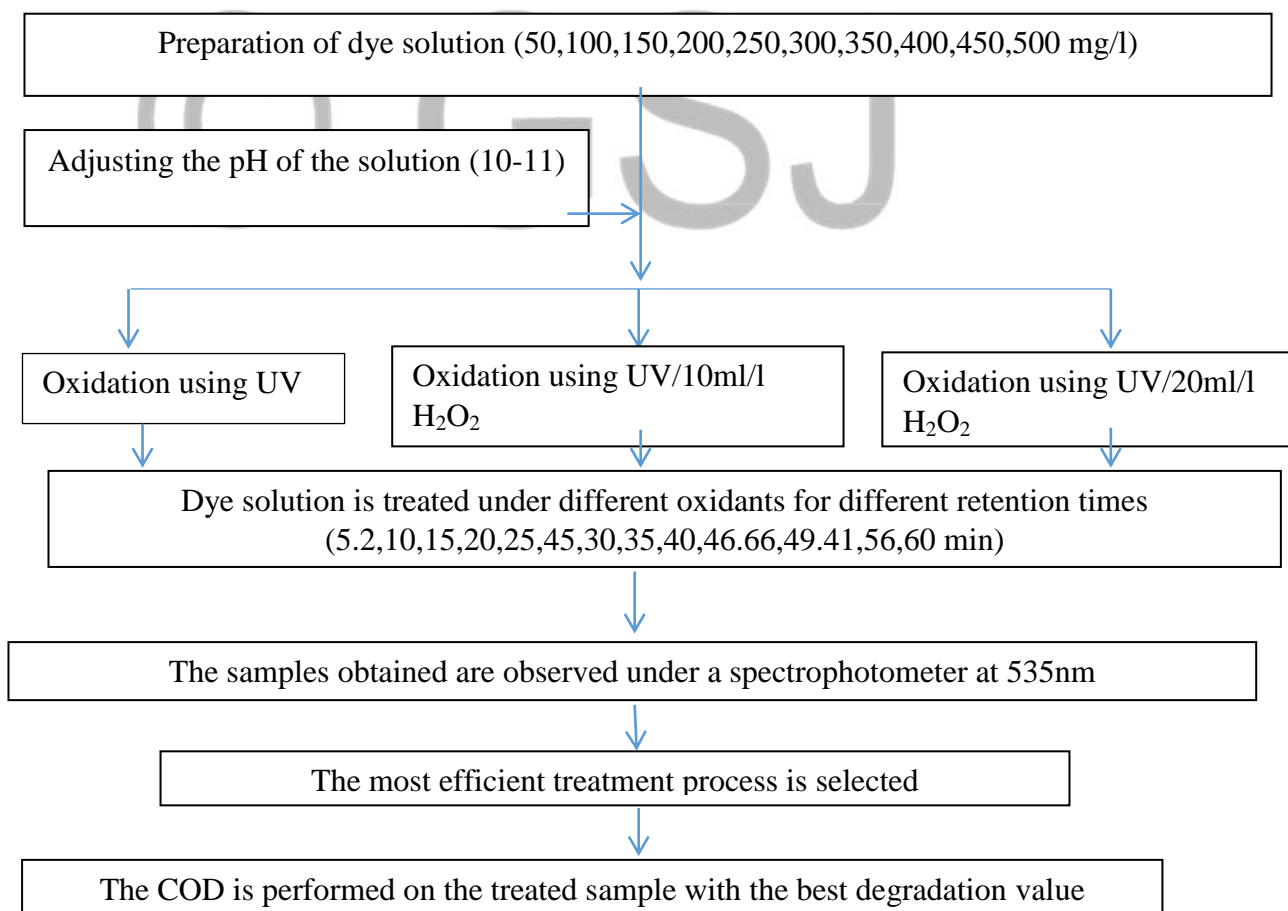


Figure 2.2: Experimental Procedure

$$\text{Reduction} = \frac{\text{Initial-Final}}{\text{Initial}} * 100 \quad (4.2)$$

3. RESULTS

3.1 Decolourization of Reactive Black 5 Dye with UV

The dye degradation percentages for different concentrations as a result of exposure to UV are shown in Table 3.1 and Figure 3.1. When the dye solution was treated with a low-pressure UV lamp (535 nm), only 27.1% of the least concentration of dye (50 mg/L) used under the maximum retention time (60 min) was degraded. Increasing the dye concentration and/or reducing the exposure time reduced the removal efficiency. Only 1.14% of the dye was removed when the lowest concentration of 50 mg/L when exposed to UV for 5.2 minutes and 0.33% of the dye was removed when the highest concentration of 500 mg/L was exposed to UV for 60 min.

Table 3. 1: Degradation percentage of reactive Black 5 under UV.

| Time (min) | 50 ppm | 100 ppm | 150 ppm | 200 ppm | 250 ppm | 300 ppm | 350 ppm | 400 ppm | 450 ppm | 500 ppm |
|------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 5.2 | 1.14 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10.0 | 3.44 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15.0 | 9.80 | 1.05 | 0.53 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20.0 | 11.47 | 4.30 | 2.27 | 1.03 | 0 | 0 | 0 | 0 | 0 | 0 |
| 25.3 | 14.82 | 5.73 | 2.45 | 2.05 | 0.62 | 0 | 0 | 0 | 0 | 0 |
| 30.0 | 15.66 | 9.01 | 3.09 | 2.10 | 1.73 | 0.82 | 0 | 0 | 0 | 0 |
| 35.0 | 18.32 | 11.42 | 4.55 | 4.50 | 3.02 | 2.01 | 0 | 0 | 0 | 0 |
| 40.0 | 22.43 | 14.75 | 5.64 | 5.40 | 4.43 | 2.52 | 0 | 0 | 0 | 0 |
| 46.6 | 22.41 | 17.45 | 6.86 | 6.55 | 6.12 | 3.20 | 0.10 | 0 | 0 | 0 |
| 49.4 | 23.71 | 17.57 | 7.95 | 7.08 | 6.98 | 5.49 | 1.06 | 0.95 | 0 | 0 |
| 56.0 | 26.28 | 20.12 | 9.98 | 7.85 | 8.25 | 6.33 | 1.86 | 1.31 | 0.83 | 0 |
| 60.0 | 27.01 | 23.49 | 11.28 | 8.23 | 9.36 | 7.40 | 2.94 | 2.51 | 2.01 | 0.33 |

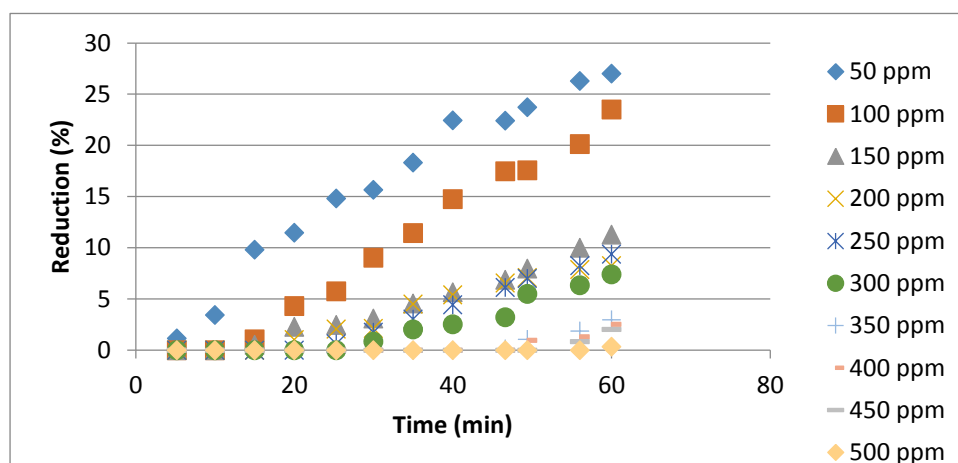


Figure 3.1: Degradation efficiency of reactive Black 5 against time when treated with UV.

3.2 Decolourization of Reactive Black 5 Dye with UV and 10 ml H₂O₂.

The dye degradation results obtained with UV and 10 ml H₂O₂ are shown in Table 3.2 and Figure 3.2. For the least dye concentration (50 mg/L), a degradation efficiency of 93.52% was observed when the dye was exposed to UV and 10 ml H₂O₂ for the minimum time of 5.2 min and a maximum degradation of 99.70% was obtained at 25.3 min. For the highest dye concentration (500 mg/L), a degradation efficiency of 20.46% was observed after 5.2 min and a maximum degradation efficiency of 99.70% was obtained after 60 min.

Table 3.2: Degradation percentage of reactive Black 5 under UV and 10ml H₂O₂.

| Time (min) | 50 ppm | 100 ppm | 150 ppm | 200 ppm | 250 ppm | 300 ppm | 350 ppm | 400 ppm | 450 ppm | 500 ppm |
|------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 5.2 | 93.52 | 92.67 | 51.51 | 48.51 | 48.19 | 45.07 | 33.33 | 24.57 | 23.21 | 20.46 |
| 10 | 96.75 | 95.37 | 69.18 | 65.37 | 59.62 | 55.74 | 52.29 | 36.15 | 31.72 | 30.59 |
| 15 | 97.64 | 97.55 | 97.48 | 82.17 | 79.38 | 69.70 | 64.59 | 48.24 | 44.32 | 40.29 |
| 20 | 99.59 | 99.30 | 98.89 | 89.29 | 88.04 | 83.43 | 70.81 | 56.82 | 50.63 | 41.68 |
| 25.3 | 99.70 | 99.72 | 99.68 | 89.40 | 87.87 | 86.60 | 76.88 | 59.29 | 57.98 | 47.97 |
| 30 | | 99.89 | 99.91 | 99.51 | 98.96 | 98.62 | 79.25 | 63.84 | 62.28 | 53.51 |
| 35 | | | 99.97 | 99.74 | 99.61 | 99.53 | 98.60 | 77.76 | 75.94 | 59.06 |
| 40 | | | | 99.97 | 99.86 | 99.80 | 99.51 | 99.28 | 84.97 | 64.6 |
| 46.6 | | | | | 99.98 | 99.96 | 99.78 | 99.64 | 99.35 | 84.75 |
| 49.4 | | | | | | | 99.94 | 99.76 | 99.43 | 89.12 |
| 56 | | | | | | | | 99.94 | 99.86 | 99.44 |
| 60 | | | | | | | | 99.96 | 99.92 | 99.70 |

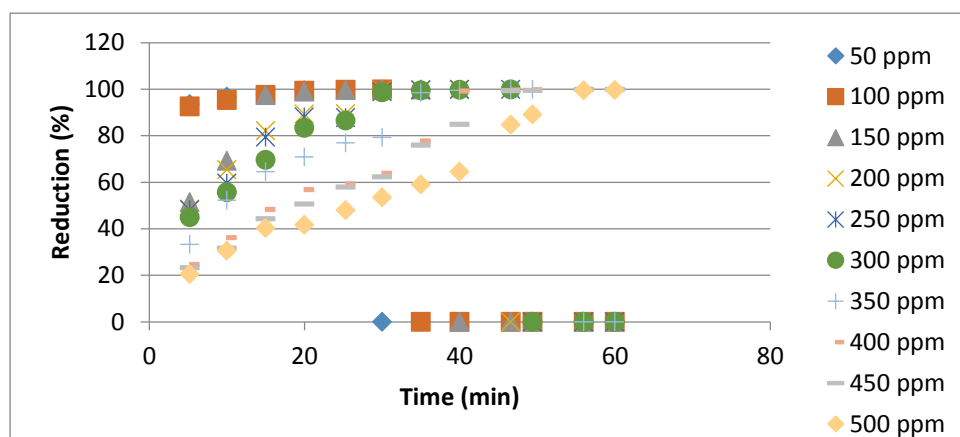


Figure 3.2: Degradation efficiency of reactive Black 5 against time when treated with UV and 10 ml H₂O₂.

3.3 Decolourization of Reactive Black 5 Dye with UV and 20 ml H₂O₂

The results obtained with UV and 20 ml H₂O₂ treatment are shown in Table 3.3 and Figure 3.3. The dye degradation percentages when the dye was treated with UV and 20 ml/L H₂O₂ was higher than that observed when using UV with 10 ml/L H₂O₂. When the dye with minimum concentration (50 mg/L) was exposed to UV and 20 ml H₂O₂ for the minimum time of 5.2 min, 94.2% of the dye was degraded. A maximum degradation efficiency of 99.96% was obtained after an exposure time of 20 min. For the highest dye concentration (500 mg/L), a degradation efficiency of 23.33% was observed with exposure time of 5.2 min and 99.95% degradation efficiency was obtained after 60 min.

Table 3.3: Degradation percentage of reactive Black 5 under UV and 20ml H₂O₂.

| Time (min) | 50 ppm | 100 ppm | 150 ppm | 200 ppm | 250 ppm | 300 ppm | 350 ppm | 400 ppm | 450 ppm | 500 ppm |
|------------|--------------|---------|---------|---------|---------|---------|---------|---------|---------|--------------|
| 5.2 | 94.20 | 55.66 | 52.11 | 51.98 | 50.72 | 46.80 | 40.49 | 34.90 | 26.66 | 23.33 |
| 10 | 98.51 | 88.02 | 70.42 | 66.42 | 62.80 | 56.59 | 52.81 | 47.71 | 41.89 | 39.43 |
| 15 | 99.62 | 99.54 | 99.48 | 92.62 | 79.46 | 70.21 | 68.48 | 65.09 | 55.35 | 52.39 |
| 20 | 99.96 | 99.94 | 99.69 | 99.49 | 98.85 | 90.85 | 87.85 | 75.84 | 68.81 | 62.77 |
| 25.3 | | 99.97 | 99.92 | 99.82 | 99.55 | 99.30 | 98.83 | 85.71 | 81.04 | 70.12 |
| 30 | | | 99.97 | 99.91 | 99.80 | 99.64 | 99.14 | 89.54 | 87.50 | 79.34 |
| 35 | | | | 99.95 | 99.94 | 99.69 | 99.69 | 99.55 | 99.41 | 99.26 |
| 40 | | | | | 99.98 | 99.94 | 99.90 | 99.86 | 99.63 | 99.62 |
| 46.6 | | | | | | 99.98 | 99.96 | 99.91 | 99.82 | 99.77 |
| 49.4 | | | | | | | | 99.96 | 99.91 | 99.89 |
| 56 | | | | | | | | 99.97 | 99.96 | 99.90 |
| 60 | | | | | | | | | | 99.95 |

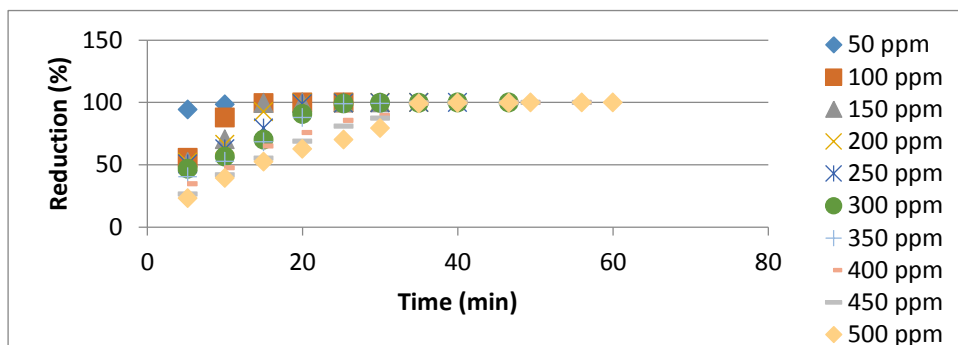


Figure 3.3: Degradation efficiency of reactive Black 5 against time when treated with UV and 20 ml H_2O_2 .

Table 3.4: Maximum removal efficiency for various treatments.

| Treatment | Dye Concentration (mg/L) | Time (min) | Maximum removal efficiency (%) |
|-------------------|--------------------------|------------|--------------------------------|
| UV | 50 | 60 | 27.01 |
| | 500 | 60 | 0.33 |
| UV/10 ml H_2O_2 | 50 | 25 | 99.70 |
| | 500 | 60 | 99.70 |
| UV/20 ml H_2O_2 | 50 | 20 | 99.96 |
| | 500 | 60 | 99.95 |

3.5 Comparative Analysis

Table 3.4 shows us the comparative analysis of the percentage of maximal removal efficiency under each oxidation mechanism from which it could be seen that UV used with 20 ml H_2O_2 provides the maximum decolourisation for the inspected time limit.

3.6 Analysis of Chemical Oxygen Demand

It appears from the results that the UV with 20 ml of H_2O_2 provided the best decolourisation. However, the amount of chemicals in the treated water was determined by performing the Chemical Oxygen Demand (COD) in order to evaluate the level of pollution in wastewater before disposal in the environment. The results obtained from COD analysis are listed in Table 3.5. Figure 3.4 shows the COD pattern in the treated water over time. The results showed that the highest COD concentration (704-1184 mg/L depending on the dye concentration) was observed at 5 minutes from the start and the COD decreased (256-416 mg/L depending on the dye concentration and exposure time) as the contact time increased. Hence, it could be concluded that a complete degradation of chemicals could be achieved if the treated samples were exposed to UV and 20 ml H_2O_2 for longer time periods.

Table 3.5: Chemical oxygen demand (COD) after treatment with UV and 20 ml H₂O₂.

| Time (min) | 50 ppm | 100 ppm | 150 ppm | 200 ppm | 250 ppm | 300 ppm | 350 ppm | 400 ppm | 450 ppm | 500 ppm |
|------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 5.2 | 704 | 832 | 864 | 864 | 928 | 1024 | 1088 | 1152 | 1152 | 1184 |
| 10 | 608 | 672 | 736 | 800 | 832 | 896 | 928 | 1056 | 1088 | 1120 |
| 15 | 512 | 512 | 608 | 704 | 672 | 736 | 800 | 832 | 1024 | 1056 |
| 20 | 416 | 384 | 448 | 544 | 576 | 672 | 704 | 800 | 800 | 864 |
| 25.3 | | 288 | 384 | 416 | 480 | 608 | 640 | 736 | 704 | 768 |
| 30 | | | 224 | 352 | 416 | 512 | 544 | 640 | 672 | 704 |
| 35 | | | | 256 | 320 | 448 | 416 | 512 | 576 | 640 |
| 40 | | | | | 224 | 288 | 320 | 448 | 480 | 544 |
| 46.6 | | | | | | 192 | 224 | 384 | 416 | 448 |
| 49.4 | | | | | | | | 288 | 352 | 416 |
| 56 | | | | | | | | 256 | 224 | 320 |
| 60 | | | | | | | | | | 256 |

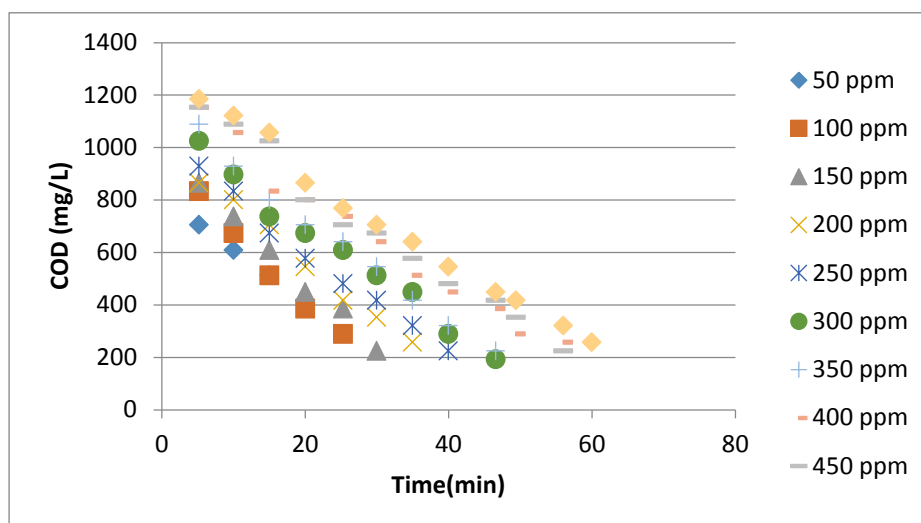


Figure 3.4: The chemical oxygen demand after treatment with UV/20 ml/L H₂O₂.

Table 3.6: Temperature of the treated effluent

| Time (min) | Temperature (°C) |
|------------|------------------|
| 5.2 | 22 |
| 10 | 23 |
| 15 | 26 |
| 20 | 28 |
| 25.4 | 29 |
| 30 | 31 |
| 35 | 33 |
| 40 | 35 |
| 46.66 | 36 |
| 49.41 | 38 |
| 56 | 40 |
| 60 | 41 |

4. DISCUSSION

4.1. Advanced oxidation using UV

The production of atomic oxygen radicals, which in turn reacts with other oxygen molecules resulting in the production of ozone. The reaction between ozone and water that results in the production of hydrogen peroxide. The production of hydroxyl radicals, which helps in the destruction of dye molecules. Kesselman et al, (1996) stated that the ozone and the hydrogen peroxide produced. These are found to be minimal and short-lived; hence, they are not that effective in degradation of the dye (Kesselman et al, 1996)

The maximum degradation achieved when 50 mg/L dye was exposed 60 min of UV was 27.01%, while the maximum degradation achieved when 500 mg/L was exposed to UV for 60 min was 0.33%. No reduction in the dye concentration was witnessed after 60 min when 500 mg/L was exposed to the UV. The very low removal efficiency is 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).

Georgiou et al. (2002) observed no colour reduction when the dye effluent was treated with just UV. Ince and Gonenc (1997) reported that when an azo dye concentration of 40 mg/L was exposed to UV in the photo reactor no significant decomposition was observed. Malik and Sanyal (2004) noted that the degradation rates of the dye when using just UV even under a lower pH was much slower when compared to using UV in a combination with other oxidants. Galindo et al (1999) stated that the disappearance of dye molecules when used with UV (in the absence of oxidants) was negligible. 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 in at pHs 7 and 11, while when used in a combination with other oxidants it resulted in a 92% decomposition rate. Mahmoud et al. (2007) reported that two UV reactors fed remazol dye solution at 25°C and 100°C achieved a maximum degradation of 12.3%, proving that the temperature had no effect on degradation of dye.

4.2. Oxidation using UV and H₂O₂

The initiation reaction between UV and H₂O₂ leading to the production of hydroxyl radicals. The propagation of the reaction involving the production of hydroxyl radicals and its reactions on H₂O₂ leading to the further production of hydroxyl radicals, which helps in the reduction of dye molecules. The termination of the reactions, which result in the formation of End Product.

When reactive Black 5 dye solution was treated with UV and 10/L ml H₂O₂, a complete degradation was observed for all the concentrations. The time required for complete degradation depended on the initial dye concentration. From the results, 99.70% degradation was achieved for the 50 mg/L dye concentration after 25 min when treated with UV/10 ml/L H₂O₂. When UV/20 ml/L H₂O₂ was used for the same dye concentration, 99.96%

degradation was achieved after 20 min. When the 500 mg/L dye concentration was treated with to UV/10 ml/L H_2O_2 , a degradation of 99.70% was obtained. After 60 min., 99.95% degradation was achieved when the 500mg/L dye concentration was treated with UV/20 ml/L H_2O_2 for 60 min.

Crittenden et al. (1999) stated that when H_2O_2 is exposed to UV, it splits to form two hydroxyl radicals which in turn react with the organics in the solution. Kdasi et al. (2004) stated that oxidation with UV/ H_2O_2 was more effective than with H_2O_2 alone. Kurbus et al. (2003) noted that the decolourisation time required for H_2O_2 /UV process was lesser than the time required for H_2O_2 / O_3 . Galindo and Kalt (1999) noted that the action of UV alone or H_2O_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_2O_2 , a dramatic increase in the degradation of the dye was observed.

Georgiou et al. (2002) reported that more than 50% degradation was obtained within 20 min for 100 mg/L reactive dyes. Percowski and Kos (2003) reported that 99% degradation of the effluents from a dye house was achieved after 2 hours. Fang et al. (1999) reported that the amount of colour removal was found to be advantageous as the reaction time increased. Yang et al. (1998) reported that a 95% colour removal was achieved on some reactive, acid, direct and basic dyes when used with H_2O_2 /UV. Verma and Ghaly (2008) reported a 99.9% degradation of 300 mg/L ramazol dye when treated with UV/ H_2O_2 at a residence time of 42 min, which was a much greater degradation than those obtained with just UV or just H_2O_2 . Shu and Chang (2005) compared the decolourization effects of six different azo dyes and determined that more than 95% degradation was achieved when treated with UV/ H_2O_2 in less than 11.5 min, which was higher than the degradation rate achieved with UV/ O_3 for the same time period.

From the results obtained it was witnessed that the degradation percentage of reactive Black 5 under UV and 20 ml/L H_2O_2 was found to be slightly higher than the degradation efficiency of UV and 10 ml H_2O_2 . Georgiou et al. (2002) noted that even a small amount of H_2O_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. Modirshala et al. (2006) reported that the improvement in decolourisation was not found to be significant above certain amount of H_2O_2 due to the recombination of hydroxyl radicals in the solution or the reaction between hydroxyl radicals and H_2O_2 creating hydroxyl radical scavenging capacity.

4.3. Comparative analysis

Treatment of the 50 mg/L dye concentration with UV/ 10 ml/L H_2O_2 provided higher degradation (99.70% after 25 min) than the treatments with UV (27.01% after 60 min). When the 500 mg/L dye concentration was treated with UV/ 10 ml/L H_2O_2 , it also provided higher degradation (99.70% after 60 min) than UV (0.33% after 60 min).

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. 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 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). Due to lack of cost effectiveness, I could not do performance in longer exposure time. It will be done for further studies

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 250 mg/L. A longer exposure time of the effluent containing 20ml/L H_2O_2 to UV was found to reduce COD further. Hence, a longer exposure time, even after complete decolourization, is recommended in order to reduce the COD to the acceptable limit of 250 mg/L.

Soutsas et al. (2010) stated that, the COD reduction potential was a function of the dye concentration, the higher the dye concentration, the lower the reduction potential. 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 potential 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 /Fe²⁺. 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. White (2011) stated that excess amount of H_2O_2 added to the effluent for treatment might not cause an environmental hazard due to its capacity to degrade under sunlight.

4.4. Effect of pH

Several researchers indicated that photo oxidation is more efficient under acidic conditions than alkaline conditions. Galindo and Kalt (1998) reported that H_2O_2 /UV oxidation was far more efficient when used under an acidic pH. They stated that when H_2O_2 is 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 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. Azbar et al. (2004) reported that the best reduction in COD and colour was obtained when treatment was performed in an acidic pH rather than an alkaline pH.

In this study, the pH was adjusted to 10-11 which is the range of pH for textile effluent. The effluent was treated at the discharge pH (10-11) in order to eliminate the acidification step and minimize the impact on the environment. under alkaline condition (99.96% after 20 min for 50 mg/L dye concentration and 99.95% after 60 min for 500 mg/L dye concentration). Higher exposure time and other pH could have tried to achieve with the better performance and it will be done for the further studies.

The difference in decolourization time does not justify the disposal problems associated with lower pH and the cost of chemical addition to the effluent to bring the lower pH value and then to the neutral value. 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. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are made from the study.

1. Out of the two treatment processes studied in this study to control the excess Azo dye, UV / H₂O₂ was found to be the more effective treatment process.
2. Any excess H₂O₂, if present, can be easily removed by the sunlight due to its instability. Hence, exposing the effluent to sunlight after treatment is highly recommended to remove the remaining H₂O₂ in the treated effluent.
3. The discharging effluent was treated at the range of pH between 10 and 11 in order to eliminate the acidification step and minimize the impact on the environment. However, higher exposure time and other pH ranges could have been tried to achieve a better performance. Therefore, further studies with other pH values are recommended before deciding on discharging the effluent to the environment.
4. From the COD results, it was evident that the reduced COD values are seen with the longer exposure time (60 min). However, it could not be tested due to high cost and the available time for this study. Therefore, further studies are highly recommended with longer exposure time even beyond 60mins.
5. The temperature after treatment was always found to be increased from 22⁰C to 41⁰C after 60 min of exposure to UV. The textile effluent from the industry has a temperature

of 27-30⁰C and treatment with UV would increase it even further. Hence, a storage unit should be used for the effluent to cool down before it is discharged into the environment in order to avoid thermal pollution.

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