Photooxidation of a reactive azo-dye from the textile industry using UV/H₂O₂ technology: process optimization and kinetics

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ABSTRACT

The homogeneous advanced oxidation process of UV/H₂O₂ was utilized to decolourize CI Reactive Red 195A (RR195A) as one of the most used dyes in the textile industry in Queensland. The UV radiation source was a low-pressure mercury arc lamp (60W emitting at 253.7nm). In this study, the effects of initial hydrogen peroxide (H₂O₂) dosage, dye concentration, pH and temperature were examined to find out the optimum operating conditions of the treatment process. Complete decolourization was achieved in the relatively short time of 20-30 minutes irradiation. Faster decolourization was achieved at low pH and high temperature. The removal rate increased with increasing initial concentration of H₂O₂ up to an optimum value. The decolourization reaction was found to follow at least initially first order kinetics with respect to the dye concentration. However, even after near complete removal of the active dye from the solution, approximately 60% of the COD was still remaining, indicating only partial breakdown of the dye molecule. In general, the result indicates that the UV/H₂O₂ technology proved to have good potential for removing dyestuff from wastewater but further treatment might be necessary to achieve complete mineralization of the organic intermediates.

KEYWORDS

Reactive azo-dye, Decolourization, Photooxidation, Textile, UV/H₂O₂ technology

1. INTRODUCTION

Synthetic dyes are produced and consumed annually in large quantities in different kinds of industries, such as textile, food, leather, paper, photography, cosmetics and pharmaceutical industries. The world production of synthetic dyes for textiles is over 7×10^5 tonnes/year and has been increasing (Zollinger, 1989), utilizing a great amount of reactive azo dyes due to the high demand for cotton fabrics with brilliant colours. Large amounts of coloured wastewater that contain synthetic dyes are generated especially from the textile finishing industry. In many cases this kind of wastewater is resistant to biodegradation because of its complex structure and it usually contains toxic metabolic products such as aromatic amines (Ince and Gonenc, 1997). Consequently, conventional activated sludge systems have difficulty in handling such wastewater, particularly in removing the colour. The ineffective treatment by conventional systems causes the release of about 20-50% of unfixed dyes into the environment (Peralta-Zamora *et al.*, 1999). Coagulation/flocculation and other conventional physical-chemical techniques are known to be costly and only transfer the pollutants from the liquid to the solid phase and thus other secondary problems arise. Therefore, a better and more appropriate method of handling coloured wastewater is needed.

Numerous advanced treatment technologies have been developed to reduce contaminants from textile wastewater. Among these technologies, advanced oxidation processes (AOPs) are known as the most popular unit operations as they show superior treatment efficiencies for removing colour and substantial organic materials from textile effluent (Hung *et al.*, 2001). The AOPs are very effective due to the generation of short-lived, very reactive hydroxyl radicals (OH[•]) that attack organic compounds with a high reaction rate. The oxidation potential of this radical is 2.80V making it the most powerful oxidizing agent after fluorine (3.03V). Additionally, the hydroxyl radical can oxidize a broad variety of organic substances 10^9 -times faster than ozone (Parsons,

2004). Some examples of AOPs are the use of ozone (O_3), UV/ H_2O_2 , UV/ O_3 , UV/ TiO_2 and Fenton reagents (H_2O_2/Fe^{2+}). The advantages of AOPs are their high treatment efficiencies, fast reaction rates, hence relatively small reactors, high flexibility and the possibility of incorporating them into water recycling processes (Colonna, *et al.*, 1999). The UV/ H_2O_2 method of treating textile wastewaters is relatively new and shows the potential to degrade toxic and/or carcinogenic compounds effectively. Through the UV/ H_2O_2 process, stable organic compounds with high molecular weights are broken down into smaller structures, which are more biodegradable (Chun & Yizhong, 1999). The treated effluent does not contain sludge (Zhang *et al.*, 1998) and foul odours are greatly reduced (Robinson, *et al.*, 2001). In addition, compared to the other AOPs, the UV/ H_2O_2 method offers several advantages as H_2O_2 is quite stable and commercially available, and fully dissolves in water without any phase transfer problems. Furthermore, the method also has simplicity of operation and lower investment costs (Colonna, *et al.*, 1999, El-Dein, *et al.*, 2001). In the present paper the photochemical method of dye degradation with UV/ H_2O_2 process was investigated. A range of experimental parameters (initial H_2O_2 dosage, dye concentration, pH and temperature) was studied to find the optimum treatment conditions for practical applications of dye removal from wastewater.

2. MATERIALS AND METHODS

2.1. Reagents

The azo dye, RR195A (Recochem, Australia), was obtained from the Logan Textile Company, Queensland, Australia, as a commercial product that is regularly utilized by the company. Analytical grade H_2O_2 (30% w/w) was obtained from Merck (Germany) and used without further purification. The pH was adjusted to the desired value using H_2SO_4 and NaOH. All the other chemicals were at reagent grade quality and solutions were prepared with MilliQ[®] water.

2.2. Photoreactor

The photoreactor is an Ultraviolet Technology of Australasia (UVTA) model LC-20 with the total volume of 585ml, which is one of a family of UV disinfection units manufactured by UVTA Pty. Ltd. (Australia). The photoreactor is covered by a metal casing. The UV light irradiates the simulated wastewater as it flows through the AFP840 tubing within the unit. The AFP840 teflon type tube is transparent, non-wettable, and chemically inert. The photoreactor is fitted with a fixed low-pressure mercury lamp (60W emitting at 253.7nm) with energy rating of more than 40,000 $\mu Ws/cm^2$. The lamp should be warmed up for a few minutes before H_2O_2 is added to get a constant UV flux and eliminate temperature variations.

2.3. Methods

In this study, the dye was hydrolyzed in an aqueous solution of 0.1 M NaOH at boiling point for 20 minutes before use (El-Dein *et al.*, 2001) as is done in the usual application process. The dye was the sole organic carbon compound in the solution. H_2O_2 concentration was determined by Reflectoquant Peroxide test strips (Merck, Germany). A spectrophotometric method (APHA, 1995) using Photometer SQ 118 (Merck, Germany) with a wavelength of 550nm was used to measure the dye concentration from filtered samples. Chemical oxygen demand (COD) was measured according to the Standard Methods (APHA, 1995) using a Thermoreactor TR 300 (Merck, Germany) and absorbance measurements were made using the Photometer SQ 118 (Merck, Germany). Temperature and pH levels were measured using a Metrohm 744. Samples were taken every 2.5 minutes, filtered (0.22 μm Millex[®] GP, Bedford, USA) and diluted when necessary. Simulated wastewater was prepared immediately just before irradiation. Control experiments were carried out under UV irradiation without H_2O_2 in the solutions and with H_2O_2 but no irradiation.

3. RESULTS AND DISCUSSION

3.1. Effect of initial H₂O₂ dosage

Different concentration of H₂O₂ (100, 200, 300, 600, 900, 1500, and 3000mg/l) were added to study the effect of H₂O₂ concentration on the decolourization rate. Figure 1 shows the decolourization of RR195A as a function of UV irradiation time for various initial H₂O₂ dosages. In general, the normalized dye concentration C_t/C_0 decreased over time in the presence of H₂O₂ and UV. The decolourization rate of RR195A as a function of H₂O₂ concentration is shown in Figure 2. The removal rate increased with increasing initial concentration of H₂O₂. However, as the initial concentration of H₂O₂ reached a certain value, the increase in decomposition rate became only small. The decolourization rate was slow at low H₂O₂ concentration, as the formation of hydroxyl radicals was insufficient. At higher H₂O₂ concentration, more OH[•] was produced leading to a faster oxidation rate. However, these free radicals preferred to react with the excess of H₂O₂ rather than with the dye (Legrini *et al.*, 1993, Galindo & Kalt, 1999). Hydroperoxyl radicals (HO₂[•]) as the competitive reaction product are much less reactive than OH[•] and do not seem to contribute to the decolourization of RR195A.

H₂O₂ with the initial concentration of 300 to 900 mg H₂O₂/L is suitable for the decolourization of RR195A using UV/H₂O₂ system as it gave a high decolourization rate. By adding 300 to 900 mg H₂O₂/L, the decolourization was about 99-100% at 30 minutes of irradiation. The most favourable initial H₂O₂ concentration that was observed for the optimum decolourization of RR195A was 300 mg H₂O₂/L. With the concentration of 300 mg H₂O₂/L about 80% of the dye was removed with a relatively short time of irradiation (17.5 minutes). Compared to an initial concentration of 600 mg H₂O₂/L, the 50% lower concentration still achieved a more favourable decolourization rate per H₂O₂ addition. The more initial H₂O₂ concentration in the system, the higher the H₂O₂ residual will be in the effluent. It is important to notice that only the combined utilization of UV and H₂O₂ achieves this high decolourization rate since control experiments showed that neither H₂O₂ nor UV alone were able to significantly reduce the RR195A concentration under comparable conditions.

Fig. 1. Effect of different initial H₂O₂ concentration dosages on the decolourization of RR195A using the UV/H₂O₂ method. Initial dye concentration=100mg/L, pH=8, temperature=30°C.

Fig. 2. Decolourization rate of RR195A as a function of different initial H₂O₂ concentration dosages. Initial dye concentration=100mg/L, pH=8, temperature=30°C.

3.2. Effect of initial pH

The effect of different pH values (3, 6, 7, 8, 9, 10, 11 and 12) on RR195A decolourization by using the UV/H₂O₂ system was examined. It is known that the pH of the solution will determine the efficiency of the UV/H₂O₂ treatment process. In this study, all experiments were conducted in unbuffered solutions. From Figure 3 we can see that during 30 minutes of irradiation, the colour removal was about 95% at pH 3 and 92 to 94% at pH 6 to 8. The decolourization rates under UV/H₂O₂ should decrease with increasing pH (Shu *et al.*, 1994). In alkaline condition, H₂O₂ will decompose into water and oxygen rather than hydroxyl radicals (Shu *et al.*, 1994, Galindo *et al.*, 1998). This causes the lower decolourization rates of azo dyes at higher pH values because the concentration of OH[•] is reduced under these conditions.

Figure 4 shows the decolourization rate of RR195A at various pH levels. The decolourization rate was increasingly less effective at pH values higher than 8. While acidic conditions achieve a more effective decolourization, the effect of pH values in the range of 8 to 11 is still relatively limited, but the reaction rate and efficiency is certainly dramatically reduced at a pH of 12. Typically, the final effluent from textile industries usually has normal to high pH (7-12). It would therefore be essential to ensure the most appropriate pH is used to get optimum reaction performance.

Fig. 3. Effect of different pH levels on the decolourization of RR195A using the UV/H₂O₂ method. Initial dye concentration=100mg/L, H₂O₂=300mg/L, temperature=30°C.

Fig. 4. Decolourization rate of RR195A as a function of different pH levels. Initial dye concentration=100mg/L, H₂O₂=300 mg/L, temperature=30°C.

3.3. Dye concentration variations

Different initial dye concentrations were tested to see the effect on RR195A decolourization using the UV/H₂O₂ method. The results are shown in Figure 5 for a H₂O₂ concentration of 300 mg/L and a pH = 8. The removal rate decreased from 100% to only 17% in 30 minutes with increasing dye concentrations from 50 to 453 mg/L. Higher dye concentrations increased the absorption of UV radiation, therefore decreasing the availability of UV light for reactions with H₂O₂ and thus lowering the formation of hydroxyl radicals in the solution (El-Dein *et al.*, 2003). The decolourization rate was found to follow first-order kinetics with respect to the dye concentration as the rate constant was affected by changing the initial concentration of RR195A.

$$\frac{-dC_t}{dt} = k_{obs} C_t \quad (4)$$

$$\ln\left(\frac{C_o}{C_t}\right) = -k_{obs} t \quad (5)$$

Where C_t is the concentration of the dye at a certain irradiation time (t), and k_{obs} is the first order rate constant. We will get Eq. 5 by integrating Eq. 4 with the restriction of $C_t = C_o$ at $t = 0$. Table 1 shows the first order rate constants of RR195A decolourization.

The rate constants dropped off with increasing dye concentrations as can be seen in Fig. 6, although the initial concentration of H_2O_2 was the same. The semi-log charts of C_t/C_o against time were linear confirming the first order reaction kinetics of the dye removal rate with respect to the dye concentration. The reaction rates changed when the C_t/C_o ratio dropped below 0.2 as the amount of UV radiation absorbed by H_2O_2 increased after removing 80% of the colour, and possibly other chemical reactions started to occur (El-Dein *et al.*, 2001). The observed initial first order rate constants for RR195A removal were determined from the slopes of the linear regression lines shown in Fig. 6. Different initial concentrations of the dye caused incomparable reaction conditions resulting in different k_{obs} values.

Fig. 5. Effect of different initial dye concentration on the decolourization of RR195A using the UV/ H_2O_2 method. Initial H_2O_2 concentration=300mg/L, pH=8, temperature=30°C.

Fig. 6. Logarithmic representation of the RR195A decolourization against irradiation time with linear regression lines demonstrating the first order kinetics of the degradation reaction. Initial H_2O_2 concentration=300mg/L, pH=8, temperature= 30°C.

Table 1.

Values of k_{obs} determined by linear regression for different dye concentration

Initial dye concentration (mg/L)	k_{obs}	r^2
50	0.150	0.9106
75	0.112	0.9860
100	0.091	0.9946
170	0.025	0.9911
453	0.007	0.9741

3.4. Effect of Temperature

To find the effect of temperature on removal rates, several runs were conducted at temperatures between 15 and 75°C, with H_2O_2 concentration of 300 mg/L, pH = 8 and initial dye concentration of 100 mg/L. The dye removal rate by using the UV/ H_2O_2 method increased with increasing temperature of the system as shown in Fig. 7. A complete decolourization of RR195A was achieved in 22.5 minutes at 75°C, 30 minutes at the temperature of 30 and 55°C. The slowest rate in this experiment was achieved at 15°C as incomplete decolourization occurred even after 30 minutes of irradiation. Heating either increased the generation rate of hydroxyl radicals or directly affected the reaction rate with the dye molecule. Given that the overall rate seems to be limited by the

availability of hydroxyl radicals (see Section 3.1 above), it is likely that the higher temperature reduced the activation energy for the H_2O_2 reaction to hydroxyl radicals.

Fig. 7. Effect of different temperature on the decolourization of RR195A using the UV/ H_2O_2 method. Initial dye concentration=100mg/L, H_2O_2 =300mg/L, pH=8.

3.5. COD removal

The COD removal was examined at the condition which is assumed as the most appropriate one based on the experimental results above. The UV/ H_2O_2 process was run at the initial H_2O_2 concentration of 300 mg/L, dye at 100 mg/L, pH = 8 and at 30°C. Even though almost all of the dye was removed (97%) from the wastewater in under these conditions after 30 minutes, only about 35-40% of COD removal was achieved (data not shown). Further organic degradation of the organic intermediates is needed to fully mineralize the wastewater. Some alternatives proposed are extending the irradiation time or combining the UV/ H_2O_2 method with other technologies that are able to remove the COD effectively.

4. CONCLUSION

In this study, the experimental results demonstrate that the UV/ H_2O_2 technology can be effectively utilized for the decolourization of RR195A in a relatively short period of time of about 30 minutes. The decolourization was strongly influenced by various parameters, particularly the initial H_2O_2 dosage, dye concentration, pH, temperature as well as irradiation time. The photooxidation of RR195A by using the UV/ H_2O_2 is more effective in an acidic medium with the initial dosage of H_2O_2 ranging between 300-900 mg H_2O_2 /L and at a high temperature. However, the final effluent of the textile industry typically has a high pH and moderately high temperature. Therefore, in this study we concluded that the operation of the UV/ H_2O_2 process at a pH of 8 and the temperature of 30°C was probably most suitable as decolourization still takes place efficiently. The decolourization of RR195A follows first order kinetics with regards to dye concentration. Further research is in progress in order to integrate the UV/ H_2O_2 method with an aerobic biological process to study the complete mineralization of RR195A since approximately 60% of the COD was still remaining even when the dye was almost completely removed from the solution.

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