Iran. J. Environ. Health. Sci. Eng., 2008, Vol. 5, No. 2, pp. 95-100

PHOTOCHEMICAL OXIDATION OF REACTIVE BLUE 19 DYE (RB19) IN TEXTILE WASTEWATER BY UV/$K_2S_2O_8$ PROCESS

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Received 14 November 2007; revised 13 January 2008; accepted 11 March 2008

ABSTRACT

In textile industry, advanced oxidation processes are used for degrading and removing color from dye baths which allow wastewater reuse. In this study, photochemical oxidation processes (UV-A/$K_2S_2O_8$, UV-C/$K_2S_2O_8$) and chemical oxidation process (dark/$K_2S_2O_8$), were investigated in a laboratory scale photoreactor for decolorization of the Reactive blue 19 (RB19) dye from synthetic textile wastewater. The effects of operating parameters such as potassium persulphate dosage, pH, reaction time and UV source, on decolorization have been evaluated. The results of direct chemical oxidation showed that 50% of the dye was been removed using $K_2S_2O_8$ in dark condition after 5h reaction time and photochemical oxidation showed that UV-C irradiation is more effective than UV-A for RB19 dye removal. The RB19 solution was completely decolorized under optimal potassium persulphate dosage of 5mmol/L and low-pressure mercury UV-C lamps (15w) in less than 30min. UV/$K_2S_2O_8$ experiments showed higher color removal performance under acidic conditions (pH=3), and in this condition with 5mmol/L of potassium persulphate, 78.5% COD has been removed after 3h irradiation time. The decolorization rate fitted to pseudo-first order kinetics with respect of dye concentration. The reaction rate constants for photochemical degradation of RB19 were 0.014 and 0.237 for UV-A/$K_2S_2O_8$ and UV-C/$K_2S_2O_8$ processes respectively.

Key words: Photochemical oxidation, UV/persulphate, Reactive Blue 19 dye, Textile Wastewater, Decolorization

INTRODUCTION

In textile industry the process of dyeing results in the production of large amounts of wastewater exhibiting intense coloration that has to be eliminated before release into natural water streams (Mohorčič *et al.*, 2006). Wastewaters from textile industries contain different types of synthetic dyes, which are mostly toxic, mutagenic and carcinogenic. Moreover, they are very stable to light, temperature and microbial attack, making them recalcitrant compounds (Kokol *et al.*, 2007). Discharging of these wastewaters into receiving streams not only affects the aesthetic aspects but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity (Çiçek *et al.*,2007).

Reactive dyes are water-soluble, anionic dyes that require relatively simple dyeing methods. They are mainly used for dyeing cellulosic fibers, such as cotton and rayon, but are also used for silk, wool, nylon, and leather (Yang and Jared McGarrahan, 2005). Reactive dyes are extensively used in textile industry, fundamentally due to the capacity of their reactive groups to bind on textile fibers by covalent bonds formation (Pelegrini *et al.*, 1999). The major environmental problem associated with the use of the reactive dyes is their loss in the dyeing process (Pelegrini *et al.*, 1999). The Reactive Blue 19 (RB-19), also known as Remazol brilliant blue, is very resistant to chemical oxidation due to its aromatic anthraquinone structure highly stabilized by resonance.In case of RB 19, the relatively low fixation efficiency (75–80%) is due to the competition between the formation of the reactive form (vinyl sulfone) and the hydrolysis reactions

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(Pelegrini *et al.*,1999 ; Lizama *et al.*, 2002).

Color removing from dye-house wastewater is currently one of the major problems faced by the textile dyeing industry. Various physical, chemical and biological treatment methods have been used for treatment of these textile effluents (Çiçek *et al.*, 2007). Oxidation processes are widely used both in industrial pretreatment and in fullscale treatment. In textile industry these processes are used for degrading and removing color from dye baths which allow wastewater reuse (Gemeay *et al.*, 2007). Photolysis of persulphate anion produces two sulfate radical anions, which are also strongly oxidizing agents, also sulphate radical anions are known to generate hydroxyl radicals (Neppolian *et al.*, 2002; Villanueva *et al.*,2007). The $S_2O_8^{2-}$ oxidant enhances mineralization of organic compounds during the degradation process compared to UV-C alone and engages in the following three possible modes of reactions with organic compounds: (i) by abstracting a hydrogen atom from saturated carbon, (ii) by adding hydrogen to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anion and from certain neutral molecules (Neppolian *et al.*, 2002; Villanueva *et al.*,2007). Reactions of dye removal under UV, $K_2S_2O_8$ and UV/$K_2S_2O_8$ processes can be presented by:

$$\mathrm{Dye} + S_2O_8^{2-} \rightarrow \mathrm{products} \qquad (1)$$

$$\mathrm{Dye} + h\nu \rightarrow \mathrm{products} \qquad (2)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\bullet} \qquad (3)$$

Photooxidation can be fitted reasonably well by an exponential decay curve suggesting a pseudo-first order reaction with respect to dye concentration (Faisal *et al.*, 2007). Kinetic pathway of color degradation could be expressed as follows:

$$-\frac{dC}{dt} = kt \qquad (4)$$

Where k is the reaction apparent rate constant (1/min); C, the dye concentration at a given time (mol/L); and t, the exposure time (min) (Aleboyeh *et al.*, 2003). This equation,after integration with initial condition C=C_0 for t=0, leads to:

$$\ln\frac{C}{C_0} = -kt \qquad (5)$$

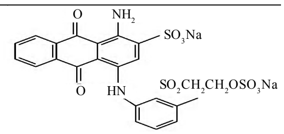
Current research has been focused on the photo-degradation of Reactive Blue 19 dye from synthetic textile wastewater by UV irradiation and UV/H_2O_2 processes.

MATERIALS AND METHODS

Materials

The RB19 was purchased from the Dystar (Germany) and used without further purification. Solutions were prepared with the dye using distilled deionized water. The Main characteristics of the dye is given in Table 1 (Kurbus *et al.*, 2002; Lee *et al.*, 2004). pH of solutions was adjusted with NaOH and HNO_3. All other reagents were analytical grade.

Table 1: Main characteristics of RB19 dye

Chemical structure	
C.I.generic name	C.I.Reactive Blue 19
Synonym	Remazol Brilliant Blue R
Molecular Formula	$C_{22}H_{16}O_{11}N_2S_3Na_2$
Molecular Weight	626.5g/moL
λ_{max}	592nm

*from Dystar. CO, Germany

UV reactor

For UV irradiation and UV/$K_2S_2O_8$ process, irradiation was carried out with 15 W (UV-A, UV-C) low-pressure mercury lamps which emits mainly at 365nm and 254nm respectively. The reactor used in this study was a batch photoreactor of 1.25L in volume. The UV-C light source was placed into a quartz sleeve. Mixing was provided by circulating the reaction solution with a peristaltic pump (Heidolph Pumpdrive 5001) at a rate of 250cm^3/min.

Procedure of study

UV-A/$K_2S_2O_8$ control and UV-C/$K_2S_2O_8$ experiments were started by turning the light on and adding appropriate amounts of persulphate into the reaction solution, respectively, which accounted for t=0. Reactions were performed at ambient temperature (25°C). Experiments were carried out with three different pHs of nominal 3, 7 and 10, corresponding to initial dye concentration (100mg/L). Different initial persulpate concentrations (0.5-10mmol/L) were also investigated. Control experiments without UV irradiation (i.e., $K_2S_2O_8$ oxidation only) were conducted at 5mmol/L $K_2S_2O_8$ concentration.

Analytical methods

Since color removal was the principal objective of this study, samples were collected at different times and immediately analyzed for dye concentration, COD and pH. In this regard, the color without filtering or centrifuging the samples was measured by spectrophotometer (based on bear-lambert law). UV-Vis spectra have been acquired between 200 and 800nm with a Unico spectrophotometer (UV 2100) as shown in Fig. 1. Dye concentrations were calculated from the calibration curve prepared from the dye concentration and the measured absorbance at λ_{max} (592nm) (Yang C and Jared McGarrahan J, 2005). Chemical oxygen demand (COD) was measured by the open reflux method according to the Standard Methods (APHA, 2005). The percentage of decolorization and COD removal were calculated as follows:

Decolorization or COD reduction (%)

$$= \left(1 - \frac{C}{C_0}\right) \times 100 \qquad (6)$$

Where C_o is initial dye concentration or COD (mg/L), C is final dye concentration or COD (mg/L) after UV or $UV/K_2S_2O_8$ processes (Şayan , 2006).

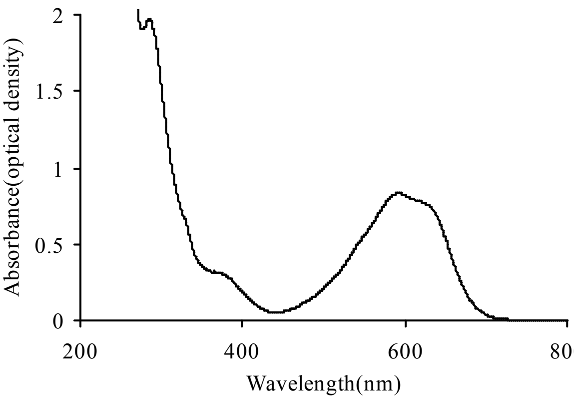


Fig. 1: Absorption spectra of the RB19 dye

RESULTS

The impact of UV-A and UV-C irradiation and pH and concentration of persulphate in dye removal under $UV/K_2S_2O_8$ process for reactive blue 19 dye was investigated. The results of this study showed that some amount of the dye (50% after 5h reaction time) was been degraded by using $K_2S_2O_8$ under dark conditions (Fig. 2). Although the rate of direct degradation of the RB19 dye in the presence of potassium persulphate was not negligible, but was slow. The effects of UV irradiation (UV-A,UV-C 15w) in various pH (3,7,10) and presence of $K_2S_2O_8$; was investigated the results of this stage showed that UV-C irradiation was more effective than UV-A for dye removal.

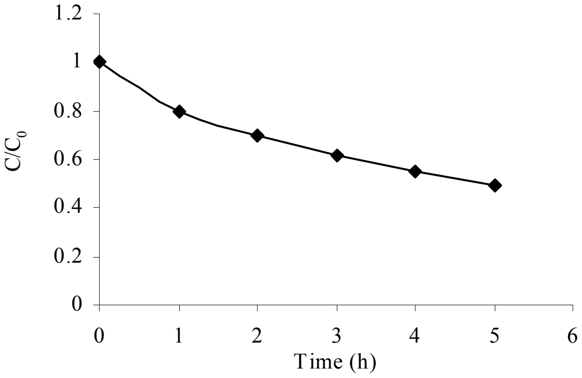


Fig. 2: Removal of RB19 in the presence of potassium persulphate (pH=5.8, C_{RB19}=100mg/L, $C_{persulphate}$=5mmol/L, Dark Conditions)

The most efficiency of decolorization in the presence of UV-A, UV-C and persulphate was shown in acidic condition (pH=3) (Fig. 3, Fig. 4). The RB19 dye removal efficiency were 31.5% and 100% (pH=3, reaction time=30min) under UV-A and UV-C irradiation, respectively. In optimum condition of pH, the effect of persulphate concentrations was investigated. The results showed that efficiency of RB19 dye removal was induced by increasing of $K_2S_2O_8$ concentration from 0.5 up to 10mmol/L (Fig. 5). The effect of 5mmol/L of persulphate for the removal of COD in pH=3 is shown in Table 2, According to these results, 78.5% COD removal was obtained after 3h irradiation time. The color removal rate constants by these processes were evaluated using a linear regression.

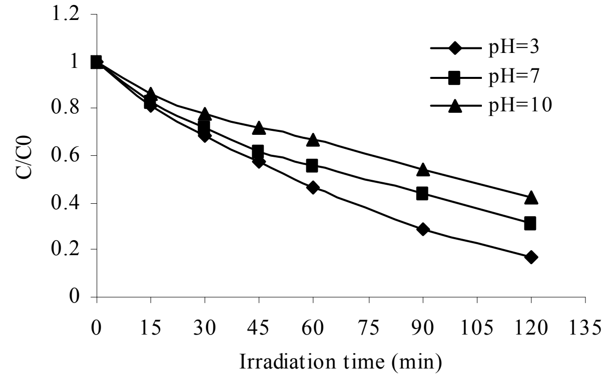


Fig. 3: Effect of pH on the dye residual fractions during UV-A/Persulphate process (C_{RB19}=100mg/L, L_{UV-A}=15w, $C_{persulphate}$=5mmol/L)

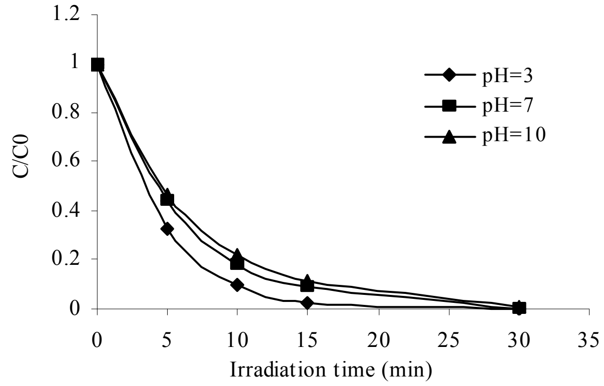


Fig. 4: Effect of pH on the dye residual fractions during UV-C/Persulphate process (C_{RB19}=100mg/L, L_{UV-C}=15w, $C_{persulphate}$=5mmol/L)

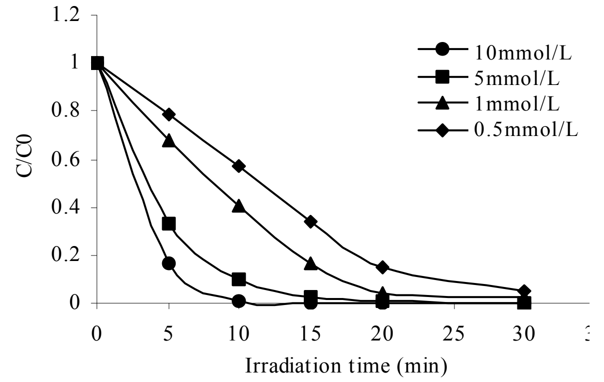


Fig. 5: Effect of potassium persulphate concentration on the dye residual fractions during UV-C/Persulphate process (pH=3, L_{UV-C}=15w, C_{RB19}=100mg/L)

Table 2: Results of COD concentration and removal by UV-C/ Persulphate process

Time (min)	COD (mg/L)	COD Removal (%)
0	121.8	0
30	108.04	11.3
60	83.19	31.7
120	41.09	66.65
180	26.18	78.5

(pH=3, $C_{persulphate}$=5mmol/L, L_{UV-C}=15w , C_{RB19}=100mg/L)

The semi-logarithmic graphs of the concentration of RB19 (100mg/L) in the presence of persulphate ion (5mmol/L) versus irradiation time yielded straight lines indicating pseudo-first order reaction. The first order plot of dye degradation with time under UV-A/$K_2S_2O_8$ and UV-C/$K_2S_2O_8$ processes are shown in Figs. 6 and 7. The reaction rate constants (k) for photochemical degradation of RB19 were 0.014 (R^2=0.9917) for UV-A/$K_2S_2O_8$ and 0.237 (R^2=0.9971) for UV-C/$K_2S_2O_8$ processes.

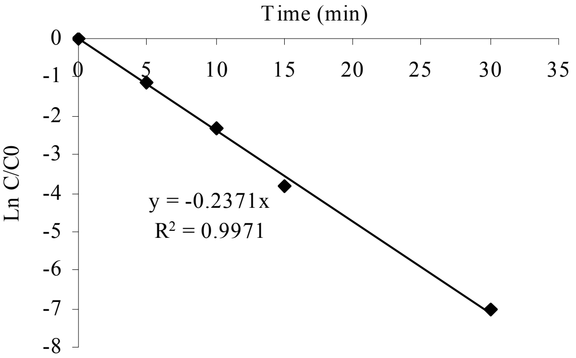


Fig. 6: First order plot of dye photochemical degradation with time (C_{RB19}=100mg/L, pH=3, L_{UV-C}=15w, $C_{persulphate}$=5mmol/L)

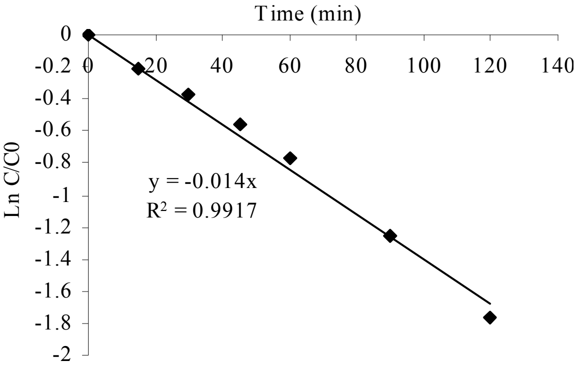


Fig. 7: First order plot of dye photochemical degradation with time (C_{RB19}=100mg/L, pH=3, L_{UV-A}=15w, $C_{persulphate}$=5mmol/L)

DISCUSSION

This work has shown that the photochemical degradation in the presence of persulphate ion is a good method for color removal and COD abatement of RB19 in synthetic textile wastewater under UV light source. The decolorization is enhanced by the presence of UV irradiation and $K_2S_2O_8$ due to the sulfate radical anions and hydroxyl radicals generated during the photochemical reactions. The reactions of dye removal under UV/$K_2S_2O_8$ process can be presented by:

$$SO_4^{-\bullet} + \text{Dye} \rightarrow SO_4^{2-} + \text{products} \qquad (7)$$

Sulfate radical anions are known to generate hydroxyl radicals according to the following equation (Neppolian *et al.*, 2002; Parida *et al.*, 2007):

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^{+} \qquad (8)$$

Hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule that can oxidize organic compounds (RH) producing organic radicals (R), which are highly reactive and can be further oxidized (Georgiou *et al.*,2002 ; Azbar *et al.*,2004).

The results showed the dependence of the decolorizing degree on the initial concentration of the potassium persulphate. Results agree with those found by Villanueva *et al.*, who reported that TiO_2 photocatalysis removed ~85% of color from the 0.2mmol acid orange 7 aqueous solution under solar light. While ~66% of color was abated using the persulphate ion as oxidant in the absence of TiO_2 under similar conditions in 2h (Villanueva *et al.*, 2007). The effective electron acceptor (oxidant) ability of persulphate ions has been observed in number of studies reported before (Abu Tariq *et al.*, 2005; Bahnemann *et al.*, 2007; Haque *et al.*, 2007). In these studies, potassium persulphate or ammonium persulphate was added to TiO2 photocatalytic reactor as an electron acceptor. The results of these studies have showed that the photodegradition rate enhanced in the presence of persulphate ions. UV/$K_2S_2O_8$ experiments showed higher color removal performance under acidic conditions (pH=3). These results agree with those reported by Villanueva *et al.*, who found that UV/$K_2S_2O_8$ and TiO_2/UV/$K_2S_2O_8$ processes require acidic conditions for high color removal performance (Villanueva *et al.*, 2007). An excess of persulphate ions reacts with dichromate in COD test, and therefore increases the apparent organic content in the sample. These results showed that the solution of persulphate (5mmol/L) in distilled water had 50mg/L COD. The results of these investigations agree with those reported by Villanueva *et al.*, who found that the persulphate ions reacts with dichromate in the COD test (Villanueva *et al.*, 2007). Results also proved that the pseudo-first order kinetic model is in good agreement with the experimental data and agree with those reported by Villanueva *et al.*, who found that the pseudo-first order kinetic model is in good agreement with the experimental data in TiO_2/UV/$K_2S_2O_8$ process (Villanueva *et al.*, 2007).

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