



# Journal of Applied Sciences

ISSN 1812-5654

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## Decolorization of Reactive Blue 19 Dye from Textile Wastewater by the UV/H<sub>2</sub>O<sub>2</sub> Process

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**Abstract:** Photo-oxidation of dyes is a new concern among researchers since it offers an attractive method for decoloration of dyes and breaks them into simple mineral forms. An advanced oxidation process, UV/H<sub>2</sub>O<sub>2</sub>, was 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 hydrogen peroxide dosage, pH, initial dye concentration and UV dosage, on decolorization have been evaluated. The RB19 solution was completely decolorized under optimal hydrogen peroxide dosage of 2.5 mmol L<sup>-1</sup> and low-pressure mercury UV-C lamps (55 w) in less than 30 min. The decolorization rate followed pseudo-first order kinetics with respect to the dye concentration. The rate increased linearly with volumetric UV dosage and nonlinearly with increasing initial hydrogen peroxide concentration. It has been found that the degradation rate increased until an optimum of hydrogen peroxide dosage, beyond which the reagent exerted an inhibitory effect. From the experimental results, the UV/H<sub>2</sub>O<sub>2</sub> process was an effective technology for RB19 dye treatment in wastewater.

**Key words:** Reactive blue 19 dye, decolorization, UV, H<sub>2</sub>O<sub>2</sub>, wastewater, textile

### INTRODUCTION

In the textile industry, the process of dyeing product of large amounts of wastewater exhibiting intense coloration that has to be eliminated before release into environment (Mohorčič *et al.*, 2006). Wastewaters from the 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). The discharge of the wastewaters into receiving streams not only affects the aesthetic nature but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity (Çiçek *et al.*, 2007). Reactive dyes are extensively used in the textile industry, fundamentally due to the capacity of their reactive groups to bind on textile fibers by covalent bonds formation. This characteristic facilitates the interaction with the fiber and reduces energy consumption. The dyes are mainly used for dyeing cellulosic fibers, such as cotton and rayon, but are also used for silk, wool, nylon and leather (Yang and Mc Garrahan, 2005). The Reactive Blue 19, also known as

Remazol brilliant blue, is very resistant to chemical oxidation due to its aromatic anthraquinone structure highly stabilized by resonance. In the particular case of the RB19, the relatively low fixation efficiency (75-80%) is due to the competition between the formation of the reactive form and the hydrolysis reactions (Pelegri *et al.*, 1999; Lizama *et al.*, 2002). Various physical, chemical and biological treatment methods have been used for the treatment of these textile effluents (Çiçek *et al.*, 2007; Daneshvar *et al.*, 2005). Advance oxidation processes are widely used both in industrial preparations and in environmental treatments. In the textile industry, these processes are used for degrading and removing color from dye baths, which allow wastewater reuse (Gemeay *et al.*, 2007). These processes are based on the production of very reactive hydroxyl radicals with an oxidation potential of 2.8 V as primary oxidizing species (Aleboyeh *et al.*, 2003; Galindo *et al.*, 2000; Mandal *et al.*, 2004). UV/H<sub>2</sub>O<sub>2</sub> process has been recognized that the efficiency of the oxidation process strongly depends on experimental conditions (García Einschlag *et al.*, 2003). The reactions of dye removal under UV, H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> processes can be presented by:

Dye+hv→products

Dye+H<sub>2</sub>O<sub>2</sub>→products

Dye+H<sub>2</sub>O<sub>2</sub>+hv→products

The aim of this study is to analyze the feasibility of discoloration of RB19 using a efficient advanced oxidation process, i.e., UV/H<sub>2</sub>O<sub>2</sub>. The influence of the pH solution and the concentration of the dyes on the decolorization were studied.

### MATERIALS AND METHODS

**Dye:** The RB19 was purchased from the Dystar (Germany) and used without further purification. Solutions were prepared with the dye using distilled deionized water. The molecular structure of the dye is shown in Fig. 1 (Kurbus *et al.*, 2002). The pH of solutions was adjusted with NaOH and H<sub>2</sub>SO<sub>4</sub>. All other reagents were analytical grade.

**Photoreactor:** All experiments were carried out in a mixed batch photoreactor of 2.5 L in volume. Mixing was provided by circulating the reaction solution with a peristaltic pump 5001 (Heidolph, Germany) at a rate of 250 cm<sup>3</sup> min<sup>-1</sup>. The radiation source was low-pressure mercury UV-C lamps (15 and 55 w, Philips, Holland). The UV lamps were inserted into a walled quartz immersion well located at the center of reactor. For the current decolorization study, 2.5 L of the colored water was initially placed in a UV/H<sub>2</sub>O<sub>2</sub> photoreactor. 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 color intensities of nominal 25 and 100, respectively. Different initial H<sub>2</sub>O<sub>2</sub> concentrations (0-250 mmol L<sup>-1</sup>) were also investigated. Control experiments without UV irradiation (i.e., H<sub>2</sub>O<sub>2</sub> oxidation only) were conducted at 2.5 mmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> concentration at the pHs. Blank experiments without H<sub>2</sub>O<sub>2</sub> dosage (i.e., UV photolysis only) were also carried out at the pH levels.

**Analytical methods:** Samples were collected at different times and immediately analyzed for color intensity and pH. Since color removal was the principal objective of this study, color intensity was the main parameter monitored. In this regard, the color without filtering or centrifuging the samples was measured spectrophotometrically. UV-Vis spectra have been acquired (200-800 nm) with a Unico

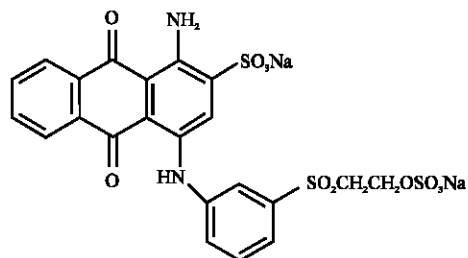


Fig. 1: RB-19 structure

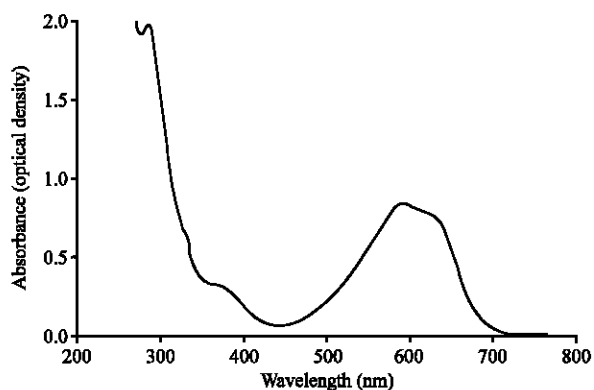


Fig. 2: Absorption spectra of the RB19 dye

spectrophotometer UV2100 (Fig. 2). Dye concentrations were calculated from the calibration curve prepared from the dye concentration and the measured absorbance at  $\lambda_{max}$  (592 nm) (Rajkumar *et al.*, 2007). The percentage of decolorization was calculated as follows:

$$\text{Decolorization (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100$$

where, C<sub>0</sub> is initial dye concentration and C is final dye concentration (Şayan, 2006).

### RESULTS AND DISCUSSION

Different H<sub>2</sub>O<sub>2</sub> concentrations were dosed to determine the effect of H<sub>2</sub>O<sub>2</sub> concentration on the decolorization rate by UV/H<sub>2</sub>O<sub>2</sub>. Blank experiments in the absence of H<sub>2</sub>O<sub>2</sub> (i.e., UV only) showed a quicker decolorization at a higher pH, although decolorization rates were slower than those for UV/H<sub>2</sub>O<sub>2</sub> systems. Control experiments with H<sub>2</sub>O<sub>2</sub> only achieved negligible decolorization (Fig. 3). The observation in the blank experiments was consistent with the results by Ince *et al.* (1997), who reported that the chemical bond of azo compounds could be directly but slowly photolyzed

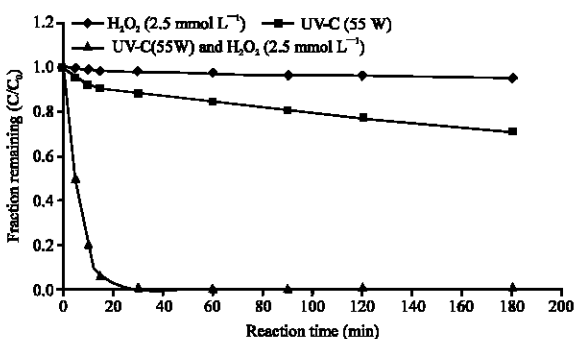


Fig. 3: Effects of UV-C Irradiation, H<sub>2</sub>O<sub>2</sub> and UV-C/H<sub>2</sub>O<sub>2</sub> process on the dye residual fractions, (C<sub>0</sub> = 25 mg L<sup>-1</sup>, pH 7, L:55W)

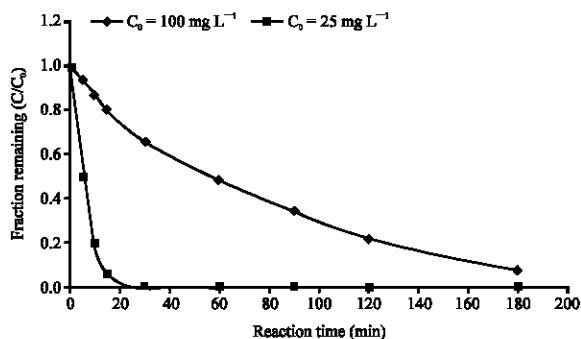


Fig. 5: Effects of initial color intensity on the dye residual fractions, (H<sub>2</sub>O<sub>2</sub> = 2.5 mmol L<sup>-1</sup>, pH 7, L:55 W)

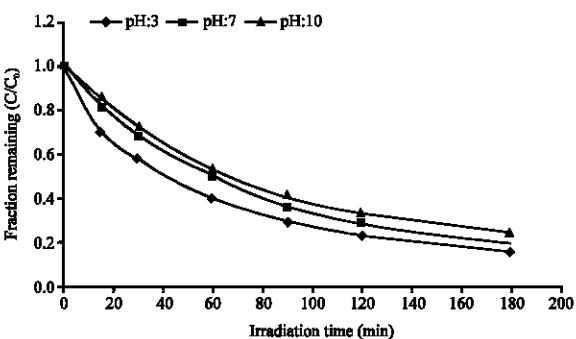


Fig. 4: Effect of pH on the dye residual fractions during UV-C/H<sub>2</sub>O<sub>2</sub> process, (C<sub>0</sub> = 100 mg L<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> = 2.5 mmol L<sup>-1</sup>, L:15W)

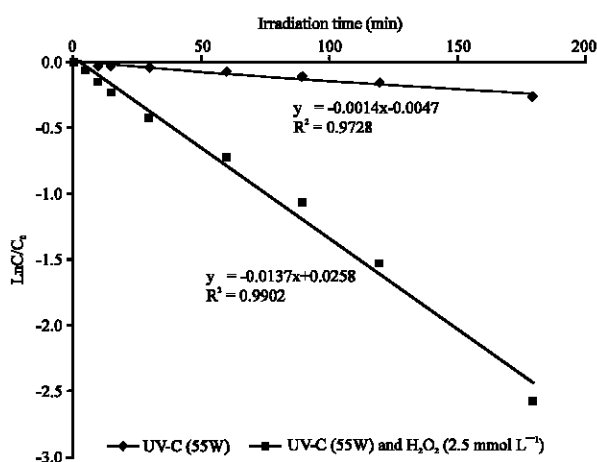
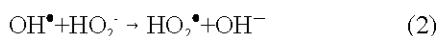
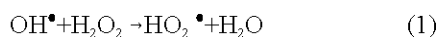


Fig. 6: First order plot of dye photochemical degradation with time, (C<sub>0</sub> = 100 mg L<sup>-1</sup>, pH 7, L:55W, H<sub>2</sub>O<sub>2</sub> = 2.5 mmol L<sup>-1</sup>)

by UV irradiation and that the process could be substantially improved by the addition of H<sub>2</sub>O<sub>2</sub>. The excess H<sub>2</sub>O<sub>2</sub> dose can reduce the oxidation rate by acting as a •OH radical scavenger itself as follows (Ku *et al.*, 1998).



Wang *et al.* (2000) reported decreased humic acid oxidation rates with the increase of H<sub>2</sub>O<sub>2</sub> concentration greater than 0.01%. Huling *et al.* (2000) also found a decreased oxidation of adsorbed 2-chlorophenol to granular activated carbon containing fixed iron oxide at the high H<sub>2</sub>O<sub>2</sub> concentration due to increased scavenging by excess H<sub>2</sub>O<sub>2</sub>. Also, the excess H<sub>2</sub>O<sub>2</sub> can absorb most of the light. The efficiency of photo-oxidation processes strongly depend upon the pH of the reaction solution. In general, the best UV/H<sub>2</sub>O<sub>2</sub> decolorization was achieved at

the pH of 3.0 (Azbar *et al.*, 2004), whereas a relatively less effective decolorization was observed in the solutions of pH 7.0 (Fig. 4). The effect of initial color intensity on decolorization efficiency was investigated. The decolorization rates were compare at pH 7.0 and different initial color intensity (Fig. 5). For the concentration 25 mg L<sup>-1</sup> decomposition was almost complete after 30 min of illumination, but for the higher concentrations the photo-oxidation process runs with some lower efficiency, however better results can be obtained by extension of reaction time. The large amount of dye inhibits the reaction of dye molecules with decrease of hydroxyl radicals. A pseudo first-order rate constant was calculated by simple least-squares regression of the natural log of color intensities versus time (Fig. 6). UV irradiation has a great influence to increase the photo-oxidation of dyes. The wastewater with high strength color is generally regarded as to be treated. Especially by the UV-irradiation technology, the strong strength of

wastewater absorbs UV resulting deduction of photo-efficiency, which irradiates hydrogen peroxide molecules into less free radical. Hence, the oxidation in UV/H<sub>2</sub>O<sub>2</sub> process is promoted positively by increasing UV power in order to overcome the treatment of color wastewater. The higher UV lamp power produced more and faster formation of OH• free radicals so as to improve the decolorization rate.

### CONCLUSIONS

The experimental results showed that the UV/H<sub>2</sub>O<sub>2</sub> process can be a suitable treatment method for decolorization of RB19 dye wastewater from textile industries under the optimal operating conditions. The decolorization rates of RB19 were determined and affected significantly by the pH, UV dosage, hydrogen peroxide dosage and initial dye concentrations. The UV/H<sub>2</sub>O<sub>2</sub> treatments were capable of decolorizing the colored wastewater at the pHs investigated (3.0, 7.0 and 10) within feasible treatment duration of less than 3 h. Enhanced decolorization was achieved with an increase in H<sub>2</sub>O<sub>2</sub> dosage and decrease in pH. An increase in H<sub>2</sub>O<sub>2</sub> concentration leads to a faster degradation up to a critical value; at a higher ratio the degradation process becomes slower. The only exception to this trend was at pH 10 where less decolorization was observed with an increase in H<sub>2</sub>O<sub>2</sub> dosage. Efficient decolorization and use of H<sub>2</sub>O<sub>2</sub> were observed at pH 3.0 conditions. It is recommended that the colored effluents be acidified prior to a decolorization step by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation. Present results prove that the pseudo-first order kinetic model is in good agreement with the experimental data. Although the decolorization rate will depend on the particular type of the dye, the technique seems to be applicable to any industrial wastewater containing dyes. These results can be taken as a starting step to establish the economical feasibility of the method, defining previously the degree of destruction and mineralization desirable for the next application of the wastewater.

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