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Decolorization of Turquoise Blue Dye by Ozonation, O₃/H₂O₂ and Fenton Processes

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Abstract: In this study, the decolorization of turquoise blue dye has been investigated by applying Advanced Oxidation Processes (AOPs) such as ozonation, O₃/H₂O₂ and Fenton. The effect of oxidant concentration on color removal has been studied for 100, 300 and 500 ppm of synthetic dye solution. It has been observed that initial dye concentration has an inverse effect on the efficiency of oxidation process for applied AOPs. The color removal efficiency using hydrogen peroxide alone was found to be 23% for 100 ppm dye solution. However, the color treatment efficiency reached to 57% when hydrogen peroxide was exposed along with FeSO₄ in Fenton process. Similarly, ozone when combined with hydrogen peroxide improved the efficacy of color removal from 72 to 90% for 100 ppm dye solution. The applied processes followed the trend O₃/H₂O₂>O₃>Fenton process>H₂O₂ for color removal at constant pH of 6 and 25°C temperature.

Key words: Decolorization, AOPs, Fenton process, O₃, O₃/H₂O₂

INTRODUCTION

Rapid industrialization with improper wastewater treatment and disposal of industrial wastes has resulted in severe pollution of the environment. Textile and dyestuff industries generate a large amount of contaminated effluent. During the last two decades, color removal from textile industry has attracted considerable attention due to color visibility in receiving water and the toxicity of certain dyes. It is estimated that between 10-15% of the total dyes used in textile production and dyeing process can be found in wastewater. The structural diversity of the synthetic dyes is derived from the use of different chromophoric groups e.g., azo, anthraquinone, triphenyl methane and polymeric compounds (Kazuaki *et al.*, 1998). These compounds have a great variety of colors and chemical structures and most of them are recalcitrant to direct microbial degradation. Although, the conventional treatment systems such as flocculation (Buschmann and Schollmeyer, 1997), sorption (Juang *et al.*, 1997), electrochemical and oxidative degradation (Nansheng *et al.*, 1997) are still widely used for wastewater treatment, yet most of them are limited due to their low performance and high cost. The degradations of a wide range of dyes by microorganisms have also been reported. However, the complexity of microbial system for degradation makes the process rather slow and costly and degradation of dyes in effluents by microorganisms yield potentially carcinogenic compounds (Ledakowicz and Gonera, 1999). Advanced oxidation processes have shown a great potential to decolorize and reduce recalcitrant wastewater loads from textile dyeing and finishing effluents (Lin and

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Lin, 1993). Advanced Oxidation Processes (AOPs) rely on the generation of very reactive and short lived hydroxyl radical (OH[•]). The hydroxyl radical has a high oxidation potential (2.8 eV) and attacks organic molecules by either abstracting a hydrogen atom or adding itself to double bonds. Thus, Advanced Oxidation Processes (AOPs) are amongst those alternative remedial technologies that have been gained widespread attention for the oxidation of the dyes in aqueous solutions and actual dye baths (Arslan, 2003; Bolanskaja *et al.*, 2006). The most common processes among AOPs are O₃, O₃/H₂O₂, O₃/UV, H₂O₂/UV, Fenton and Photo Fenton processes (Arslan and Balcioglu, 1999). In this study an attempt has been made to evaluate the effectiveness of O₃, O₃/H₂O₂ and Fenton processes for color removal, in terms of initial dye concentrations.

MATERIALS AND METHODS

Turquoise Blue (cationic basic) reactive dye was obtained from Panreac Co. (Barcelona, Spain) and was chosen as a model compound of triarylmethane dyes, whose structure can be depicted from Fig. 1.

Hydrogen peroxide (35% w/w) and FeSO₄·7H₂O were obtained from Merck (Germany) and were used without further purification. Three different concentrations of the dye solutions (100, 300 and 500 ppm) were used for each AOP and were prepared by dissolving requisite amount of the dye in deionized water. A UV-Vis spectrophotometer (Perkin Elmer 2000, England) was used for the determination of color removal at 613 nm. All the experiments were carried out for 0.5 L sample in batch mode at constant pH of 6, which was adjusted manually by adding 0.1 N NaOH/0.1 N HCl and at 25°C temperature.

Ozonation and O₃/H₂O₂ Processes

The ozonation and O₃/H₂O₂ processes were conducted in a bubble column type reactor made of Pyrex glass with internal diameter of 3.3 cm. A JQ-6M Puretech model ozone generator was used to produce ozone at the rate of 250 mg h⁻¹ for feeding into the reactor through a fine bubbling stone. The effect of ozone exposure time on decolorization of the sample was observed for above half an hour (36 min). The optimized dosage of H₂O₂ (0.5 ml L⁻¹) i.e., where maximum color removal was observed for all concentrations of the synthetic dye samples (Fig. 2) employed for O₃/H₂O₂ and Fenton processes.

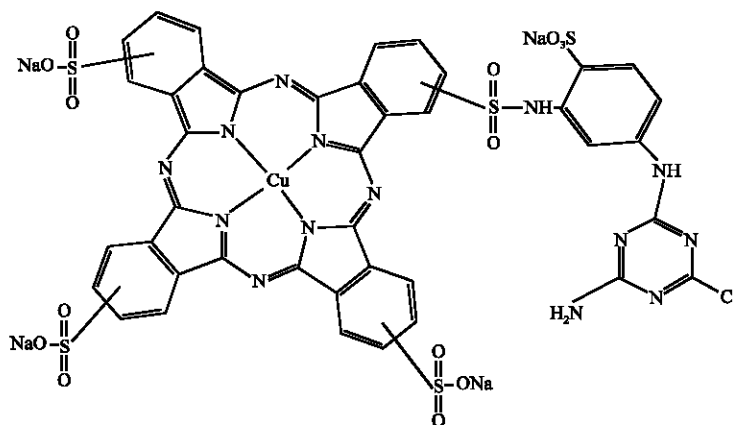


Fig. 1: Molecular structure of turquoise blue dye (reactive)

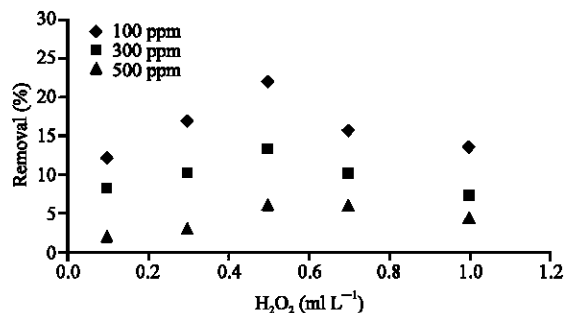


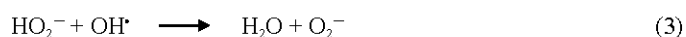
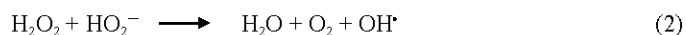
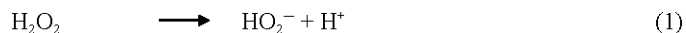
Fig. 2: Optimization of H₂O₂ concentration for O₃/H₂O₂ and Fenton process

Fenton Process

A graduated Pyrex glass vessel with magnetic stirring set up was used for Fenton process by using optimised dosage of H₂O₂ i.e., 0.5 ml L⁻¹. The mixing of sample dye solution with H₂O₂ and Ferrous sulfate was performed at 200 rpm for 10 min. The sample solution was then allowed to settle the unmixed amount of ferrous sulfate for 20 min. The concentration of ferrous sulfate was varied from 10 to 100 mg L⁻¹ to investigate its effect on decolorization of dye solution.

Optimization of H₂O₂ Dosage

The presence of excess H₂O₂ in the reaction mixture to inhibit further oxidation could be attributed from the following mechanism proposed by Beltran *et al.* (1996). According to this mechanism the hydroperoxy anions (HO₂⁻) are initially formed which is the conjugated base of H₂O₂ (Eq. 1). These HO₂⁻ anions then react with OH[•] radical and residual H₂O₂ (Eq. 2 and 3). Hence the presence of excess H₂O₂ could depress the applied process efficiency.



It is, therefore, important to optimize the applied dosage of H₂O₂ for improving the treatment performance. For this purpose, a jar-test was performed by rapid mixing of dye solution with H₂O₂ at 200 rpm for 10 min. The amount of H₂O₂ was varied from 0.1 to 1 ml L⁻¹ for 100, 300 and 500 ppm of dye solutions. Figure 2, shows the optimal dosage of H₂O₂ (0.5 ml L⁻¹) at which maximum color removal was observed for all the concentrations of dye solutions. Therefore, the optimized value of H₂O₂ dosage was employed for O₃/H₂O₂ and Fenton processes.

RESULTS AND DISCUSSION

The degree of dye decomposition increases with an increase in ozonation time that is with the dose of ozone administered. Hence the color removal was maximum i.e., 70, 50 and 25% for 100, 300 and 500 ppm of synthetic dye solutions respectively at 36 min of ozone exposure time. The experimental outcomes are shown in Fig. 3 that are in good agreement of results of Kos and Perkowski (2003). After 36 min no appreciable color removal was observed even with increase in ozonation time to 42 min in all concentrations of synthetic dye solutions. This could be explained by the fact that an

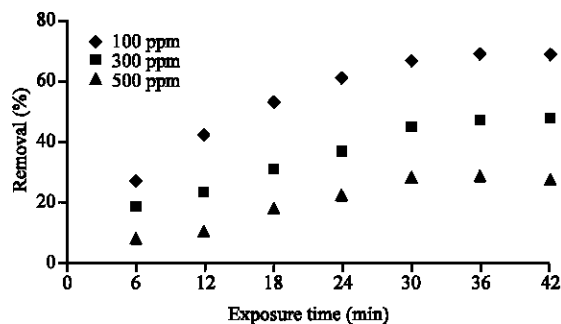


Fig. 3: Effect of ozone exposure time on color removal (at pH = 6; 0 zone dose = 250 mg L⁻¹)

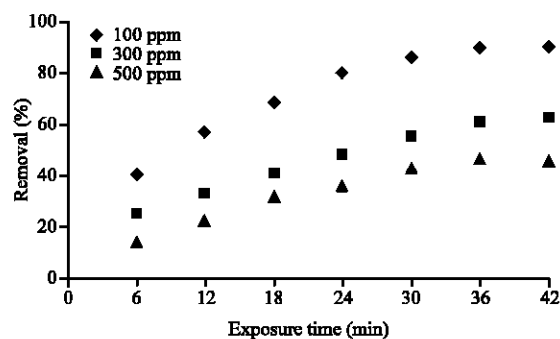


Fig. 4: Effect of ozone exposure time on color removal in O₃/H₂O₂ process (pH = 6, H₂O₂ = 0.5 ml L⁻¹ and ozone dose = 250 mg L⁻¹)

increase in ozone exposure time enhanced the mass transfer and reaction rate of dye solution. The decrease in color removal efficiency with increase in dye concentration may be attributed due to the competition of ozone between parent dye molecules and the reaction by-products.

The capability of ozone in oxidizing various pollutants by direct attack on aromatic rings is further enhanced in the presence of hydrogen peroxide due to the generation of highly reactive OH[•] radicals (Stowell and Jensen, 1991). Thus, combining H₂O₂ with ozone, the results for decolorization could be improved instead of using ozone only for the treatment of dyes. Figure 4, shows improved decolorization results i.e., 90% for 100 ppm dye solution for H₂O₂ when used in combination with ozone. An increase in color removal is observed with the increase in ozonation exposure time in all concentrations of dye solutions at optimal H₂O₂ dosage. Initially hydrogen peroxide is dissociated into hydroperoxide ions, which further attack the ozone molecules resulting in the formation of hydroxyl radicals. A significant decrease in the residual concentration of ozone also confirms that ozone consumes hydrogen peroxide effectively to generate OH[•] radicals (Kuo, 1992). The decrease in color removal with increase in dye concentration is due to the fact that number of dye molecules increased for a fixed no of OH[•] radicals.

Initially an increase in color removal was observed with the increase in FeSO₄ amount for all concentrations of synthetic dye solutions. However, the removal of color is decreased beyond 50 mg L⁻¹ of FeSO₄ concentration. Maximum value of color removal was found to be 55, 38 and 27% in case of 100, 300 and 500 ppm dye solution respectively at 50 mg L⁻¹ of FeSO₄ as shown in Fig. 5. Usually the rate of decolorization increases with an increase in the concentration of ferrous ions though the extent of increase is sometimes observed to be marginal above a certain concentration as reported

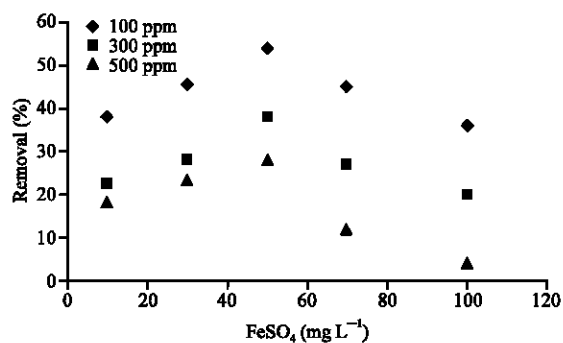


Fig. 5: Effect of FeSO₄ concentration on color removal (pH = 6 and H₂O₂ = 0.5 ml L⁻¹)

by Rivas *et al.* (2001). The decrease in color removal after pertaining a specific concentration of FeSO₄ could be explained as ferrous ions catalyze H₂O₂ to form hydroxyl radicals quickly at the initial stage of reaction. The amount of unutilized iron salt increases, which would result in an increase in the TDS and color contents of the effluent stream (Azbar *et al.*, 2004).

CONCLUSION

The color removal from various concentrations of synthetic dye (turquoise blue) solutions was carried out to reveal the efficacy of ozonation, O₃/H₂O₂ and Fenton processes at constant pH of 6 and 25°C temperature. The result outcomes showed that the color removal (100 ppm dye solution) was maximum in case of O₃/H₂O₂ i.e., 90% at 36 min ozone exposure time with optimal dosage of H₂O₂. Ozonation of 100 ppm dye solution essayed as second option with 72% color removal. While in Fenton Process, maximum color removal was observed at 50 mg L⁻¹ of FeSO₄ concentration. All the treatment processes showed a decrease in color removal with increase in initial dye concentration.

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