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Kinetics of UV, Fenton and Photo Fenton Processes for Decolorization of Various Red CL-5B Dye Concentrations

Abdullah Yasar, Nasir Ahmad, Aamir Amanat Ali Khan, Hajira Khan and Mehwish Khalid
Directorate of Research and Development, University of the Punjab, Lahore, Pakistan

Abstract: Decolorization of Red CL-5B azo dye was studied using UV, Fenton and Photo Fenton processes. The effect of initial dye concentration, FeSO_4 dose, pH and variation in UV time on decolorization was investigated. UV radiation was carried out with a 108 W low-pressure mercury lamp. Increase in the ferrous dose beyond the optimal dose resulted in significant decrease in color removal efficiency. The optimal doses were found to be 20, 30 and 50 mg L^{-1} for 100, 300 and 500 mg L^{-1} dye concentrations, respectively. The highest decolorization was observed at pH 2. However, in acidic range (2-6) removal efficiency for particular dye concentration was almost same at particular settling time. For photo Fenton process UV irradiation time was doubled as the dye concentration was increased to furnish more than 90% removal efficiency. Color removal curves obeyed first order kinetics irrespective of dye concentration.

Key words: Fenton, photo fenton, color removal, red CL-5B, dye concentrations

INTRODUCTION

Color in textile industry wastewaters has long been recognized as an environmental problem. Color, depending on its origin, is not only a problem of aesthetics but also of toxicity and reduced biodegradability (Gahr *et al.*, 1994; Georgiou *et al.*, 2003). Color is also the primary obstacle for water reuse and materials recovery in dyeing operations. Among dyes used reactive dyes are most troublesome (Soon *et al.*, 2005), because they are found in relatively high concentrations in textile industry effluents.

Several strategies for the removal of color from such effluents have been studied. These included physical and chemical methods involving flocculation, sorption electrochemical and oxidative degradation or the use of microorganisms, however, using traditional techniques are generally considered inadequate (Sameiro *et al.*, 2005), as modern dyes have a great degree of chemical and photolytic stability. Also reactive dyes are very soluble in water and large quantities of adsorbents are required to decolorize the dye that is practically not viable (Brown and Roberts, 2004). Activated sludge treatment is most commonly used treatment technique, though it was not originally intended for industrial wastes, particularly for textile waste containing dyes and surfactants (Yang *et al.*, 1998). Reactive dyes are indeed refractory to microbial degradation (Chao and Lee, 2000) because of their toxic effect on microorganism rendering biological processes

ineffective (Correia *et al.*, 1994; Shah *et al.*, 2003). The research and development in Advanced Oxidation Technologies (AOTs) for water remediation have made great progress in recent years (Zhang *et al.*, 2004; Shu and Chang, 2005; Shu, 2006), especially the H_2O_2 based processes (Ksibi, 2006). The nonspecific reactivity of hydroxyl radicals make them potentially useful for degradation of a wide range of organic compounds (Yasar *et al.*, 2006a). Fenton reagent and its modifications have also received great attention as means for decolorization of synthetic dyes (Neamtu *et al.*, 2004). During UV application, UV light exposure time has an incremental effect on color removal (Hanzon and Vigilia, 1999). Colour reduction is also a function of initial dye concentration and is not significantly improved even by the use of high intensity lamp when dye concentrations are high (Shu *et al.*, 1994).

In this study an attempt has been made to investigate the influence of process conditions (dye concentration, oxidant dose, pH and UV irradiation time) on the performance of Fenton and Photo Fenton process for the decolorization of synthetic solution of Red CL-5B dye. Reaction kinetics was determined in terms of reaction rate.

MATERIALS AND METHODS

Materials: The hydrogen per oxide solution (35% w/w) and Ferrous Sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were obtained from Merck, Germany. For adjustment of pH of dye solutions,

H₂SO₄ (0.1 N), NaOH (0.1 N) and NaOH (1N) were prepared using standard laboratory procedures (APHA, 1998).

Reactive concentrated azo dye Red CL-5B was obtained from Clariant Pakistan. The flasks containing dye solutions were covered with aluminum foil to avoid degradation by laboratory fluorescent lights. The research was conducted during April, 2005 to March 2006, in the advanced wastewater treatment laboratory, Directorate of Research and Development, University of the Punjab, Lahore-Pakistan.

Fenton and photo fenton treatment: The reactor was consisted of a graduated Pyrex glass beaker and a magnetic stirring set up. A 200 mL dye solution sample was used in each run. The experimental matrix included 100, 300, 500 mg L⁻¹ dye concentration, H₂O₂ dose of 170 mg L⁻¹ and Iron Sulfate (FeSO₄.7H₂O) as catalyst (Fig. 1a). Color analysis was made by Spectrophotometer (MN-Micron 970) at wavelength (542 nm). Then to observe the effect of initial pH, solution pH was varied (2, 4, 6 and 8) in 100, 300 and 500 mg L⁻¹ dye concentration solutions.

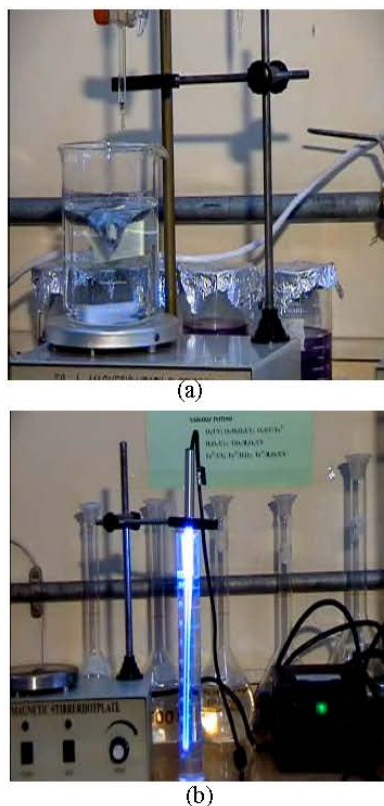


Fig. 1: Experimental set up for (a) fenton and (b) photo fenton processes

A photo reactor was set up for the experiments in batch mode (Fig. 1b). A UV lamp model PENRAY 3SC9 UPLAND USA with radiation intensity of 5 mWcm⁻² and wavelength of 254 nm was positioned in the center of reactor (with the internal diameter of 3.3 cm and height of 30 cm). After the application of H₂O₂/Fe⁺², UV irradiation time was varied from 1, 2, 3 to 21 min.

Reaction kinetics: Reaction kinetics was studied by plotting a graph between -ln (A/A₀) against oxidation time (t). If a straight line appears it shows that reaction is 1st order. The following kinetic equation was used.

$$\ln (A/A_0) = K_d(t)+C$$

Where A is absorbance at time t, A₀ is absorbance of untreated sample, K_d is pseudo 1st order decolorization rate constant.

RESULTS AND DISCUSSION

Optimization of ferrous dose: Several researchers (Yasar *et al.*, 2006b; Bali *et al.*, 2004; Kang *et al.*, 2000) have reported that the rate of decolorization by H₂O₂ alone is extremely low for many dyes, especially azo dyes. Addition of Fe⁺² accelerates the generation of hydroxyl radicals (OH[•]), however, in excess it can lower the effectiveness of Fenton oxidation. This situation accentuates the need to find the optimal dose (concentration) of FeSO₄.7H₂O. Various ferrous Sulphate doses (10, 20, 30, 40, 50 and 100 mg L⁻¹) were applied at constant H₂O₂ content of 170 mg L⁻¹. Figure 2 clearly show that increase in the ferrous concentration beyond optimal dose results in decrease in color removal efficiency. Results demonstrated that Fe⁺² dose of 20 mg L⁻¹ gave 86% color removal at 20 min settling time for 100 mg L⁻¹ dye concentration (Fig. 2a), with while 30 mg L⁻¹ was found optimal for 300 and 500 mg L⁻¹ dye concentration, with 90 and 80% removal at min setting time, respectively.

Effect of pH on fenton process: The high color removal under acidic conditions (due to more OH[•] radicals generation) and low color removal in basic conditions (due to Fe(OH)₃ formation) has already been reported (Legrini *et al.*, 1993; Perez *et al.*, 2002). Results show that initial pH has significant effect on the color removal by Fenton's process especially for higher initial dye concentrations (300 and 500 mg L⁻¹), an initial pH of 2 gave maximum removal efficiency after a settling time of 10 min. However, with an increase in post settling to 20, 40 and 60 min for 100, 300 and 500 mg L⁻¹ initial dye

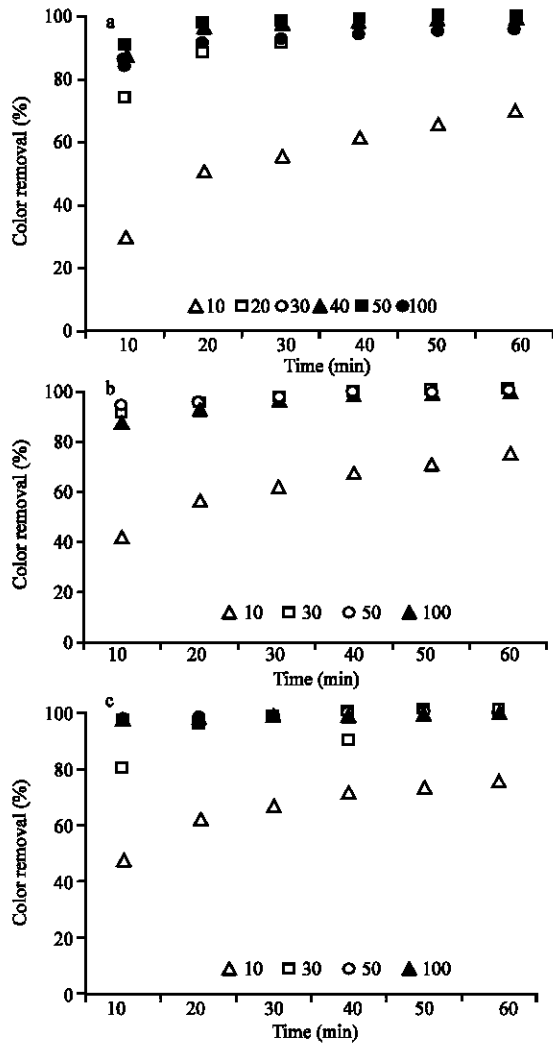


Fig. 2: Effect of various doses of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (mg L^{-1}) on (a) 100 mg L^{-1} , (b) 300 mg L^{-1} and (c) 500 mg L^{-1} Red-CL 5B concentrations ($C_{\text{H}_2\text{O}_2} = 170 \text{ mg L}^{-1}$)

concentration, the effect of pH was decreased as almost same removal efficiency for that particular concentration was achieved in acidic range (Fig. 3).

UV irradiation: The effect of UV irradiation on various initial dye concentrations for decolorization is shown in Fig. 4. Increase in the initial concentration of dye from 100 to 500 mg L^{-1} decreased the color removal from 99.9 to 36.4% at 40 min UV irradiation. This can be attributed to the fact that an increase in initial dye concentration decreases the penetration of photons entering into the solution, consequently lowering the cleavage of azo double bonds (Muruganandham and Swaminathan, 2004).

Photo-fenton's process: The photo-activated chemical reactions are characterized by a free radical mechanism

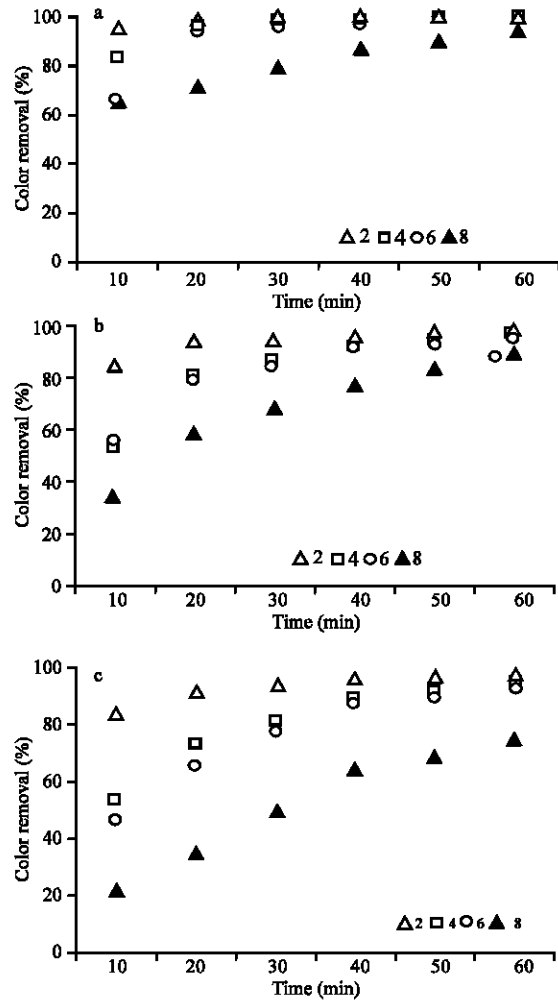


Fig. 3: Effect of pH on (a) 100 mg L^{-1} , (b) 300 mg L^{-1} and (c) 500 mg L^{-1} dye concentrations ($C_{\text{H}_2\text{O}_2} = 170 \text{ mg L}^{-1}$, $C_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 30 \text{ mg L}^{-1}$)

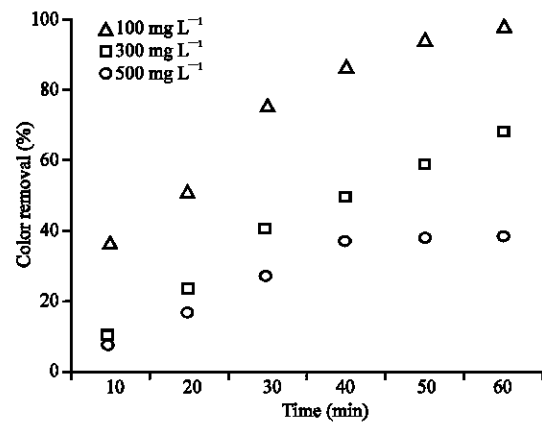


Fig. 4: Effect of UV irradiation time on color removal of Red CL-5B dye

initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the

Table 1: Effect of UV irradiation on (a) 100 mg L⁻¹, (b) 300 mg L⁻¹ and (c) 500 mg L⁻¹ dye concentration (C_{H₂O₂} = 170 mg L⁻¹, C_{FeSO₄.7H₂O} = 5 mg L⁻¹)

Time (min)	Removal (%)	pH	Temp.
(a) 100 mg L ⁻¹			
2	92.3	3.5	32.8
3	95.2	3.4	33.4
4	98.2	3.3	34.0
5	99.0	3.3	35.0
6	99.9	3.2	37.9
(b) 300 mg L ⁻¹			
1	65.7	3.3	32.6
2	67.9	3.1	34.2
4	80.0	3.1	34.7
8	88.9	2.9	38.1
12	96.1	2.8	36.0
(c) 500 mg L ⁻¹			
3	79.8	2.8	34.3
6	83.1	2.8	35.5
9	87.6	2.7	37.9
15	93.1	2.53	41.2
21	96.0	2.40	44.3

solution, with or without the presence of the catalyst (Gogate and Pandit, 2004). Experiments were carried out by addition of H₂O₂ (170 mg L⁻¹) and FeSO₄.7H₂O (5 mg L⁻¹). For initial dye concentration of 100 mg L⁻¹ 92% color removal was obtained for 2 min, however, complete decolorization was obtained at 6 min UV exposure (Table 1). For 300 and 500 mg L⁻¹ dye concentration, up to 6 min UV exposure resulted in insignificant color removal, however, 96% color removal was obtained for UV exposure of 12 and 21 min, respectively. The high efficiency of photo-Fenton process at lower dose of ferrous Sulphate owed to the formation of more hydroxyl radical than the Fenton process. This signifies that UV lamp of 108 W and irradiation intensity of 5 mW cm⁻² has a significant effect on dye decolorization (Lucas and Peres, 2006).

Kinetic studies: The decolorization of dissolved dyes in wastewater is a complex process with many reactions which are difficult to distinguished individually. Therefore an approximate kinetic study for the color removal of dye solution was performed. Several investigations (Bali *et al.*, 2004; Neamtu *et al.*, 2003; Wu and Wang, 2001; Balcioglu and Arslan, 2001) reported that most of the color removal curves obey first-order kinetics. In all the experiments the disappearance of dye could be described as a first order reaction kinetics with regard to dye concentration. Figure 5 and 6 show that rate of decolorization for photo-Fenton process when compared to Fenton process is better and for photo-Fenton initial lower rate of decolorization is due to the comparatively lower effect of UV radiation during initial minutes of the reaction. However the decolorization was significantly increased after few minutes. This is because with the passage of time as the dye

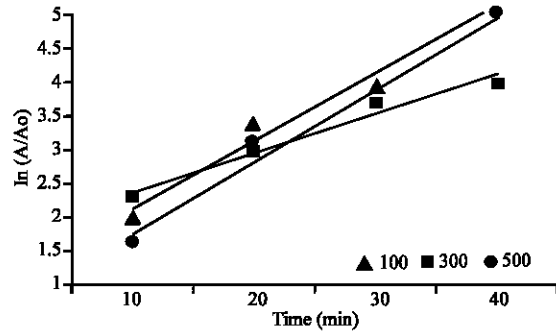


Fig. 5: Reaction kinetics of optimized dose of ferrous Sulphate (30 mg L⁻¹) for various dye concentrations

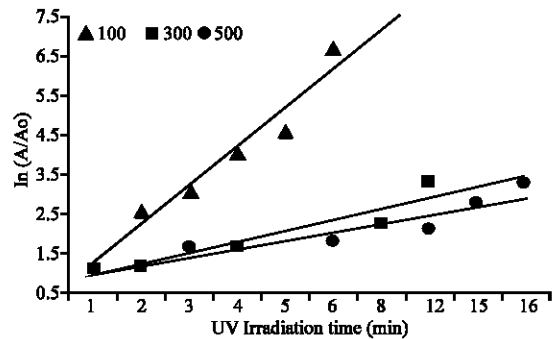


Fig. 6: Reaction kinetics of Photo Fenton process for various dye concentrations

concentration decreases UV light wavelength can significantly influence direct formation of OH radicals as well as the photo-reduction rate of Fe⁺³ to Fe⁺², which enables process to furnish its maximum rate (Lucas and Peres, 2006).

CONCLUSIONS

From results of this study the following conclusion can be drawn.

- Increase in dye concentration requires increase in ferrous dose for optimal results. However, further increase in the dose significantly lowers the efficiency of the process. Post settling enhances the efficiency irrespective of the dye concentration and it is more effective for lower ferrous dose.
- Initial pH greatly influences the color removal efficiency by Fenton oxidation and this effect is more pronounced for higher dye concentrations. However, in acidic range removal efficiency becomes almost similar after an optimal post settling time, which appears to be directly proportional to the dye concentration.

- Photo-Fenton process is more effective than Fenton process even at lower dose of ferrous Sulphate due to additional benefit of UV radiations. However, initially higher dye concentration inhibits the UV irradiation and increases the UV time for same color removal efficiency.
- The decolorization of Red CL-5B appeared to be first order reaction kinetics irrespective of dye concentration.

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