

Comparative Study of Degradation of Azo Dyes by Photo-Fenton Process

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ABSTRACT

In a laboratory study, degradation of two azo dyes (Amaranth and Evans blue) by photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process under visible light irradiation has been examined. The dyes have been chosen as model pollutant and the effects of various parameters such as effect of pH, concentration of ferrous ion, concentration of amaranth and Evans blue dye, concentration of hydrogen peroxide and effect of light intensity on degradation of dyes were investigated. The degradation of dye depends on its structure. It was observed that Evans blue degraded faster than amaranth.

Keywords- Advanced oxidation process, Azo dyes, Photo-Fenton process, Dye degradation.

1. INTRODUCTION

The Fenton reaction [1, 2] is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalyst. These radicals are a very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions. The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide [2]. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. The Fenton reagent has been found to be effective in treating various industrial wastewater components. More than two thousand azo dyes are known and over half of the commercial dyestuffs are azo dyes. Azo dyes are broadly used in the textile industry, and also widely employed to color solvents, inks, paints, varnishes, paper, plastic, rubber, foods, drugs, and cosmetics [3].

Ledakowicz et al. [4] observed the kinetics of the decolorization by Fenton's reagent. El-Dein et al. [5] demonstrated the kinetics of decolorization and mineralization of the azo dye reactive black 5 by hydrogen peroxide and UV light. Baldrian et al. [6] reported the decolorization of synthetic dyes by hydrogen peroxide with heterogeneous catalysis by mixed iron oxides. Decolorization and mineralization of C.I. acid yellow 23 by Fenton and photo-Fenton processes observed by Modirshahla et al. [7]. Huang et al. [8] reported a comparative study of oxidation of dye-reactive black B by different advanced oxidation processes as Fenton, electro-Fenton and photo-Fenton. A comparative study on oxidation of dispersed dyes by electrochemical process, ozone, hypochlorite and Fenton reagent has been reported by Lidia et al. [9].

The aim of the present investigation is to examine the effect of various parameters on the degradation of dyes and to compare the degradation rate of the two dyes.

2. EXPERIMENTAL SETUP

Samples of azo dyes amaranth and Evans blue (Central drug house, CDH), FeSO_4 (CDH) and H_2O_2 (30% Merck), HCl, NaOH were used in the present investigation. The photochemical degradation of both dyes was studied in presence of Fe^{2+} ion, H_2O_2 and visible light. Stock solutions of dyes (1.0×10^{-3} M) and FeSO_4 (5.0×10^{-3} M) were prepared in doubly distilled water (1000 mL). For the photochemical degradation of dyes, 22.0 mL of Evans blue solution was taken in a beaker and 0.3 mL of ferrous sulphate solution was added to it, the total volume was made to 50.0 mL, so the concentrations of ferrous ions and dye were 3.0×10^{-5} M and 4.4×10^{-4} M respectively in the reaction mixture. 13 mL of amaranth was taken in a beaker and 0.3 mL of ferrous sulphate solution was added to it. The total volume was made to 50.0 mL, so that the concentrations of Fe^{2+} and amaranth were 2.6×10^{-4} M and 3×10^{-5} M, respectively in a reaction mixture.

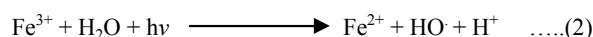
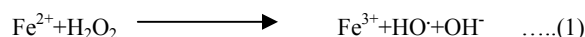
The pH of the solution was adjusted to 3.0 for Evans blue and 4.0 for amaranth by adding HCl, 0.75 and 1.0 mL H_2O_2 was added to reaction mixtures then the solution was exposed to a 200 W tungsten lamp (Philips). The intensity of light is measured with the help of solarimeter (Suryamapi Model no. CEL 201).

An aliquot of 2.0 mL was taken out from reaction mixture for analysis. The optical density of Evans blue and amaranth was determined at wavelength $\lambda_{\text{max}} = 610\text{nm}$ and 520 nm respectively by spectrophotometer (Labtronix).

3. RESULTS AND DISCUSSION

3.1 Effect of pH Variation

The effect of pH on the degradation of dyes was observed in the pH range 2.0 to 9.0. At pH 3.0 the discoloration of Evans blue and at pH 4.0 the discoloration of amaranth give the best results compared with the other pH's and it has been found that the rate of degradation of dyes increases with an increase in pH upto optimum pH which can be explained as the hydroxyl radicals may generated by two steps: (i) the reaction between ferrous ions and hydrogen peroxide. (ii) The photochemical reaction of ferric ions and water.



At high pH, degradation is lower due to precipitation of $\text{Fe}(\text{OH})_3$. In this form iron decomposes H_2O_2 into water and oxygen, so less hydroxyl radicals are available. At pH less than 2, formation of oxonium ion (H_3O^+) enhanced the stability of hydrogen peroxide and restricted the generation of $\cdot\text{OH}$ radicals. The scavenging of hydroxyl radicals by the excess of H^+ is another reason for lower degradation efficiency.

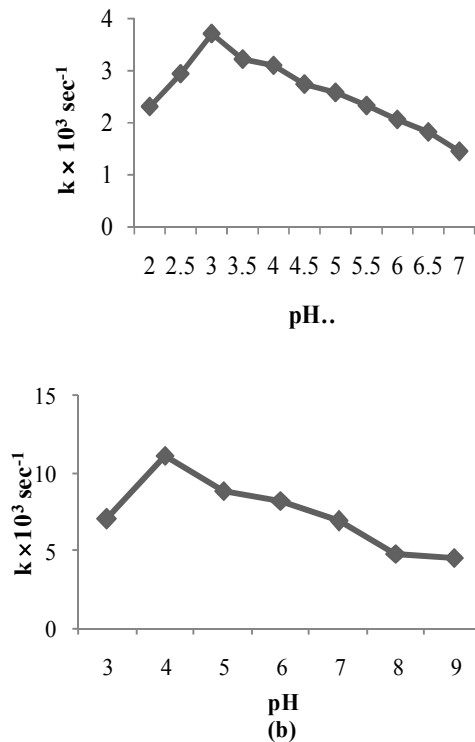


Figure 2. Effect of pH (a) [Evans Blue] = 4.4×10^{-4} M, $[\text{Fe}^{2+}] = 2.0 \times 10^{-5}$ M, $\text{H}_2\text{O}_2 = 0.5$ mL, Light Intensity = 40.0 mWcm^{-2} , (b) [Amaranth] = 2.6×10^{-4} M, $[\text{Fe}^{2+}] = 3 \times 10^{-5}$ M, $\text{H}_2\text{O}_2 = 1$ ml, Light Intensity = 60.0 mW cm^{-2}

3.2 Effect of Dye Concentration

As shown in Figure 3, the rate of photochemical degradation was found to increase with the increase in Evans blue concentration up to 4.4×10^{-5} M and amaranth concentration up to 2.6×10^{-4} M. On further increasing its concentration, the rate of degradation was found to decrease. On increasing the concentration of dyes, more molecules of dye are available for excitation and degradation. Above optimum concentration, the rate of reaction was found to decrease because at the high concentration of dye, it may start acting like a filter for the incident light and the dye will not permit the desired light intensity to reach the dye molecules and decrease in the rate of photochemical degradation of dyes was observed.

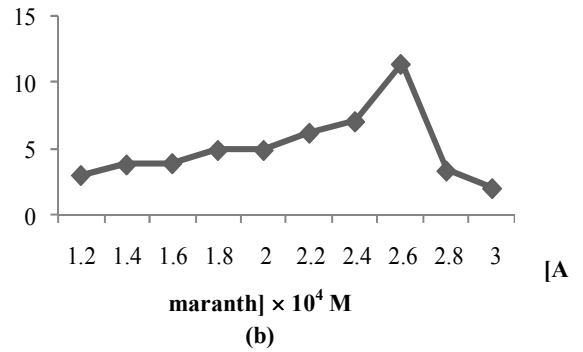
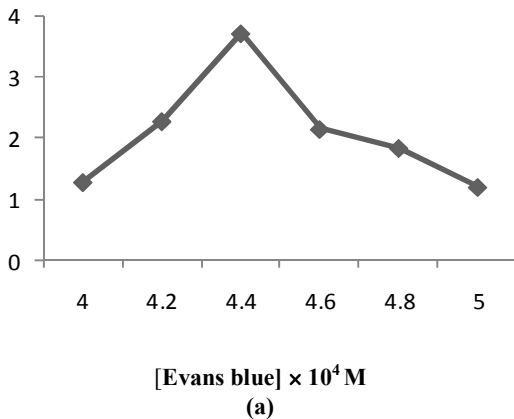


Figure 3. Effect of Evans blue concentration (a) pH = 3.0, $[\text{Fe}^{2+}] = 2.0 \times 10^{-5}$ M, $\text{H}_2\text{O}_2 = 0.5$ mL, Light Intensity = 40.0 mWcm^{-2} , (b) pH = 4, $[\text{Fe}^{2+}] = 3 \times 10^{-5}$ M, $\text{H}_2\text{O}_2 = 1$ ml, Light Intensity = 60.0 mW cm^{-2}

3.3 Effect of Ferrous Ion Concentration

Keeping all other factors identical, the effect of the concentration of Fe^{2+} ions on the rate of photochemical degradation of dyes was observed. The range of concentration of ferrous ions in the present case was kept between 1.0 to 8.0×10^{-5} M. As graphically presented in Figure 4, the rate of reaction increases on increasing the concentration of Fe^{2+} ions up to 3.0×10^{-5} .

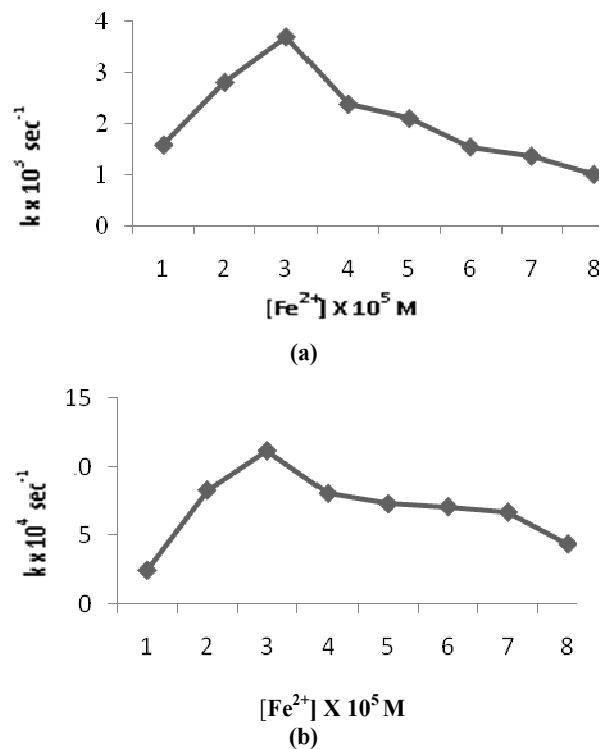
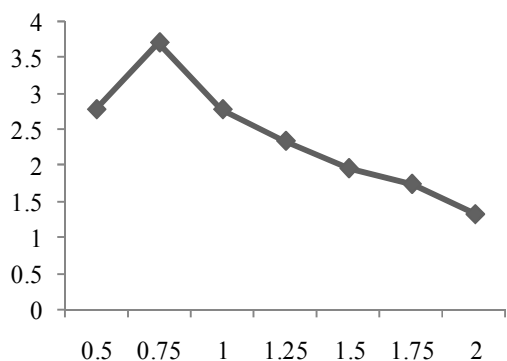
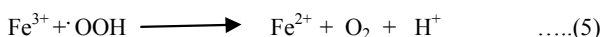
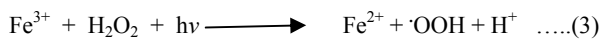


Figure 4. Effect of ferrous ion concentration (a) [Evans Blue] = 4.4×10^{-4} M, pH = 3.0, $\text{H}_2\text{O}_2 = 0.5$ mL, Light Intensity = 40.0 mWcm^{-2} , (b) [Amaranth] = 2.6×10^{-4} M, pH = 4, $\text{H}_2\text{O}_2 = 1$ ml, Light Intensity = 60.0 mW cm^{-2} ,

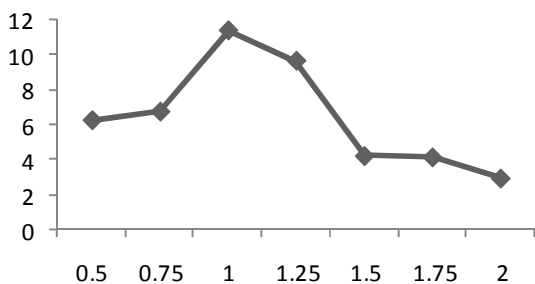
On increasing the concentration of Fe^{2+} ion in the reaction mixture, the rate of photochemical degradation also increases. However, on increasing the ions further, the rate of reaction found to decrease because Fe^{2+} ions impart yellow colour to the solution and at high concentration, it may also act as a filter for the incident light.

3.4 Effect of Amount of Hydrogen Peroxide

Amount of H₂O₂ is one of the operating parameters as it is significantly influence the final degradation of dye. The results are graphically shown in Figure 5. The rate of reaction for evans blue and amaranth increases with an optimum rate at 0.75 mL and 1 mL H₂O₂ respectively, the rate of degradation of dyes decreases above optimum H₂O₂ amount because the rate of reaction in eq. 3 and 4 become fast and hydroxyl radicals are consumed rapidly due to greater availability of H₂O₂ molecules. ·OOH radicals produce H⁺ ions (eq. 5), slightly decreasing the pH at the end of the reaction. As a consequence, the rate of photo degradation decreases.



(a)

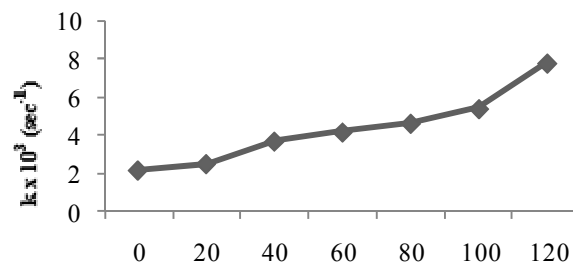


(b)

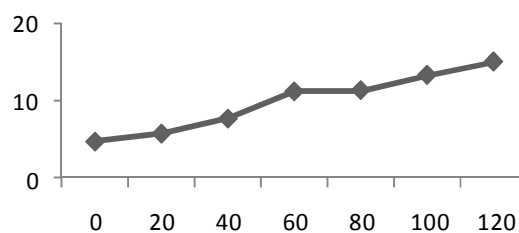
Figure 5. Effect of amount of hydrogen peroxide (a) [Evans Blue] = 4.4 × 10⁻⁴ M, pH = 3.0, [Fe²⁺] = 3.0 × 10⁻⁵ M, Light Intensity = 40.0 mWcm⁻², (b) [Amaranth] = 2.6 × 10⁻⁴ M, pH = 4, [Fe²⁺] = 3 × 10⁻⁵ M, Light Intensity = 60.0 mW cm⁻²

3.5 Effect of Light Intensity

A linear relationship was observed between the rate constant and light intensity, which is shown graphically in Figure 6, which indicates that an increase in the light intensity increases the rate of reaction. This may be attributed to the fact that increased number of photons reacts with Fe³⁺ ions and as a result, there is an increase in the number of hydroxyl radicals and a corresponding increase in the rate of reaction.



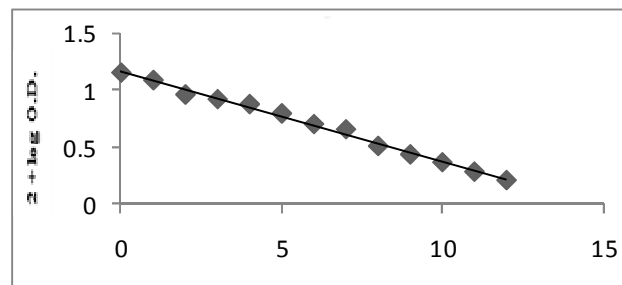
(a)



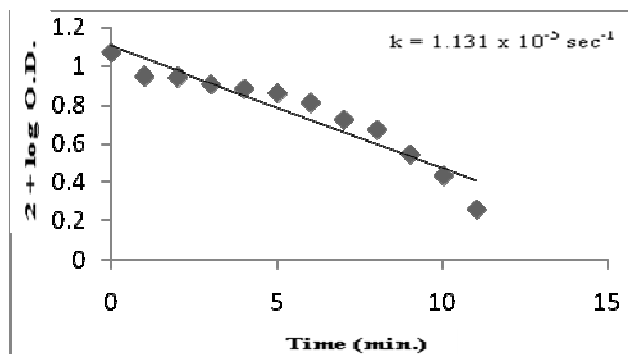
(b)

Figure 6. Effect of light intensity (a) [Evans Blue] = 4.4 × 10⁻⁴ M, pH = 3.0, H₂O₂ = 0.75 mL, [Fe²⁺] = 3.0 × 10⁻⁵ M, (b) [Amaranth] = 2.6 × 10⁻⁴ M, pH = 4, H₂O₂ = 1 mL, [Fe²⁺] = 3 × 10⁻⁵ M

A plot of 2 + log O.D. against time was linear therefore it followed pseudo-first order kinetics. The rate constant was measured with the expression k = 2.303 × slope. The rate constant for evans blue and amaranth were found 3.71 × 10⁻³ sec⁻¹ and 1.131 × 10⁻⁵ sec⁻¹ and are presented in Figure 7.



(a)



(b)

Figure 7. A Typical Run (a) [Evans Blue] = 4.4 × 10⁻⁴ M, pH = 3.0, H₂O₂ = 0.75 mL, [Fe²⁺] = 3.0 × 10⁻⁵ M, Light Intensity = 40.0 mWcm⁻², (b) [Amaranth] = 2.6 × 10⁻⁴ M, pH = 4.0, H₂O₂ = 1 mL, [Fe²⁺] = 3.0 × 10⁻⁵ M, Light intensity = 60.0 mWcm⁻²

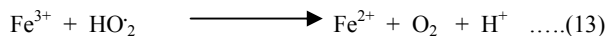
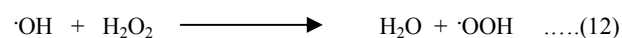
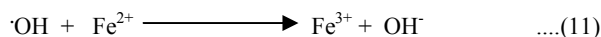
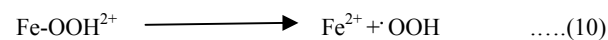
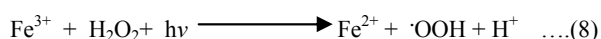
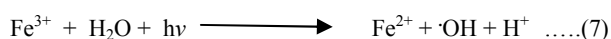
Optimum conditions for effectively degradation of dyes are presented in Table (1).

Table 1. Optimum conditions for degradation of Evans blue and Amaranth in photo-Fenton process

Dyes	Evans blue	Amaranth
Variables		
H₂O₂ concentration	0.75 mL	1 mL
Ferrous ion concentration	3.0×10^{-5} M	3.0×10^{-5} M
Dye concentration	4.4×10^{-4} M	2.6×10^{-4} M
pH	3.0	4.0
Degradation degree (DD %) in 12mins.	88.7%	85%

4. MECHANISM

On the basis of experimental observations a tentative mechanism has been proposed for degradation of dyes with photo-Fenton's reagent.



The aqueous solution of ferrous ion decomposes hydrogen peroxide into hydroxyl radicals and hydroxyl ions, while ferrous ions undergo oxidation to ferric ions. Ferric ion on exposure to light dissociates water into a proton and hydroxyl radical and ferric ion is reduced to ferrous ions.

The ferric ion generates HO₂ radical due to dissociation of hydrogen peroxide in presence of light. The incorporation of hydroxyl radicals with H₂O₂ also produces HO₂ radicals. Ferrous ions undergo oxidation to ferric ion by addition of hydroxyl radicals, while ferric ions get reduced to ferrous ions by incorporation of HO₂ radicals and producing H⁺ ions. HO₂ radicals are highly unstable in water and reacts slowly with dye molecules.

5. CONCLUSION

A comparison was made for degradation rates of evans blue and amaranth with photo-Fenton. Based on the above results, it can be concluded that, the degradation degree of the two azo dyes are strongly dependent on ferrous ion concentration, amount of hydrogen peroxide, dye concentration and pH. It was observed that the rate of degradation of evans blue is higher as compared to amaranth dye in presence of photo-Fenton reagent. The estimation of degree (DD) was calculated by the following relation:

$$\text{DD}\% = \frac{A_i - A_t}{A_i} \times 100$$

Here, A_i = Initial intensity of colour and A_t = intensity of colour at t time of the oxidation.

The % colour removal of evans blue and amaranth dye by photo-Fenton were 88.7% and 85% in 12 minutes, respectively. The results indicated that evans blue was degraded faster than amaranth.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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