



# **DEGRADATION AND DECOLOURATION OF AMARANTH DYE BY PHOTO-FENTON AND FENTON REAGENTS: A COMPARATIVE STUDY**

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## **ABSTRACT**

Among the available advanced oxidation processes, Fenton and photo-Fenton reagents are of special interest, because of effective and economic degradation of azo dyes. One of the main cause of water pollution is, release of effluents from textile and dyeing industries in fresh water, which is toxic and carcinogenic in some cases. The present paper investigates the degradation of azo dye Amaranth by the photo-Fenton and Fenton reagents. The dye has been chosen as a model pollutant and the effects of various parameters such as effect of pH, effect of concentration of ferrous ion, effect of concentration of amaranth dye, effect of concentration of hydrogen peroxide and effect of light intensity on degradation of amaranth were investigated.

**Key words:** Water pollution, Amaranth, Photo-Fenton reagent, Fenton reagent, Degradation, Advanced oxidation process.

## **INTRODUCTION**

A wide range of organic pollutants has been detected in industrial wastewater, which pose severe problems in biological systems. Dyes and pigments present in water, introduce colour and chemicals, which is a clear indication of water pollution. Azo dyes constitute the largest class of dye used in industries, more than two thousand azo dyes are known and over half of the commercial dye stuffs are azo dyes. Azo dyes are broadly used in the textile industry and also widely employed to colour solvents, ink, paints, varnishes, paper, plastic, rubber, foods, drugs and cosmetics<sup>1</sup>.

Conventional techniques such as coagulation/flocculation, membrane separation, absorption by activated carbon are based on phase transfer of the pollutants. These methods transferred the contaminant from waste water to solid wastes and they are not efficient for

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removal of dyes. Biological methods are also ineffective for decolourization of azo dyes because of its stability and complex aromatic structure<sup>2</sup>.

Meric et al.<sup>3</sup> observed the colour and COD removal from waste water containing reactive black-5 using Fenton's oxidation process. Fongsatitkul et al.<sup>4</sup> used the sequencing batch reactors and Fenton's reagent to treat waste water from a textile industry. Degradation of methyl red using Fenton's reagent and the effect of various salts was studied by Ashraf et al.<sup>5</sup> Vinh et al.<sup>6</sup> investigated the degradation of basic blue-41 dye by Fenton reaction. Ameta et al.<sup>7</sup> reported a comparative study of Fenton's and photo-Fenton's and other related reagents in resorcinol-TiO<sub>2</sub> system.

Recently, advanced oxidation processes (AOPs) have been introduced to treat waste water, which has been developed to oxidize organic pollutants into carbon dioxide, water and inorganic ions or transform into less complex structures. AOPs are based on the generation of highly reactive species such as hydroxyl radicals (\*OH), which have strong oxidation potential and oxidise a large number of organic pollutants<sup>8</sup>.

## EXPERIMENTAL

Stock solution of amaranth ( $1 \times 10^{-3}$  M) and ferrous sulphate ( $5 \times 10^{-3}$  M) were prepared in doubly distilled water. 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<sup>2+</sup> and amaranth were  $2.6 \times 10^{-4}$  M and  $3 \times 10^{-5}$  M, respectively in a reaction mixture. The pH of the solution is adjusted to 4.0 by adding HCl and 1 mL H<sub>2</sub>O<sub>2</sub> was added to it. The solution was exposed to a 200 W tungsten lamp (Philips). The intensity of light is measured with the help of solarimeter (Suryamapi Model CEL 201).

An aliquot of 2.0 mL was taken out from reaction mixture for analysis. The optical density of amaranth was determined at wavelength  $\lambda_{\max} = 520$  nm by a spectrophotometer (Labtronix). It was observed that the optical density decreases with time. A plot of  $2 + \log$  O.D. against time was linear therefore it followed pseudo-first order kinetics (Fig. 6). The rate constant was measured with the expression  $k = 2.303 \times \text{slope}$ . The results are summarized in different figures.

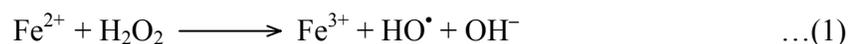
## RESULTS AND DISCUSSION

### Effect of pH variation

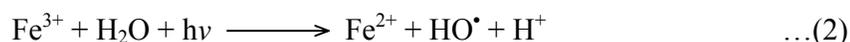
The effect of pH on degradation of amaranth was investigated. It is evident from Fig. 1 that the rate of degradation of amaranth increases with increase in pH upto 4.0 and

then it decreases with increasing pH. The effect of pH on the degradation of amaranth was observed in the pH range 3 to 10. At high pH, the generation of hydroxyl radicals get slower, which may be explained by following reactions –

- (i) The reaction of ferrous ions with hydrogen peroxide.

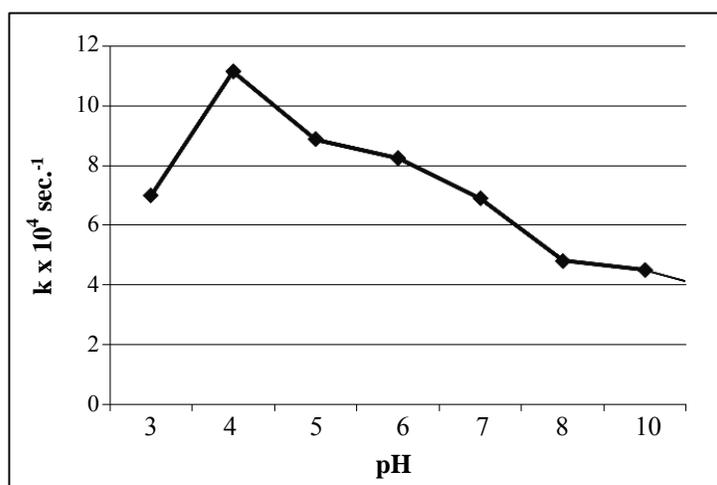


- (ii) Photochemical reaction of ferric ions with water.



The increase in the pH of the medium will favour the (i) step where  $\text{OH}^-$  ions are formed and in (ii) step protons are generated. Below 4 pH (1) step dominates over (2) step. Above 4 pH (2) step dominates (1) step. The Fenton like decomposition is much more pH sensitive and is applicable only in the systems with pH higher than 2.0.

$$[\text{Fe}^{2+}] = 3 \times 10^{-5} \text{ M}, [\text{Amaranth}] = 2.6 \times 10^{-4} \text{ M}, \text{Light Intensity} = 60.0 \text{ mW cm}^{-2}, \\ \text{H}_2\text{O}_2 = 1 \text{ mL}$$



**Fig. 1: Effect of pH variation**

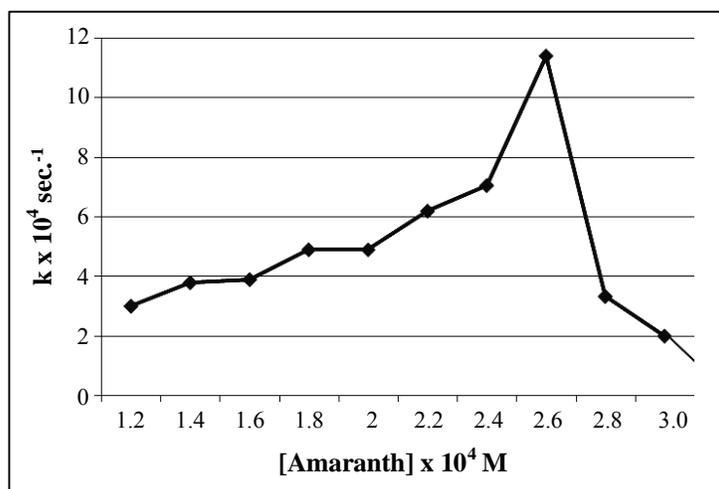
### Effect of dye concentration

The effect of concentration of dye on the rate of degradation of dye was studied by keeping all other factors identical. The concentrations of dye varied from  $1.2 \times 10^{-4} \text{ M}$  to

$3 \times 10^{-4}$  M and it was observed that degradation increases with increasing concentration of amaranth upto  $2.6 \times 10^{-4}$  M. A further increase in concentration shows decrease in the rate of degradation as shown in Fig. 2.

On increasing the concentration of amaranth, more molecules are available for excitation and degradation. On increasing the concentration above  $2.6 \times 10^{-4}$  M, the rate of reaction decreases, which can be explained as at higher concentration the dye may start act as a filter for the incident light. The dark colour of dye will not permit the desired light intensity to reach at the dye molecule as a result decrease in the rate of degradation of amaranth was observed.

$$[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}, \text{ pH} = 4, \text{ Light Intensity} = 60.0 \text{ mW cm}^{-2}, \text{ H}_2\text{O}_2 = 1 \text{ mL}$$



**Fig. 2: Effect of amaranth concentration**

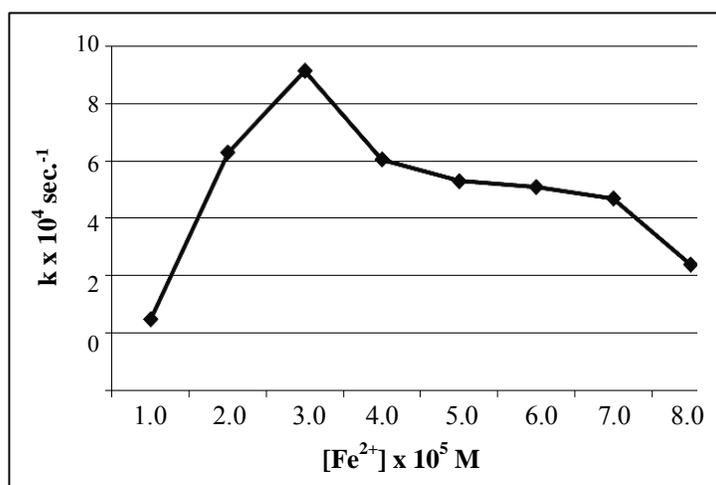
### **Effect of ferrous ion concentration**

The degradation of dye efficiency by photo-Fenton process is also influenced by the concentration of  $\text{Fe}^{2+}$  ions, which catalyze  $\text{H}_2\text{O}_2$  decomposition resulting in generation of  $\cdot\text{OH}$  radicals and consequently the degradation of dye molecule<sup>9</sup>. According to the literature, on increasing ferrous ion concentration, the degradation rate of organic compound also increases, upto certain level where further addition of iron becomes inefficient<sup>10</sup>.

The effect of concentration of  $\text{Fe}^{2+}$  ion on the rate of degradation of amaranth was observed by keeping all other factors identical. The effect of ferrous ion concentration on degradation of dye was observed between  $1 \times 10^{-5}$  M to  $8 \times 10^{-5}$  M concentration. The rate of

photodegradation increases on increasing the concentration of  $\text{Fe}^{2+}$  ions up to  $3.0 \times 10^{-5}$  M, beyond this limit rate of photodegradation of dye decreases. The results are reported in Fig. 3.  $\text{Fe}^{2+}$  ions is accompanied by enhanced generation of the active species hydroxyl radicals and as a consequence, the rate of degradation also increases. However, on increasing the concentration of  $\text{Fe}^{2+}$  ions further, the rate of reaction was decreased. This is because of the  $\text{Fe}^{2+}$  ions impart a yellow colour to the solution and at higher concentrations, it may also act as a filter for the incident light.

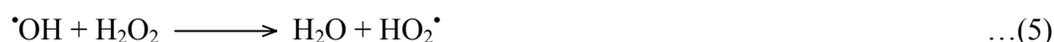
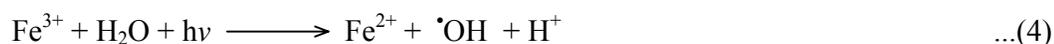
[Amaranth] =  $2.6 \times 10^{-4}$  M, pH = 4, Light Intensity =  $60.0 \text{ m W cm}^{-2}$ ,  $\text{H}_2\text{O}_2$  = 1 mL



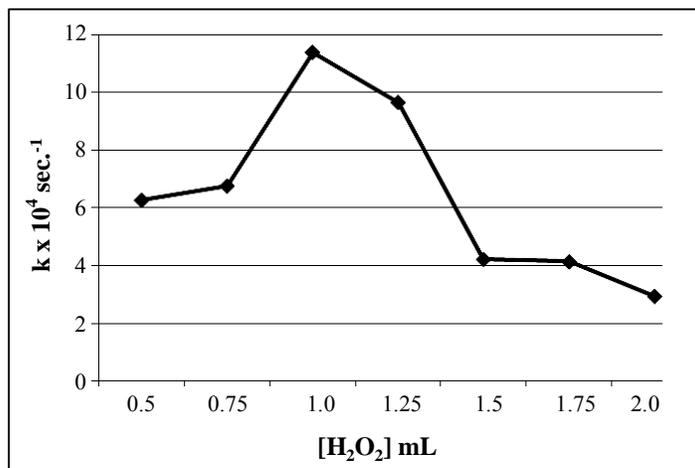
**Fig. 3: Effect of ferrous ion concentration**

### Effect of $\text{H}_2\text{O}_2$ concentration

Concentration of hydrogen peroxide is one of the operating parameters, which significantly influence the final degradation of dye. The results are shown in Fig. 4. The rate of reaction increases upto 1.0 mL  $\text{H}_2\text{O}_2$ . On further increasing the volume of hydrogen peroxide, the rate of degradation of dye decreases due to scavenging nature of  $\text{H}_2\text{O}_2$  towards  $\cdot\text{OH}$  radical (Eq. 5).



[Amaranth] =  $2.6 \times 10^{-4}$ , pH = 4, Light Intensity =  $60.0 \text{ m W cm}^{-2}$  [Fe<sup>2+</sup>] =  $3.0 \times 10^{-5}$

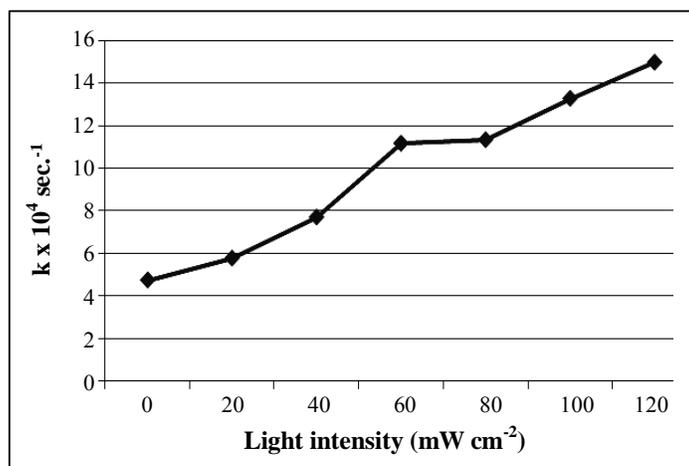


**Fig. 4: Effect of hydrogen peroxide**

### Effect of light intensity

The effect of light intensity on degradation of dye was also investigated. Light intensity was varied from  $20 \text{ mWcm}^{-2}$  to  $120 \text{ mWcm}^{-2}$ . A linear relationship was observed between the rate constant and light intensity. It indicates increase in the light intensity increases the rate of photodegradation of dye due to increasing number of photons reacting with ferrous ions results increase in number of the hydroxyl radicals therefore a corresponding

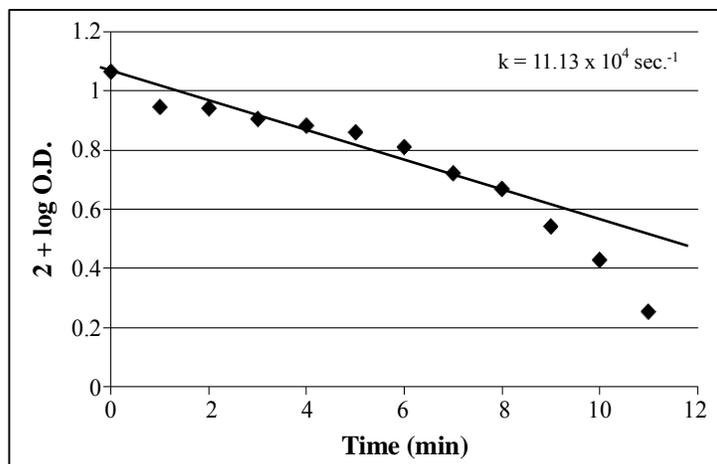
[Amaranth] =  $2.6 \times 10^{-4}$  M, pH = 4, H<sub>2</sub>O<sub>2</sub> = 1 mL, [Fe<sup>2+</sup>] =  $3.0 \times 10^{-5}$  M



**Fig. 5: Effect of light intensity**

increase in the rate of reaction was observed. Higher light intensities were rejected due to possible thermal effects.

pH = 4.0, [Amaranth] =  $2.6 \times 10^{-4}$ ,  $[\text{Fe}^{2+}] = 3.0 \times 10^{-5}$ ,  $\text{H}_2\text{O}_2 = 1$  mL, Light intensity =  $60.0 \text{ mW cm}^{-2}$

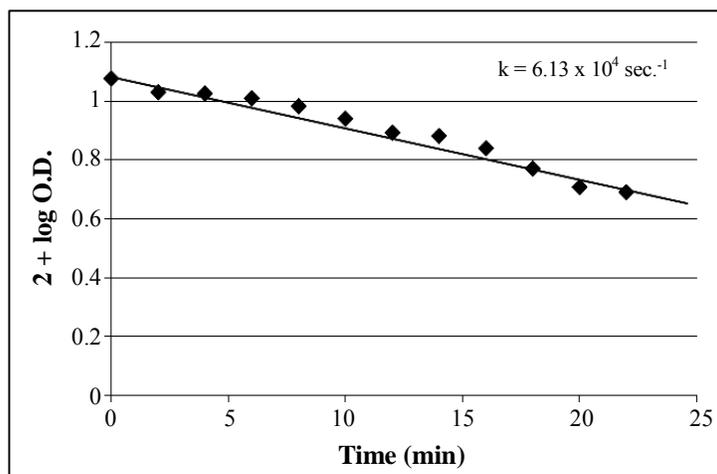


**Fig. 6: A typical run (photo-Fenton reagent)**

### Effects of Fenton reagent

The rate of degradation of amaranth dye in presence of Fenton reagent were also

[Amaranth] =  $2.6 \times 10^{-4}$  M,  $[\text{Fe}^{2+}] = 3.0 \times 10^{-5}$  M, pH= 4.0,  $\text{H}_2\text{O}_2 = 1$  mL,  
Light intensity =  $60.0 \text{ mW cm}^{-2}$



**Fig. 7: A typical run [Fenton reagent]**

investigated keeping optimum conditions of pH, dye concentration,  $\text{Fe}^{2+}$  ion concentration and amount of  $\text{H}_2\text{O}_2$ . A typical run is shown in Fig. 7. In Fig. 6, typical run for the degradation of dye is also given with photo-Fenton reagent.

## CONCLUSION

A comparison was made for degradation rates of amaranth with Fenton and photo-Fenton reagents.

The order of the effectiveness of both reagents is as follows:

- (i) Photo-Fenton reagent > Fenton reagent
- (ii) It was observed that the rate of degradation of dye in presence of photo-Fenton reagent is higher as compared to Fenton reagent. The estimation of degradation 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 amaranth dye by photo-Fenton reagent and Fenton reagent were 85% and 59% in 11 minutes and 22 minutes, respectively.

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