

# Kinetic and Thermodynamic Study for Fenton-Like Oxidation of Amaranth Red Dye

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## Abstract

Oxidation by Fenton like reactions ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ) is economically process for destructive hazardous pollutants in waste water. The effects of different parameters such as, amaranth red dye, ferric chloride, hydrogen peroxide concentrations, pH value of solution, temperature and the presence of inorganic ions (carbonate, nitrate, chloride) on oxidative decolorization of amaranth were investigated. Amaranth degradation by ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ) reagent was found to follow first order kinetic model. Under optimum condition, pH = 2.6 and  $[\text{FeCl}_3] = 3.75 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ , the amaranth in aqueous solution with an initial concentration of  $5 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$  was degraded by 95% within 6 minutes. Increasing temperature in the range of 298 - 308 K increases the rate of dye degradation. Thermodynamic constants,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  were evaluated. The results implied that the oxidation process was favorable and endothermic.

## Keywords

Amaranth Red, Decolorization, Kinetics, Fenton-Like

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## 1. Introduction

The need of industry for dye has shown a high pollutant potential, specially the use of azodyes [1], for example, tartrazine [2], amaranth [3] and others. Amaranth is used as food dye; cosmetic dye and can applied for natural and synthetic fibers, leather, paper, phenol formaldehyde resins [4]. The FDA in the United States has banned amaranth and it is also banned in Russia, Norway and Austria [5]. Owing to their toxicity, many studies have been done to remove them from water source. Biological (biodegradation) [6] and chemical methods (chlorination, ozonation) [7] are the most frequently used methods for removal of dyes from effluent water streams. But, these traditional processes for treatment of the effluents prove to be insufficient to purify waste water after the different operations of waste waters dyeing and washing.

Advanced oxidation processes (AOPs) are alternative methods for the complete degradation of dye. The usage of the advanced oxidation processes (AOPs) have improved during the last decade since they are able to eliminate the problem of dye destruction in aqueous systems. AOPs were based on the generation of very reactive species such as hydroxyl radicals ( $\bullet\text{OH}$ ) that oxidize a broad range of pollutants quickly and non-selectively. AOPs such as Fenton and Photo-Fenton catalytic reactions [8] [9],  $\text{H}_2\text{O}_2/\text{UV}$  processes [9].

The aim of this work was to find out the potential of Fenton-like for the decolorization of amaranth as model azo dye and examine the effect of the major system parameters on the decolorization kinetics of amaranth dye. Such parameters are the pH, concentration of ferric chloride,  $\text{H}_2\text{O}_2$ , dye and temperature of ambient. Also the study gave attention to the effect some inorganic electrolytes.

## 2. Experimental

### 2.1. Reagents and Materials

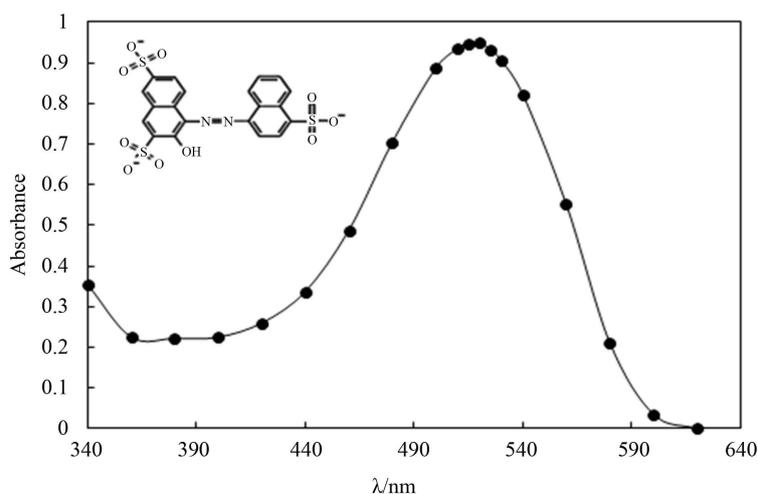
All chemicals were of pure grade and were used without further purification. Amaranth Red purchased from Fisher Scientific company chemical manufacturing division Fair town, New Jersey (molecular weight = 604.47,  $\lambda_{\text{max}} = 520 \text{ nm}$ ). The chemical structure and uv-vis spectrum of amaranth red dye is given in **Figure 1**.  $\text{FeCl}_3$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{CO}_3$  were purchased from Merck. Hydrogen peroxide solution (35%) was of analytical grade. All solutions were prepared using bidistilled water. Stock solutions of dye (1 mM),  $\text{FeCl}_3$  (10mM) were prepared in 0.01 M of HCl. All experiments were performed at pH below 3.

### 2.2. Kinetic Experiments

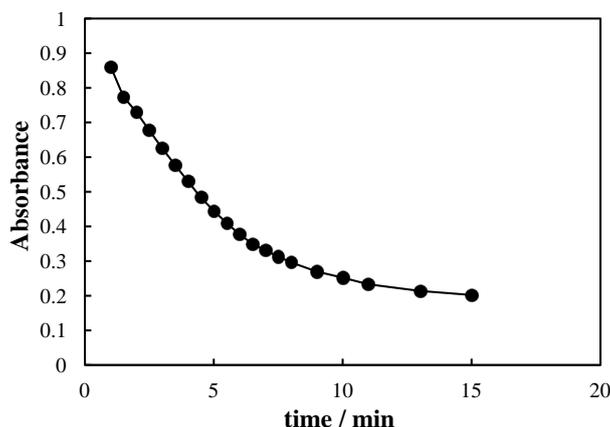
The kinetic measurements were carried out spectrophotometrically using 292 Cecil spectrophotometer was equipped with constant temperature cell holder attached to thermostatic controlled bath with temperature stability of  $\pm 0.1^\circ\text{C}$ . The reactants were thermostated for 15 min, then mixed thoroughly and quickly transferred to an absorption cell. The progress of the reaction was monitored at 520 nm. The pH of the reaction was adjusted using Griffin pH-meter fitted with a combined glass calomel electrode.

## 3. Results and Discussion

The present study concerns with the oxidative decolorization of amaranth by Fenton-like reaction. The absorbance of amaranth at  $\lambda_{\text{max}} = 520 \text{ nm}$  decreased with time as shown in **Figure 2**. The kinetics measurements were carried out under pseudo first order conditions, where hydrogen peroxide concentration was in excess than that of dye. The plot of logarithmic absorbance vs. time was linear. This indicates the pseudo first-order kinetics of the reaction with respect to the Amaranth concentration.



**Figure 1.** Chemical structure, uv-vis spectrum of amaranth red dye. [dye] =  $5 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ .



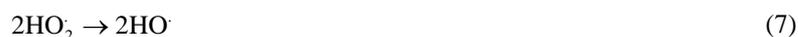
**Figure 2.** The change in absorbance of amaranth vs time at  $\lambda = 520$  nm.  $[\text{dye}] = 5 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[\text{H}_2\text{O}_2] = 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[\text{Fe}^{3+}] = 5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  and  $\text{pH} = 2.6$ .

### 3.1. Effect of pH

Advanced oxidation processes are powerful alternative methods of wastewater treatment. This method based on the production of powerful oxidant,  $\text{HO}\cdot$  ( $E = 2.8$  V versus NHE). These radicals are capable to degrade recalcitrant organic compounds under mild experimental conditions [10]. The general mechanism of Fenton reaction [11] is



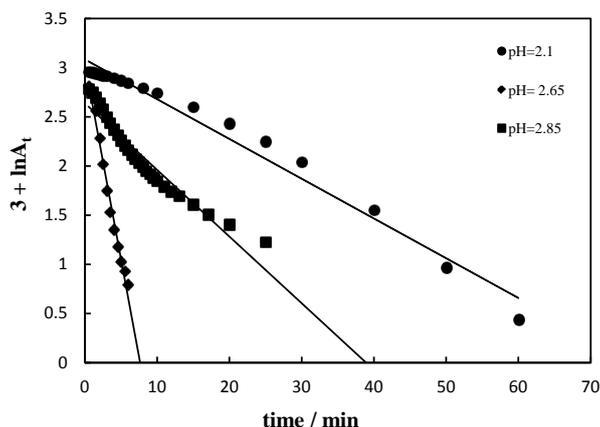
Then,  $\text{Fe}^{3+}$  ions can be reduced by excess  $\text{H}_2\text{O}_2$  to form  $\text{Fe}^{2+}$  ions and more  $\text{HO}\cdot$  radicals. Second reaction is called Fenton-like [12] allowing  $\text{Fe}^{2+}$  regeneration leading to catalytic mechanism (reactions, 2 - 6),



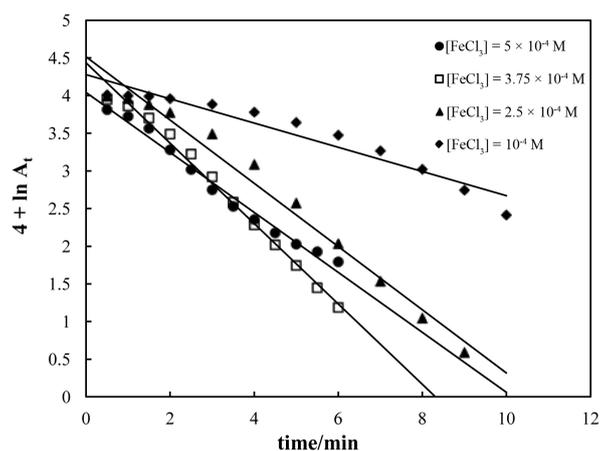
As clear from above mechanism the amount of  $\text{HO}\cdot$  depends on the pH of solution. The effect of pH was studied in pH range of 2 - 3. The results showed that increasing pH from 2 to  $2.6 \pm 0.1$  increases the observed rate constant,  $k_{\text{obs}}$ , from  $0.45 \times 10^{-3} \text{ s}^{-1}$  to  $8.9 \times 10^{-3} \text{ s}^{-1}$  (Figure 3). The drastic decrease in the rate of decolorization at  $\text{pH} = 2$  is attributed to drastic reduction of hydroxyl radicals resulted from the stabilization of hydrogen peroxide. Also Figure 3 showed that increasing pH above 2.6 decreases the observed rate constant. Therefore, the optimal pH value for the decolorization of amaranth is 2.6. This is in agreement with earlier results [8] [11]-[15]. These studies showed that there is optimum pH value ( $\text{pH} = 3$ ).

### 3.2. Effect of Ferric Chloride Concentration

No reaction was observed between amaranth and hydrogen peroxide in absence of ferric ions. Ferric ion concentration shows acceleration effect on the decolorization rate of amaranth. Keeping temperature at  $35^\circ\text{C}$ ,  $[\text{dye}] = 5 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$  and  $[\text{H}_2\text{O}_2] = 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$  using different concentrations of ferric chloride namely,  $1 - 3.75 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ , the decolorization rate increased by increasing ferric ions concentrations. This is attributed to increase  $\text{HO}\cdot$  concentrations. Above that concentration the rate decreased, Figure 4. This could be at-



**Figure 3.** First order plots for decolorization of amaranth at various pH. [dye] =  $5 \times 10^{-5}$  mol·dm<sup>-3</sup>, [H<sub>2</sub>O<sub>2</sub>] =  $5 \times 10^{-3}$  mol·dm<sup>-3</sup>, [Fe<sup>3+</sup>] =  $5 \times 10^{-4}$  mol·dm<sup>-3</sup> and T = 35°C.



**Figure 4.** First order plots for decolorization of amaranth at various Fe<sup>3+</sup> concentrations. [dye] =  $5 \times 10^{-5}$  mol·dm<sup>-3</sup>, [H<sub>2</sub>O<sub>2</sub>] =  $5 \times 10^{-3}$  mol·dm<sup>-3</sup>, pH = 2.65 and T = 35°C.

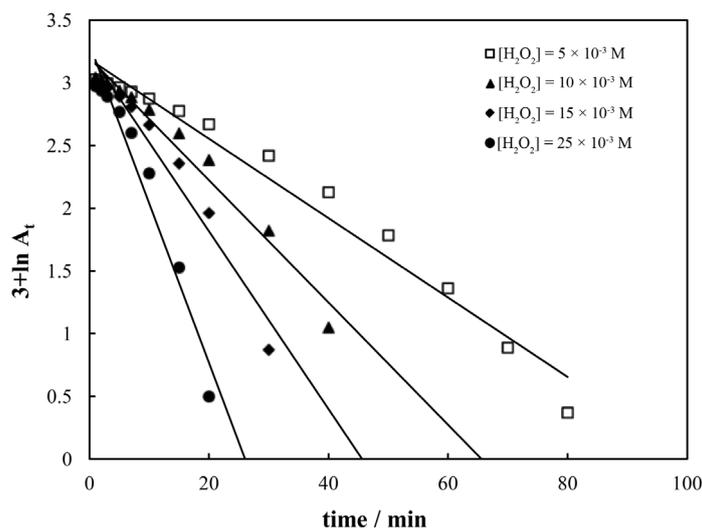
tributed to the increasing in [Fe<sup>3+</sup>] increases [Fe<sup>2+</sup>] which scavenging the HO<sup>•</sup> [8] [15]. Maximum rate at [Fe<sup>3+</sup>] =  $3.75 \times 10^{-4}$  mol·dm<sup>-3</sup>, almost, 95% color removed was observed. Khataee *et al.* [16] reported that increasing the concentration of Fe<sup>3+</sup> ions increases the decolorization rate of brilliant blue and maximum rate was at [Fe<sup>3+</sup>] =  $2 \times 10^{-4}$  mol·dm<sup>-3</sup>.

### 3.3. Effect of H<sub>2</sub>O<sub>2</sub> Concentration

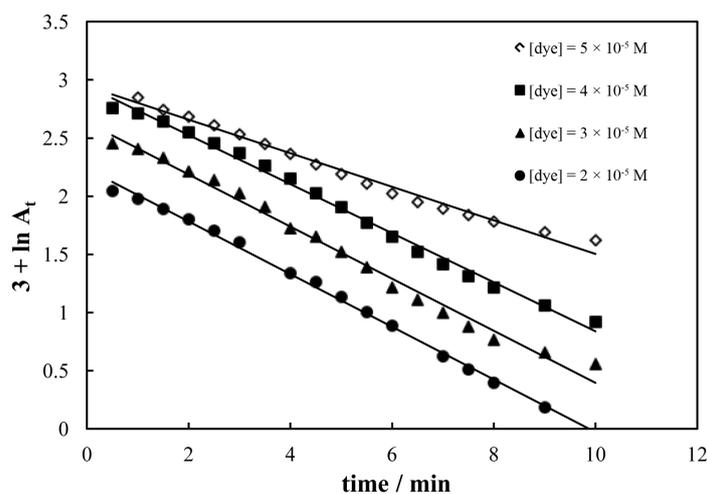
The effect of hydrogen peroxide concentration on the rate of decolorization of amaranth studied at pH equals 2, [dye] =  $5 \times 10^{-5}$  mol·dm<sup>-3</sup> and [Fe<sup>3+</sup>] =  $5 \times 10^{-4}$  mol·dm<sup>-3</sup>. Figure 5 showed that the decrease in dye concentration as function of time was dependent of hydrogen peroxide concentration. Increases of hydrogen peroxide concentrations in range of  $5 - 25 \times 10^{-3}$  mol·dm<sup>-3</sup> increases the rate constant of decolorization from  $0.5 \times 10^{-3}$  to  $2 \times 10^{-3}$  s<sup>-1</sup>. This is due to the increase of HO<sup>•</sup> radicals [8] [15]. Plot of  $\ln k_{\text{obs}}$  versus  $\ln[\text{H}_2\text{O}_2]$  yields straight line with slope of unity indicates the reaction is first order in hydrogen peroxide.

### 3.4. Effect of Amaranth Concentration

The effect of initial dye concentration of aqueous solution of amaranth on Fenton-like process was investigated since pollutant concentration is important parameter in wastewater treatment. Increasing the initial amaranth concentration from  $2$  to  $4 \times 10^{-5}$  mol·dm<sup>-3</sup> did not show any effect on the decolorization rate, Figure 6. Also



**Figure 5.** First order plots for decolorization of amaranth at various  $\text{H}_2\text{O}_2$  concentrations.  $[\text{dye}] = 5 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[\text{Fe}^{3+}] = 5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ,  $T = 35^\circ\text{C}$  and  $\text{pH} = 2$ .



**Figure 6.** First order plots for decolorization of amaranth at various dye concentrations.  $[\text{H}_2\text{O}_2] = 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[\text{Fe}^{3+}] = 5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ,  $T = 30^\circ\text{C}$  and  $\text{pH} = 2.65$ .

**Figure 6** shows that increasing the concentration of dye above  $(4 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3})$  decrease the rate of decolorization. This attributed to relatively lower of  $\text{HO}^\cdot$  results from the increasing of amaranth concentration while concentration of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$  remains the same. The obtained results were in good agreement with earlier reported [11] [13]-[15].

### 3.5. Effect of Temperature

The variation of the temperature in range of 298 - 308 K increases the rate of decolorization of amaranth. No optimal temperature in this study was detected as opposed to the literature reports [17] [18] in which  $30^\circ\text{C}$  are stated as optimal temperature for Fenton oxidation. Another optimal temperature,  $50^\circ\text{C}$  was reported on decolorization of some dyes by Fenton-like reaction [8]. The activation energy was calculated from Arrhenius plot and Eyring equation and was found to be  $104.79 \text{ kJ}\cdot\text{mol}^{-1}$ . The other thermodynamic parameters are given in **Table 1**. As observed from **Table 1** positive value of  $\Delta S^\ddagger$  indicates reaction is favor. The  $\Delta H^\ddagger$  positive value indicates that the process is endothermic.

### 3.6. Effect of Inorganic Anion Concentration

Inorganic anions occur naturally in waste water (e.g.  $\text{NO}_3^-$ ) or may be added to facilitate the dyeing (e.g.  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ ). The presence of inorganic anions in textile wastewaters plays an important role in the oxidation kinetics of different dyes. Inorganic anions may induce or reduce the rate of oxidation.

#### 3.6.1. Influence of $\text{NaNO}_3$ Concentration

Decolorization rate of amaranth did not affect by addition of  $\text{NaNO}_3$  (Table 2).

#### 3.6.2. Influence of $\text{Na}_2\text{CO}_3$ Concentration

Different concentrations of  $\text{Na}_2\text{CO}_3$  were used to study the effect of carbonate ions on the oxidation of amaranth. Carbonate ions were present mainly as  $\text{H}_2\text{CO}_3$ , since the experiments were performed at  $\text{pH} \leq 3$ . Presence of bicarbonate ions in the course of oxidation may decrease the decolorization rate due to scavenging of  $\text{OH}^\bullet$  by  $\text{HCO}_3^-$  ( $\text{HCO}_3^- + \text{OH}^\bullet \rightarrow \text{CO}_3^{\bullet-} + \text{H}_2\text{O}$ ). Production of  $\text{CO}_3^{\bullet-}$  which is less reactive than hydroxyl radical [19] lowered the levels of  $\text{OH}^\bullet$  during the course of the reaction hence decreasing the decolorization rate. It was observed that the decolorization rate constant ( $5.295 \times 10^{-3} \text{ s}^{-1}$ ) in the absence of carbonate ions decreased to  $1.74 \times 10^{-3} \text{ s}^{-1}$  due to the presence of  $8 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$   $\text{Na}_2\text{CO}_3$ , Table 2.

#### 3.6.3. Influence of $\text{NaCl}$ Concentration

Addition of  $0.085 \text{ mol}\cdot\text{dm}^{-3}$  of  $\text{NaCl}$  decreased rate constant from  $5.32 \times 10^{-3} \text{ s}^{-1}$  (in absence of chloride) to  $1.6 \times 10^{-3} \text{ s}^{-1}$ . The inhibitive effect of chloride can be explained by scavenging effect of chloride ion on  $\text{OH}^\bullet$  (Equation (9)).



Increasing the concentration of chloride up to  $0.340 \text{ mol}\cdot\text{dm}^{-3}$  had no significant effect (Table 2). The obtained results were in good agreement with earlier reported [8] [11] [14].

**Table 1.** Thermodynamic parameters for decolorization of Amaranth by Fenton-like reagent.

parameters	value
$E_a$	$104.79 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ$	$102.23 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta S^\circ$	$38.76 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$\Delta G^\circ$	$90.29 \text{ kJ}\cdot\text{mol}^{-1}$

**Table 2.** Observed first order rate constants for the decolorization of Amaranth by Fenton-like reagent at temperature =  $35^\circ\text{C}$  at different concentration of inorganic anions.

Inorganic electrolyte	Concentration/ $\text{mol}\cdot\text{dm}^{-3}$	$k_{\text{obs}} \times 10^3/\text{s}^{-1}$
$\text{NaNO}_3$	0	5.295
	0.059	5.207
	0.118	6.2
	0.236	6.032
$\text{NaCl}$	0	5.322
	0.085	1.6
	0.170	1.928
$\text{Na}_2\text{CO}_3$	0	5.295
	0.004	3.848
	0.008	1.740

## 4. Conclusion

The decolorization kinetics of amaranth red in aqueous solution was studied using Fenton like reaction in dark environment. The results showed that the Fenton-like is powerful method for decolorization of amaranth red dye. The reaction was first order in dye and  $\text{H}_2\text{O}_2$ . The Fenton-like oxidation of amaranth red dye showed maximum rate at  $\text{pH} = 2.6$  and  $[\text{Fe}^{3+}] = 3.75 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ .

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