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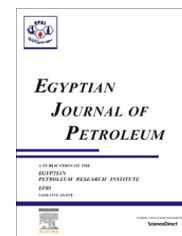
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FULL LENGTH ARTICLE

Degradation of methyl orange using Fenton catalytic reaction

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Abstract   Oxidation by Fenton reactions a proven and economically feasible process for destruction of a variety of hazardous pollutants in wastewater. We report herein the oxidation of methyl orange using a Fenton reaction at normal laboratory temperature and at atmospheric pressure. The effects of different parameters like the dosages of H_2O_2 and Fe^{2+}, initial concentration of dye and pH of the solution, on the oxidation of the dye present in dilute aqueous solutions are found. The results indicate that the dye can be most effectively oxidized in aqueous solution at dye: Fe^{2+}:H_2O_2 molar ratio of 1:3.5:54.2. It was found that more than 97.8% removal of the dye could be achieved in 15 min in the pH 2.79 at room temperature. The results will be useful for designing the treatment systems of the various dyes containing wastewater.
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1. Introduction

Dye pollutants from the dyestuff manufacturing, dyeing, printing and textile industries are important sources of environmental contamination. The effluents discharged from these industries are usually strongly colored, and the direct release of the wastewater into receiving water body will cause damage to both aquatic life and human beings due to their toxic, carcinogenic and mutagenic effects [1,2]. Azo dyes, characterized by the presence of one or more azo groups (N=N) bound to aromatic rings, are the largest and most important class of synthetic organic dyes. It has been estimated that more than 50% of all dyes in common used are azo dyes because of their chemical stability and versatility [3].

A variety of physical, chemical, and biological methods are presently available for treatment of wastewater discharged from various industries. Biological treatment is a proven technology and cost-effective, but it suffers from a number of disadvantages. Physical methods such as liquid–liquid extraction, ion-exchange, adsorption, air or steam stripping, etc. are also ineffective on pollutants which are not readily adsorbable or volatile, and have further disadvantage that they simply transfer the pollutants to another phase rather than destroying them. In contrast, chemical oxidation methods can result in almost complete mineralization of organic pollutants and are effective for a wider range of organics. The oxidation with

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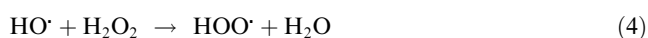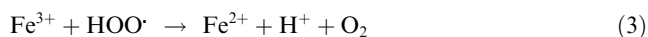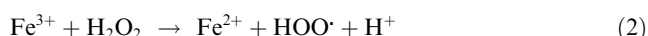URL: http://www.epri.sci.eg (S.A. Shaban).
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Fenton reaction based on ferrous ion and hydrogen peroxide is an effective technology for destruction of a large number of hazardous and organic pollutants [4].

Fenton reaction is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in an acidic medium, which was firstly discovered by Fenton in the 1890s [5]. In the last decades, Fenton's reaction has been introduced into wastewater treatment processes, and it has been shown that a variety of refractory organics could be effectively degraded through Fenton reaction without producing any toxic substances in water environment [6,7]. The mechanism that describes Fenton reaction mainly includes the following reactions [6,8]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^{+} \tag{2}$$

$$Fe^{3+} + HOO^{\cdot} \rightarrow Fe^{2+} + H^{+} + O_2 \tag{3}$$

$$HO^{\cdot} + H_2O_2 \rightarrow HOO^{\cdot} + H_2O \tag{4}$$

$$HO^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} \tag{5}$$

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \tag{6}$$

$$HO^{\cdot} + HOO^{\cdot} \rightarrow O_2 + H_2O \tag{7}$$
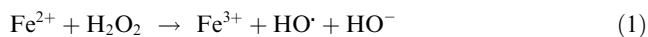
There are several studies related to using of Fenton reaction for the treatment of azo dyes wastewaters [9–12].

The previous researches have shown that a number of azo dyes could be effectively degraded by Fenton reaction. And the degradation efficiency of dyes was mainly dependent on their chemical characteristics, the generation rate and concentration of $HO^{\cdot}$ in the process.

2. Materials and methods

2.1. Reagent

Methyl orange ($C_{14}H_{14}N_3NaO_3S$) provided from Aldrich Chemical Company; ferrous sulfate ($FeSO_4 \cdot 7H_2O$) provided from LOBA Chemic; Hydrogen peroxide (30% v/v); and hydrochloric acid provided from BIO CHEM.

All the chemicals were of analytical grade and were used without further purification. A known dye concentration was prepared in distilled water and used as the stock solution for all studies. The properties of MO are shown in Table 1.

2.2. Experimental procedures

All experiments were carried out at room temperature and pH of the solution was adjusted by using hydrochloric acid or sodium hydroxide using a pH meter.

The required amount of Fe^{2+} and H_2O_2 was added to the dye solution. The Fenton reaction was started by the addition of H_2O_2. Immediately after the addition of H_2O_2 the concentrations of the dye were determined spectrophotometrically at 464 nm, at different times in order to study the degradation of the methyl orange.

2.3. Analytical methods

The UV–Vis spectra of the MO were recorded from 200 to 800 nm by using Thermo Scientific Evolution 300 UV–Vis Spectrophotometer. The spectrum showed that the maximum absorbance wavelength (λ_{max}) of MO was at 464 nm. Therefore the absorbance of MO in the experiment can be determined at 464 nm. Before the measurement, a calibration curve was obtained using the standard MO solution with a series of known concentrations.

The dye degradation efficiency was used in the study:

$$\text{Degradation efficiency } \% = \left(1 - \frac{C_{dye,t}}{C_{dye,0}}\right) \times 100$$

where $C_{dye,t}$ and $C_{dye,0}$ are the concentration of dye at λ_{max} reaction time t and 0, respectively.
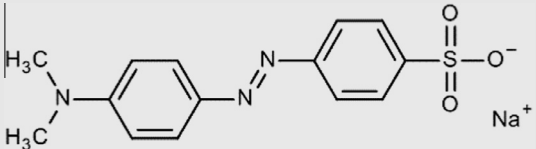
3. Results and discussion

3.1. Optimization of system parameters

3.1.1. Effect of H_2O_2 dosage on the degradation of methyl orange

H_2O_2 plays a very important role as a source of $HO^{\cdot}$ generation in Fenton's reaction. The effect of H_2O_2 dosage on the

Table 1 Properties of methyl orange.

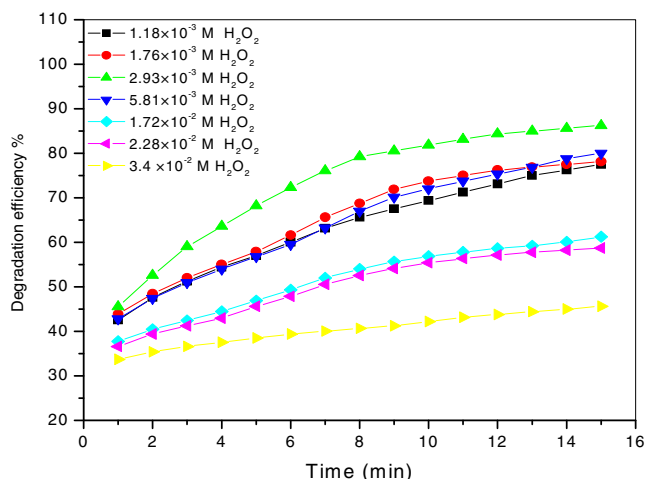| Properties of methyl orange	
IUPAC name	Sodium 4-[(4-dimethylamino) phenyldiazenyl] benzenesulfonate
Molecular formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass	327.33 g/mole
Density	1.28 g/cm^3, solid
Melting point	> 300 °C
Boiling point	Decomposes
Solubility in water	Soluble in water

Figure 1 Effect of [H_2O_2] on the degradation of methyl orange by Fenton reaction. Experimental condition: [MO] = 5.4×10^{-5} M; [Fe^{2+}] = 1.9×10^{-4} M; pH = 6.69.

degradation of methyl orange was examined by varying initial concentration of H_2O_2 from 1.18×10^{-3} to 3.4×10^{-2} M and the results are shown in Fig. 1. From the figure, it can be observed that increasing the dosage of H_2O_2 from 1.18×10^{-3} to 2.93×10^{-3} M could enhance the degradation of methyl orange from 77.5% to 86.25% within 15 min of reaction. However, with a further increase of the dosage above 2.93×10^{-3}–3.4×10^{-2} M, the degradation of methyl orange was not improved but dropped down. For example, the degradation efficiencies within15 min of reaction reduced from 86.25% to 45.65% as an increasing dosage of H_2O_2 from 2.93×10^{-3} to 3.4×10^{-2} M. Indeed, the decrease of the degradation efficiency of MO at high dosage of H_2O_2 was mainly caused by the scavenging effect of excessive H_2O_2 to HO· (Eq. (4)). In addition, the recombination of HO· (Eq. (6)) also contributed for the declining of the degradation efficiency of MO [6,8]. From the experimental results, therefore, a suitable H_2O_2 dosage as 2.93×10^{-3} M was selected.
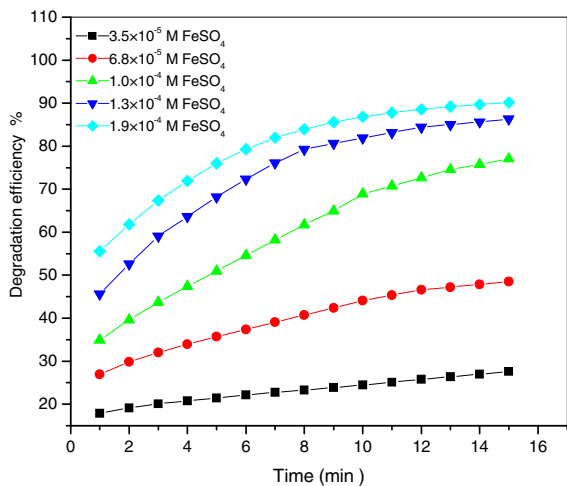
3.1.2. Effect of Fe^{2+} dosage on the degradation of methyl orange

Fe^{2+} is another main parameter in Fenton reaction that catalytically decomposes H_2O_2 to generate HO·. Fig. 2, shows the effect of Fe^{2+} dosage on the degradation of MO with different initial concentration from 3.5×10^{-5} to 1.9×10^{-4} M. It can be seen that the degradation was limited at 3.5×10^{-5} and 6.81×10^{-5} M Fe^{2+}, there is only 27.59% and 48.46%, respectively of MO was degraded within 15 min of reaction. In the presence of 1.0×10^{-4}, 1.3×10^{-4} and 1.9×10^{-4} M of Fe^{2+}, a great improvement of the degradation of methyl orange could be observed and the degradation efficiencies within 15 min of reaction achieved were 77.01%, 86.25% and 90.12%, respectively. The fact is that higher degradation efficiency achieved at high Fe^{2+} dosages was mainly attributed to the higher production of HO· with more Fe^{2+} in Fenton
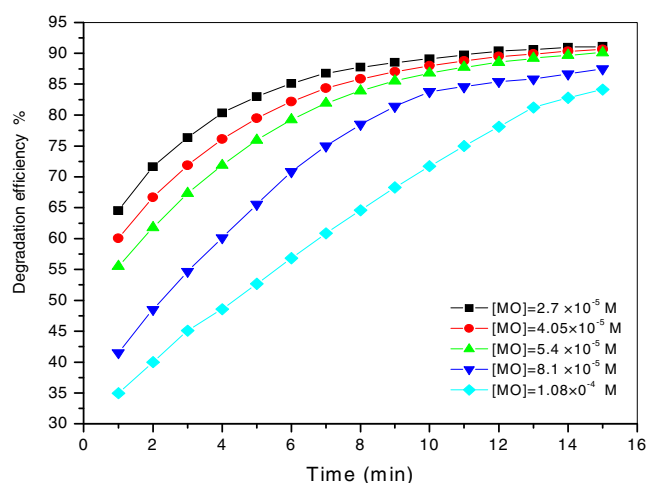

Figure 3 Effect of the concentration of methyl orange on the degradation by Fenton reaction. Experimental condition: [Fe^{2+}] = 1.9×10^{-4} M; [H_2O_2] = 2.93×10^{-3} M; pH = 6.69.

Figure 2 Effect of Fe^{2+} on the degradation of methyl orange by Fenton reaction. Experimental condition: [MO] = 5.4×10^{-5} M; [H_2O_2] = 2.93×10^{-3} M; pH = 6.69.
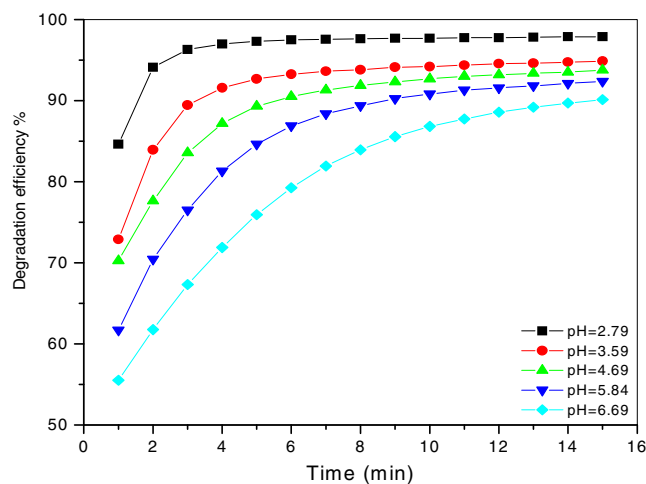

Figure 4 Effect of initial pH on the degradation of methyl orange by Fenton oxidation. Experimental condition: [MO] = 5.4×10^{-5} M; [H_2O_2] = 2.93×10^{-3} M; [Fe^{2+}] = 1.9×10^{-4} M.

reaction. So that, 1.9×10^{-4} M of Fe^{2+} was considered to be a suitable dosage for the degradation of MO.

3.1.3. Effect of concentration of methyl orange on the degradation

The degradation of different concentrations of methyl orange was studied; the results are shown in Fig. 3. It can be seen that the degradation efficiency of methyl orange was decreased with increasing the concentrations of MO. As increasing the concentration of MO from 2.7×10^{-5} to 1.08×10^{-4} M, the degradation efficiency of MO within 15 min of reaction decreased from 91.12% to 84.13%. This is due to a relative lower concentration of $HO^{\bullet}$ results from increasing the concentration of MO.
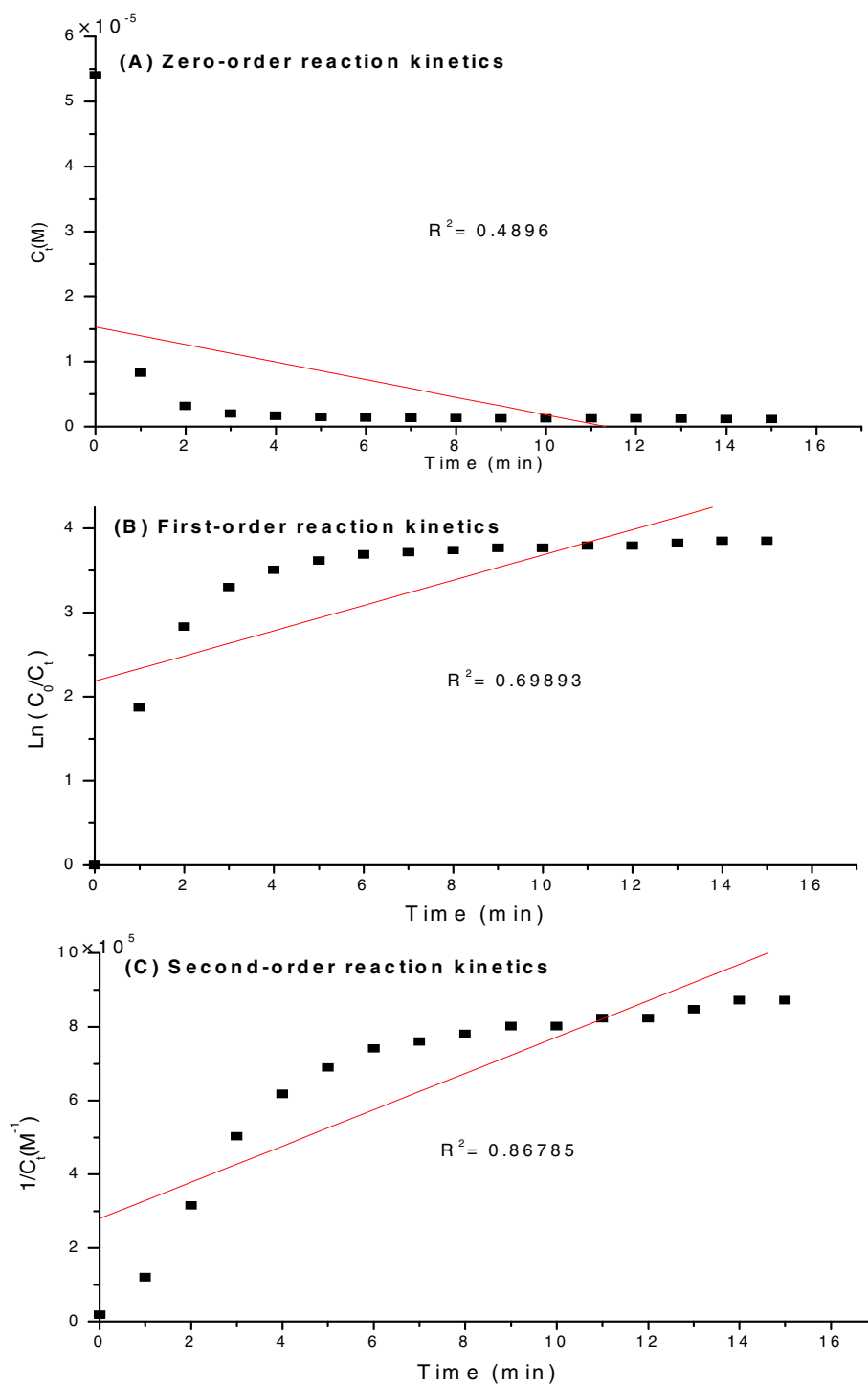

Figure 5   (A) Zero-, (B) first- (C) second- order reaction kinetics for degradation of MO by Fenton reaction. Experimental condition: [MO] = 5.4×10^{-5} M; [H_2O_2] = 2.93×10^{-3} M; [Fe^{2+}] = 1.9×10^{-4} M and pH = 2.79.

3.1.4. Effect of initial pH on the degradation of the methyl orange

The effect of initial pH of solution on the degradation of methyl orange by Fenton reaction was studied in the pH range of 2.79–8 and the results are shown in Fig. 4. A direct influence of initial pH on the degradation of MO could be observed and the best degradation efficiency was obtained at pH of 2.79. At initial pH of 8.0, the degradation of MO almost could not be observed in 15 min of reaction. It is principally due to the formation of ferrous/ferric hydroxide complexes which leads to the deactivation of ferrous catalyst, and a small amount of HO· was generated [13,14]. When the initial pH was decreased from 6.69 to 2.79, the degradation efficiency of MO within 15 min increased significantly from 90.12% to 97.8%.

3.2. Kinetic study

In the present study, zero, first- and second-order reaction kinetics were used to study the degradation kinetics of MO by Fenton oxidation process. The individual expression was presented as below (Eqs. (8) and (9)):

• Zero-order reaction kinetics:

$$\left(\frac{dc}{dt}\right) = -k_0 \tag{8}$$

• First-order reaction kinetics:

$$\left(\frac{dc}{dt}\right) = -k_1 C \tag{9}$$

• Second-order reaction kinetics:

$$\left(\frac{dc}{dt}\right) = -k_2 C^2 \tag{10}$$

where C is the concentration of MO; k_0, k_1 and k_2 represent the apparent kinetic rate constants of zero-, first- and second-order reaction kinetics, respectively; t is the reaction time.

By integrating the Eqs. (8)–(10), Eqs. (11)–(13) could be obtained.

$$C_t = C_0 - k_0 t \tag{11}$$

$$C_t = C_0 e^{-k_1 t} \tag{12}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \tag{13}$$

where C_t is the concentration of MO at reaction time t.

Regression analysis based on the zero-, first- and second-order reaction kinetics for the degradation of MO in Fenton oxidation process was conducted and the results are shown in Fig. 5. Comparing the regression coefficients (R^2) obtained from Fig. 5(A)–(C), it can be seen that R^2 based on the second-order reaction kinetics (Fig. 5(C)) was 0.86785, which was obviously much better than that based on the zero-order ($R^2 = 0.48960$) and the first-order ($R^2 = 0.69893$) reaction kinetics. The results indicated that the degradation kinetics of MO followed the second-order kinetics well.

The apparent kinetic rate constants, k_2, of the degradation of MO were found to be $4.9273 \times 10^4 \, \mathrm{M^{-1} \, min^{-1}}$ at an optimal condition of [MO] = 5.4×10^{-5} M, [H$_2$O$_2$] = 2.93×10^{-3} M, [Fe^{2+}] = 1.9×10^{-4} M, pH = 2.79 at room temperature.

4. Conclusions

In this work, the degradation of MO in aqueous solution by Fenton reaction has been studied on different experimental conditions, including, dosages of H$_2$O$_2$ and Fe^{2+}, different of dye concentration, and different pH value of solutions. A suitable operating condition was selected as: [MO] = 5.4×10^{-5} M, [Fe^{2+}] = 1.9×10^{-4} M; [H$_2$O$_2$] = 2.93×10^{-3} M and pH = 2.79 at room temperature. In the given conditions, more than 97.8% of degradation efficiency was achieved within 15 min of reaction. And when the initial pH was decreased from 6.69 to 2.79, the degradation efficiency of MO within 15 min increased significantly from 90.12% to 97.8%. The Kinetic study indicated that the degradation kinetics of MO followed the second-order kinetics.

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