Research article

Kinetic and thermodynamic studies of the degradation of methylene blue by photo-Fenton reaction

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A B S T R A C T

Syrian natural magnetite has been utilized for the removal of methylene blue from aqueous solutions by photo-Fenton reaction. Experiments were carried out to evaluate the kinetic and thermodynamic parameters.

Pseudo-first order, pseudo-second-order models were used to analyze the kinetic data obtained at different initial MB concentrations and temperatures.

The photo-Fenton degradation process of MB is better described by the pseudo-first-order model. The activation energy Ea = 16.89 and 18.02 kJ/mol for MB degradation at concentrations 40 and 80 mg/l respectively, and that suggesting the degradation reaction proceeded with a low energy barrier, the values obtained (ΔG^*, ΔS^*, and ΔH^*) indicate that the process is endothermic and spontaneous.

1. Introduction

Industrial water is known to contain large quantities of organic pollutants the most common of which are dyes. Dyes are widely used in industry, such as cosmetics, paper, leather, pharmacy, food industries, and textile industry in particular. More than 7×10^5 tons of these dyes are produced annually around the world. It is estimated that about 10–15% of these chemical compounds are discharged into waterways by the textile industries [1].

Many literature works showed that the colored dyes have biodegradation resistant to conventional physical and biological oxidation treatments because they have a complex aromatic molecular structure [2, 3, 4, 5, 6].

Organic dyes like Methylene blue (MB) which has a high solubility in water and is widely used in textile industries. However, MB may be responsible for permanent injury to the eyes [7].
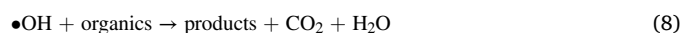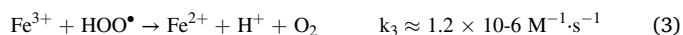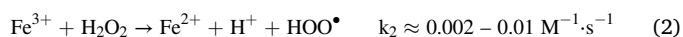
Several treatment processes - such as physical separation, chemical oxidation, biological dissociation, and Photo-Fenton reactions - have been used in the process of removing dyes from wastewater [8].

Traditional Fenton, consisting of H_2O_2 and ferrous ions, is verified to be rapid and nonselective in contaminants degradation for the generation of hydroxyl radicals (•OH) [9, 10].

The free radical •OH has the oxidation potential of 2.8 eV [11, 12] and that is higher than 1.78 eV the oxidation potential of H_2O_2. The

equipment for traditional Fenton was achieved at pH 2–4 [13, 14, 15, 16].

The process of free radical •OH generation can be described as following equations [17, 18, 19]:

$$Fe^{2+} + H_2O_2 \rightarrow {}^\bullet OH + OH^- + Fe^{3+} \qquad k_1 \approx 70 \text{ M}^{-1}\cdot\text{s}^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \qquad k_2 \approx 0.002 - 0.01 \text{ M}^{-1}\cdot\text{s}^{-1} \qquad (2)$$

$$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad k_3 \approx 1.2 \times 10\text{-}6 \text{ M}^{-1}\cdot\text{s}^{-1} \qquad (3)$$

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \qquad k_4 \approx 3.2 \times 108 \text{ M}^{-1}\cdot\text{s}^{-1} \qquad (4)$$

$${}^\bullet OH + H_2O_2 \rightarrow H_2O + HOO^\bullet \qquad k_5 \approx 3.3 \times 107 \text{ M}^{-1}\cdot\text{s}^{-1} \qquad (5)$$

$$Fe^{2+} + HOO^\bullet \rightarrow HOO^- + Fe^{3+} \qquad (6)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \qquad (7)$$

$$\bullet OH + organics \rightarrow products + CO_2 + H_2O \qquad (8)$$

The exhaustion rate of Fe^{2+} (70 M^{-1} s^{-1}), is much higher than that of generation (0.002–0.01 M^{-1} s^{-1}), and that will slow down the reaction. Disadvantages, traditional Fenton can't use in wide applications because of the narrow pH range and inability to reused the catalysts [20, 21, 22].

The second pollution as iron sludge which produced from the treatment process can affect the water quality [23, 24, 25].

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Because of the disadvantages mentioned previously, the scientists had to modify the Fenton reactions to become more effective and efficient, and during this process the hydrogen peroxide reacts with the solid metal catalyst to avoid formulating iron sludge in addition to the wide range of pH.

The photo-Fenton process is a promising class of advanced oxidation processes (AOPs) used for wastewater treatment [9, 26].

Since the use of solid catalysts is more chemically effective, it is more easily separable and recyclable [27].

Magnetite (Mag.) is one of the most important natural iron compounds and has a variety of uses, and it is found in the form of natural ores scattered in different places of the earth's crust and the form of different dimensions particles [28].

It consists of iron oxides (II, III) and has the formula Fe_3O_4. This can be expressed in the form Fe (II) Fe (III)$_2O_4$, which is classified as Spinels and consists of tetrahedral and octahedral building units that stack to form a compact cubic crystal structure. It generally expresses the spinel structure $A^{2+} B_2^{3+} O_4^{2-}$ where A, B have (II, III, or IV) equivalent elements such as Mg, Zn, Fe, Mn, Al, Cr, Ti, Si [29].

Most countries care about their natural ore reserves to invest them in many fields. Natural magnetite is found in many countries such as Syria. This paper aims to employ this natural magnetite as a catalyst in photo-Fenton processes to degrade organic pollutants from aqueous solutions at a low economic cost. This is the first time Syrian natural magnetite is studied, whereas we previously studied its physiochemical properties by characterizing its adsorption ability [30]. In this paper, the thermodynamic and kinetics parameters had been detected by photo-Fenton reactions.

2. Materials and methods

2.1. Chemical

Natural magnetite ores in Wadi-Kandyl coast north Latakia city, Syria.
Methylene Blue (MB) $C_{16}H_{18}N_3SCl$.
Hydrogen peroxide H_2O_2 35% w/v.

2.2. Instruments

An electric drying oven heats up (300 °C) produced by the R-LABINCO company.
Calcination muffle heats (1200 °C) produced by Carbolite company.
SpectroPhotoMeter 150W (T60 U) produced by PG Instruments Limited company, to determine the concentration of a methylene blue solution at 665 nm wavelength.
UV lamp (10 W).
Water bath produced by Julabo company.

2.3. Magnetite characterization

The natural magnetite samples were collected from the Wadi-Kandyl coast, and then mechanically separated from other substances by the magnet, and then washed by deionized water to get rid of dissolved substances, and then powdered and dried in an electrical oven at 110 °C for 5 h, and finally calcined in Calcination muffle at 550 °C for 5 h, where XRD and FTIR analysis was performed in the previous study [30].

2.4. Batch degradation experiments

The degradation of MB dye was carried out in a batch operation. The MB solution was prepared in deionized water. The batch tests of the photo-Fenton reaction were performed in a 100 mL glass beaker at different experimental conditions that include a 25 ml of MB aqueous solution with two MB concentrations of 40, 80 mg/l, the temperature of 303–333 K (using water bath), 0.15g dosage of Mag, and 2 m mol of H_2O_2, at natural pH. The degradation of MB 40, 80 mg/l took 60, 120 min respectively.

3. Results and discussions

3.1. Kinetic studies

To determine the degradation kinetic of Methylene Blue (MB) on natural magnetite using Photo-Fenton reaction, the pseudo-first-order and pseudo-second-order kinetic models were examined. On the other hand, some of the thermodynamic parameters were determined. The methylene blue degradation depends on time and temperature which was studied at)303, 313, 323, 333 K (for the solution with $C_0 = 40$ and 80 mg/l, and 2 m mol of H_2O_2 + 0.15 g of magnetite were added to 25 ml of each solution, the solution was left in a water bath under UV lamp (10 W).

The residual MB concentration was determined by the spectroscopic method (UV-Vis) at 665 nm. The uptake values for removal of MB from solution are shown in Figure 1.

Removal ratio was calculated using the following equation:

$$\text{Removal \%} = \frac{A_0 - A_e}{A_0} \cdot 100 \tag{9}$$

A_0: initial concentration of MB (mg/l).
A_e: residuals concentration of MB (mg/l).

The optimal conditions for MB degradation from our previous study were: 0.15g dosage from magnetite, 2 m mol of H_2O_2 at natural pH [31].

It is seen from Figure 1 that the degradation of MB increases by increasing the temperature for both concentrations and this tendency may be due to the increase of the reaction between hydrogen peroxide and Fe II ions to produce the hydroxyl radicals. Similar behavior was found in other studies [32].

From Figure 1 we can say that the degradation process of MB takes place in two steps. The first step accurses at the beginning stages i.e. approx. in the first 30 min for concentration 40 mg/l and 50 min for 80 mg/l.

After these periods degradation process exhibits a slower rate and reaches equilibrium and maximum removal about 95% after 60 min and 120 min for concentrations 40 and 80 mg/l respectively [33].

The data from Figures 1 and 2 were analyzed using the pseudo-first equation:

$$\ln \frac{[A]_0}{[A]} = k_1 t \tag{10}$$

And pseudo-second equation:

$$\frac{1}{[A]} = k_2 t + \frac{1}{[A]_0} \tag{11}$$

$[A]_0$: initial concentration of MB (mg/l).
$[A]$: residuals concentration of MB (mg/l).
t: time (min).
k_1, k_2: constant of pseudo-first equation (min^{-1}) and pseudo-second equation (M^{-1}.min^{-1}) respectively.

The results of the two equations are presented in Figures 2 and 3.
Calculated rate constants k_1, k_2, and correlation coefficients R^2 were summarized in Tables [1 and 2].

From Tables 1 and 2 values correlation coefficients, R^2 for pseudo-first-order is higher than R^2 for pseudo-second-order and closer to 1 and the k_1 rate constant increases with temperature from 0.048 to 0.088 and also increased from 0.046 to 0.088 at the MB concentration 40, 80 mg/l respectively, While the k_2 rate constant variables.

The Fenton degradation process of MB is better described by the pseudo-first-order model. From the result in Tables 1 and 2 we can say that the process accurses according to the film diffusion and interaction particles diffusion mechanism and these results were in close agreement with the literature [34].
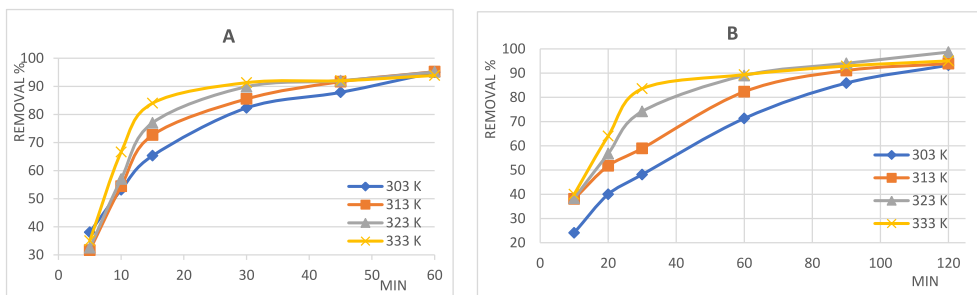
Figure 1. Dissociation of the methylene blue at different temperatures (UV, 0.15 g Mag + 2 m mol H_2O_2) (A 40 mg/l, B 80 mg/l).
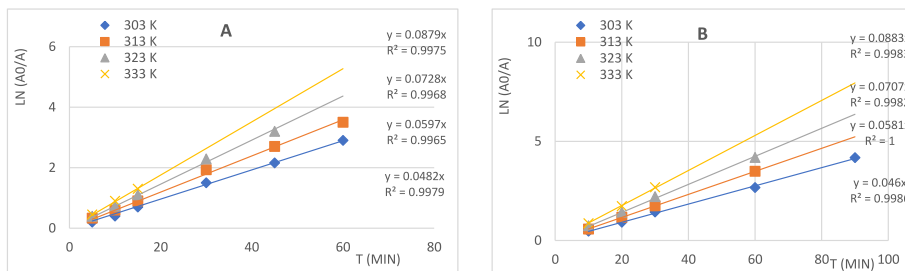

Figure 2. Plots of the pseudo-first-order model (A for MB 40 mg/l, B for MB 80 mg/l).
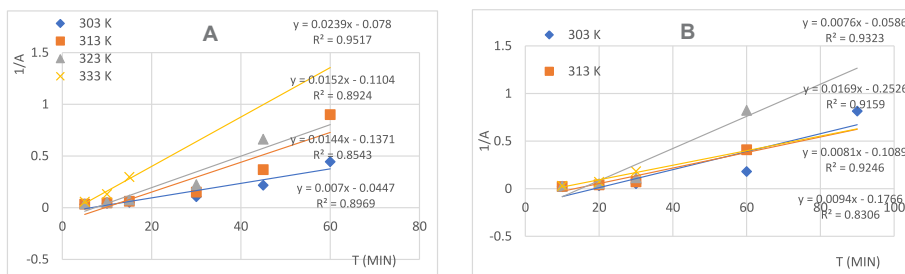

Figure 3. Plots of pseudo second-order model (A for MB 40 mg/l, B for MB 80 mg/l).

Table 1. Experimental results for photo-Fenton degradation of MB (40 mg/l).

T (K)	Pseudo first order model		Pseudo second order model	
	k_1, min^{-1}	R^2	k_2, $M^{-1}.min^{-1}$	R^2
303	0.048	0.998	0.007	0.897
313	0.059	0.997	0.014	0.854
323	0.073	0.997	0.015	0.892
333	0.088	0.998	0.024	0.952

Table 2. Experimental results for photo-Fenton degradation of MB (80 mg/l).

T (K)	Pseudo first order model		Pseudo second order model	
	k_1, min^{-1}	R^2	k_2, $M^{-1}.min^{-1}$	R^2
303	0.046	0.999	0.009	0.831
313	0.058	1	0.008	0.925
323	0.071	0.998	0.017	0.916
333	0.088	0.998	0.008	0.932

3.2. Thermodynamic studies

The variation of k_1 with temperature in the (303, 313, 323, 333 K) was used for the calculation of the activation energy (Ea) and some thermodynamic parameters.

The activation energy of the degradation was calculated using the Arrhenius equation

$$ln k_{app} = -\frac{Ea}{RT} + \ln A \qquad (12)$$

Ea: activation energy (kJ/mol).
A: Arrhenius constant (min^{-1}).
T: temperature (k).
K_{app}: Apparent rate constant (min^{-1}).
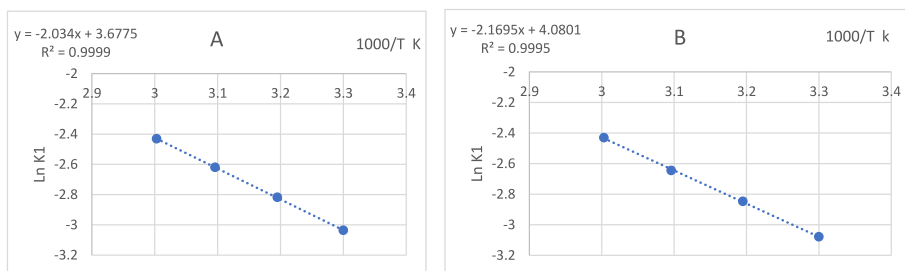R: universal gases constant 8.314 (j/mol.k). As shown in Figure 4.

Figure 4. Plots of ln k versus 1000/T for the degradation of MB (A for MB 40 mg/l, B for MB 80 mg/l).

To calculate the activation energy, we had to draw log(k) vs 1/T, where we got a straight line, and from its slope, we can calculate the activation energy.

The values of the activation energy have moderate values and it was 16.890 and 18.020 kJ/mol for concentrations 40 and 80 mg/l of MB respectively.

This value suggested that the oxidative reaction proceeded with a low energy barrier.

The results show that the photo-Fenton degradation of MB is physical process, because the values of activation energy less than 20 kJ/mol, and these values is in agreement with thermodynamic results in Table 3 [35].

The data obtained from the degradation experiments at (303, 313, 323, 333 K) and the initial MB concentrations of 40 and 80 mg/l were used to the calculation of thermodynamic properties using the flowing equation:

$$ln\frac{k}{T} = \frac{-\Delta H^*}{R} \cdot \frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^*}{R} \tag{13}$$

k_B: Boltzmann constant 1.3806×10^{-23} m^2 kg s^{-2} K^{-1}
ΔH^*: enthalpy (kJ/mol).
ΔS^*: entropy (kJ/mol.K).
T: temperature (K).
k: constant (min^{-1}).

R: universal gases constant 8.314 (J/mol.k).
h: Blank constant 6.626×10^{-34} m^2 kg/s.

The plot of $ln\frac{k}{t}$ vs $\frac{1}{T}$ in Figure 5 gave a straight line, and the values of ΔS^* and ΔH^* can be obtained from the intercept and slope, respectively, and the value of ΔG^* can be calculated from the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{14}$$

ΔG^*: free energy (kJ/mol)
ΔH^*: enthalpy (kJ/mol)
T: temperature (K)
ΔS^*: entropy (J/mol.K)

The thermodynamic parameters are presented in Table 3.

The negative ΔS^* values in Table 3 (-233.2 and -219.8 J/mol.k for concentration 40 and 80 mg/l of MB respectively) indicate to decrease the randomness in the system where the degradation happened.

The negative values of ΔG^* in Table 3 show that the degradation process of MB on magnetite using Fenton reaction occurs spontaneously and the extent of the spontaneity of the reaction increased by increasing the temperature, but it slightly decreases when the concentrations of MB shifted from 40 mg/l to 80 mg/l [35].

The MB degradation is endothermic because of positive values of enthalpy (14.25 and 15.38 kJ/mol for concentration 40 and 80 mg/l of MB respectively).

Table 3. The thermodynamic parameters for MB degradation (40, 80) mg/l.

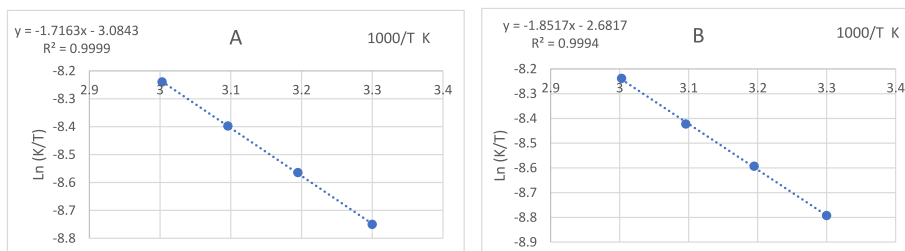| C_0	T (K)	k_1	R^2	ΔH^* (kJ/mol)	ΔS^* (J/mol.K)	ΔG^* (kJ/mol)
40 mg/l	303	0.048	0.998	14.25	-233.2	-53.38
	313	0.059	0.997			-55.61
	323	0.073	0.997			-57.84
	333	0.088	0.998			-60.07
80 mg/l	303	0.046	0.999	15.38	-219.8	-51.24
	313	0.058	1			-53.44
	323	0.071	0.998			-55.64
	333	0.088	0.998			-57.84

Figure 5. Plots of ln (k/T) versus 1/T for the degradation of MB (A for MB 40 mg/l, B for MB 80 mg/l).

4. Conclusion

In the present study, natural magnetite has been successfully used in the photo-Fenton reaction for degradation of Methylene Blue from its aqueous solution. The maximum removal of MB about 95% after 60 min and 120 min for concentrations 40 and 80 mg/l respectively, and that is at different temperatures (303, 313, 323, 333 K). The Fenton degradation process of MB is better described by the pseudo-first-order model, values correlation coefficients R^2 for pseudo-first-order is closer to 1, and the k_1 rate constant increases quite slightly with temperature. The values of the activation energy have moderate values and it was 16.89 kJ/mol for concentration 40 mg/l of MB and 18.02 kJ/mol for concentration 80 mg/l the values obtained (ΔG^*, ΔS^*, and ΔH^*) indicate that the process is endothermic and spontaneous. The values of enthalpy and entropy were 14.25 kJ/mol, -233.2 J/K.mol respectively for concentration 40 mg/l of MB and 15.38 kJ/mol, -219.8 J/K.mol respectively for concentration 80 mg/l. While the ΔG^* values were changing from -53.38 kJ/mol at 303 K to -60.07 kJ/mol at 333 K for concentration 40 mg/l of MB, and -51.24 kJ/mol at 303 k to -57.84 kJ/mol at 333 K for concentration 80 mg/l of MB.

Declarations

Author contribution statement

Ibrahim Raheb: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Mohammad Sameh Manlla: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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