Research Article

Fenton-Like Oxidation of Malachite Green Solutions: Kinetic and Thermodynamic Study

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Oxidation by Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) reactions is proven to be an economically feasible process for destruction of a variety of hazardous pollutants in wastewater. In this study, the degradation and mineralization of malachite green dye are reported using Fenton-like reaction. The effects of different parameters like pH of the solution, the initial concentrations of Fe^{3+} , H_2O_2 , and dye, temperature, and added electrolytes (Cl^- and SO_4^{2-}) on the oxidation of the dye were investigated. Optimized condition was determined. The efficiency of 95.5% degradation of MAG after 15 minutes of reaction at pH 3 was obtained. TOC removal indicates partial and insignificant mineralization of malachite green dye. The results of experiments showed that degradation of malachite green dye in Fenton-like oxidation process can be described with a pseudo-second-order kinetic model. The thermodynamic constants of the Fenton oxidation process were evaluated. The results implied that the oxidation process was feasible, spontaneous, and endothermic. The results will be useful for designing the treatment systems of various dye-containing wastewaters.

1. Introduction

Dyes in wastewater are of particular environmental concern since they not only give an undesirable color to the waters but also in some cases are harmful compounds and can originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase. Environmental research has paid special attention to dye compounds because of the extensive environmental contamination arising from dyeing operations. Various attempts have been made for the removal of dyes from water and wastewater. There are several methods applicable for the reclamation of dyeing wastewaters [1, 2]. Commonly applied treatment methods for color removal from dye-contaminated effluents consist of various processes involving biological, physical and chemical decolorization methods. The biological treatment is not a complete solution to the problem due to biological resistance of some dyes [3]. The traditional treatment techniques were applied in wastewaters, such as ozonation [4], membrane [5], oxidation [6, 7], photochemical [8], and adsorption [9–13]. Various Fenton processes were used for oxidation of dyes. Homogenous Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) is one of the most important processes to

generate hydroxyl radicals $\cdot\text{OH}$ [14–16]. These processes are involved in the generation of highly reactive radicals (especially hydroxyl radicals) in enough quantity to affect water purification, and their use is justified by the low organic content of the wastewaters to be treated. They have low reaction temperatures and thus require the presence of very active oxidation agents. In particular, the oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants [17–21].

The Fenton process completely destroys contaminants and breaks them down into harmless compounds, such as carbon dioxide, water, and inorganic salts. However, its applications are limited due to the generation of excessive amounts of ferric hydroxide sludge that requires additional separation process and disposal [22].

Malachite green is classified in the dyestuff industry as a triarylmethane dye. Malachite green (MAG) is usually used as a dye for materials such as silk, leather, and paper. Removal of malachite green by different methods such as oxidation [23], catalytic oxidation [24], electrooxidation [25], and adsorption by agro-industry waste [26], peel [27], and solid agricultural waste [28, 29] was studied.

Fenton's reagent is a mixture of ferrous ion and hydrogen peroxide generating hydroxyl radical ($\cdot\text{OH}$) in situ according to the following equation:

Fe(III) can catalyze the decomposition of H_2O_2 . The reaction of H_2O_2 with Fe^{3+} (the so-called Fenton's-like reagent) goes through the formation of hydroperoxyl radical $\text{HO}_2\cdot$ [30]:

The specific objectives of this study are the investigation of removal efficiencies of malachite green (MAG) by Fenton-like process. Important variables such as oxidation time, effect of pH, dosages of H_2O_2 , and ferrous ions were examined. The kinetics and thermodynamic of process also were determined.

2. Experimental

2.1. Material and Methods. The basic dye, MAG, has molecular formula $\text{C}_{23}\text{H}_{25}\text{ClN}_2$ and molar mass 364.911 g/mol with λ_{max} 620 nm and was used as received without further purification to prepare simulated wastewater. 5.0×10^{-3} stock solution of MAG was prepared, and working solutions are prepared by the dilution. Experimental solutions of the desired concentration were obtained by successive dilutions. The chemical structure of malachite green (4-[(4-dimethylaminophenyl)phenyl-methyl]-N,N-dimethylaniline) is shown in Figure 1.

All the reagents used in the experiments were in analytical grade (Merck) and were used without further purification. All the experiments were conducted at room temperature. The dye oxidation was achieved by Fenton-like reagent which was composed of a mixture of $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ and H_2O_2 (30%). The necessary quantities of Fe^{3+} and H_2O_2 were added simultaneously in the dye solution. All experiments were conducted in a 500 mL thermostated batch glass reactor equipped with the magnetic stirrer. The kinetics of oxidation was followed by taking samples at regular time interval.

The residual concentration of the MAG in the solution at different times of sampling was determined. The residual concentration of the dye was deducted from the calibration curves which were produced at wavelength corresponding to the maximum of absorbance (620 nm) on an UV-visible spectrophotometer apparatus (Shimadzu 160 A). The cells used were in quartz 1 cm thick. The discoloration efficiency

FIGURE 1: Chemical structure of malachite green (MAG).

of the dye (X) with respect to its initial concentration is calculated as

$$\%X = ([\text{MAG}]_0 - [\text{MAG}] / [\text{MAG}]_0) \times 100, \quad (8)$$

where $[\text{MAG}]_0$ and $[\text{MAG}]$ are the initial and appropriate concentrations of dye at any reaction time t , respectively.

3. Results and Discussion

3.1. Effect of pH on Decolorization. pH has a major effect on the efficiency of MAG treatment. The oxidation was done for 120 min under controlled pH condition with constant dose of Fe^{3+} (1.0×10^{-4} M) and H_2O_2 (5×10^{-2} M). The effect of pH on the removal of malachite green using 50 mg L^{-1} of dye was studied. The oxidation of MAG as a function of pH is shown in Figure 2. It is evident that change in the pH of the solution to Fenton-like value of 3 leads to increases in the extent of MAG oxidation. It is apparent from that extent of decolorization decreases with increase in pH, and at pH 3.0 almost >95% color removal was observed. Therefore, the results demonstrate that the pH value for the most effective oxidation of MAG is approximately 3. The decrease in oxidation rate at $\text{pH} > 3$ could be explained by the formation of $\text{Fe}(\text{OH})_3$, which has lower catalytic activity in the decomposition of H_2O_2 [30]. The low activity detected for high pH has been reported, and the results closely agreed with those in the literature [19, 30–32].

3.2. Effect of Fe^{3+} Ferrous Dosage. The concentration of Fe^{3+} is one of the critical parameters in Fenton processes. In the present study, the influence of different iron concentrations ($\text{Fe}^{3+} = 1.0 \times 10^{-6}$ – 1.0×10^{-3} M) expressed as MAG removal is illustrated in Figure 3. The concentration of hydrogen peroxide is fixed as 0.05 M, and MAG concentration is 3.0×10^{-5} M. It can be seen from results that MAG degradation increased with increasing Fe^{3+} concentrations. This is due to the fact that Fe^{3+} plays a very important role in the decompositions of H_2O_2 to generate the $\cdot\text{OH}$ in the Fenton process. The lower degradation capacity of Fe^{3+} at small concentration is probably due to the lowest $\cdot\text{OH}$ radicals producing a variable for oxidation [16, 19], for higher concentration of Fe^{3+} oxidation of dye will decrease. This can be explained by

FIGURE 2: Effect of pH on the discoloration efficiency for Fenton-like oxidation process, ($[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2} \text{ M}$, $[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$).

FIGURE 3: Effect of Fe^{3+} concentration on the discoloration efficiency for Fenton-like oxidation process, ($[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2}$, $[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$).

the fact that, when the concentrations of Fe^{3+} are high, can react with the $\text{HO}_2^\bullet$ and finally reduce consumed the very reactive $^\bullet\text{OH}$ radical according to (3).

3.3. Effect of H_2O_2 Concentration. H_2O_2 plays the role of an oxidizing agent in this process. The selection of an optimal H_2O_2 concentration for the decolorization of MAG is important from practical point of view due to the cost of H_2O_2 [33].

Oxidation of dyes by Fenton and Fenton-like process is carried out by $^\bullet\text{OH}$ radicals that are directly produced from the reaction between H_2O_2 , Fe^{2+} , and Fe^{3+} . To determine the concentration of H_2O_2 giving the maximum MAG discoloration efficiency, experiments were conducted, and results obtained are represented in Figure 4. The discoloration efficiency according to time for different concentrations of

FIGURE 4: Effect of H_2O_2 concentration on the discoloration efficiency for Fenton-like oxidation process ($[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$, $[\text{Fe}^{3+}] = 1.0 \times 10^{-4}$).

H_2O_2 shows that the dye degradation yield increases with increasing concentration of H_2O_2 . For the oxidation process, the addition of H_2O_2 from 5.0×10^{-3} – $1.0 \times 10^{-1} \text{ M}$ increases the decolorization from 68 to 95% at 10 min. The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H_2O_2 [17]. However at higher H_2O_2 concentration, efficiency of dye removal showed no significant efficiency, which is due to recombination of hydroxyl radicals, and scavenging the OH radicals will occur, which can be expressed by (2), (5), and (6).

3.4. Effect of Relation $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$. The main process variables affecting the rate of a Fenton-like reaction are the molar concentrations of the oxidant (H_2O_2) and catalyst (Fe^{3+}), particularly the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio. Therefore, color removal as a function of the initial molar ratio of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was investigated. The different ratios of $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ 1–400 are reported from the literature. The experimental results showed that the optimum $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio for the removal of MAG was 1:50 [19, 34]. The reaction of Fe^{3+} with H_2O_2 leads to the formation of Fe^{2+} ions, which can further react with H_2O_2 to produce OH radical. Therefore, a low Fe^{3+} concentration decreases MAG degradation. MAG removal actually ceased when the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio increased from 1:50 to 1:500 for 1 mM Fe^{3+} , indicating that H_2O_2 was overdosed when its concentration rose tenfold. In the presence of 50 mM of H_2O_2 , the ionic liquid is probably eliminated solely by the reaction with $^\bullet\text{OH}$, but at 500 mM; as it is expected, most of the H_2O_2 dosage applied was consumed in the first stage of the fast reaction. The oxidation of ionic liquids was done not only by reaction with $^\bullet\text{OH}$ radicals but also by other radical species generated in vigorous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reactions such as FeO^{3+} [35] and $\text{Fe}^{3+}\text{HO}_2^{2+}$ [30] which then decrease.

3.5. Effect of Dye Concentration. The efficiency of the Fenton-like process as a function of initial concentration of dye was

evaluated. Figure 5 shows the changes of MAG concentration with the reaction time. The results indicated that decolorization efficiency increased when the initial dye concentration increased. Concentration plays a very important role in reactions according to the collision theory of chemical reactions. Two reactants were in a closed container. All the molecules contained within are colliding constantly. By increasing the concentration of one or more reactants, the frequency of collisions between reactant molecules is increased, and the frequency of effective collisions that causes a reaction to occur will also be high. The lifetime of hydroxyl radicals is very short (only a few nanoseconds), and they can only react where they are formed; therefore, as increasing the quantity of dye molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency [36].

3.6. Effect of Temperature. The influence of reaction temperature on the decolorization efficiency of MAG was investigated by varying temperature from 20°C to 70°C. Temperature is critical to the reaction rate, product yield, and distribution. The result is illustrated in Figure 6. It can be seen that raising the temperature has a positive impact on the decolorization of MAG. The decolorization efficiency within 10 min reaction increased from 78% to 95% as the different temperatures. This is due to the fact that higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as $\cdot\text{OH}$ radical or high-valence iron species [34]. In addition, a higher temperature can provide more energy for the reactant molecules to overcome reaction activation energy [37]. Although the decolorization efficiency for $T = 30^\circ\text{C}$ is lower than those obtained at $T = 40^\circ\text{C}$, the values of dyes removal achieved at 30°C might be considered satisfactory. At higher temperature, the efficiency of MAG oxidation decreases. This phenomenon may be due to the decomposition of H_2O_2 at the relatively high temperatures (9). This is consistent with results found in the literature [38]:

3.7. Mineralization Study. The complete mineralization of 1 mol MAG dye molecule implies the formation of the equivalent amount (23 moles) of CO_2 at the end of the treatment. However, the depletion in TOC (shown in Figure 7) clearly indicates that the reaction does not go to completion. Extent of mineralization of the dye by Fenton-like process can be evaluated by measuring Total Organic Carbon (TOC). To determine the change in the TOC of reaction medium, initial TOC (pure dye solution) and the TOC of a sample at different intervals during the reaction were measured. TOC reduction was determined as follows:

$$\text{TOC}_{\text{removal}} = \frac{1 - \text{TOC}_t}{\text{TOC}_0} \times 100, \quad (10)$$

where TOC_t and TOC_0 (mg L^{-1}) are values at time (t) and at time (0), respectively. 70% TOC reduction is achieved for MAG dye in 30 min. In fact, after 30 min of reaction,

FIGURE 5: Effect of MAG concentration on the discoloration efficiency for Fenton-like oxidation process.

FIGURE 6: Effect of temperature on the discoloration efficiency for Fenton-like oxidation process.

about 70% of the initial organic carbon had been transformed into CO_2 , which implied the existence of other organic compounds in the solution and the partial mineralization of dyes [39, 40].

3.8. Effect of Cl^- and SO_4^{2-} on Fenton Effectiveness. Cl^- and SO_4^{2-} are common coexisting anions with dyes in wastewater; therefore, the effect of Cl^- and SO_4^{2-} ions on MAG removal by Fenton-like process was investigated. It was found that the presence of Cl^- at the concentration range of $0\text{--}0.1\text{ mol L}^{-1}$ did not have a significant effect on removing MAG. The effect of SO_4^{2-} on the removal of MAG was significant at the concentration range of $0\text{--}0.1\text{ mol L}^{-1}$. The removal of MAG decreased at a concentration of 0.02 mol L^{-1}

FIGURE 7: TOC removal for MAG dye by Fenton-like oxidation process.

of SO_4^{2-} . The removal of MAG decreased to 45% for concentration of 0.02 mol L^{-1} of SO_4^{2-} .

3.9. Kinetic of Fenton Reaction. The general elementary rate law for reaction of a target organic compound (MAG) can be written as follows:

$$\frac{-dC_{\text{MAG}}}{dt} = k_{\text{HO}}k_{\text{OH}}k_{\text{RH}} + \sum K_{\text{oxi}}C_{\text{oxi}}C_{\text{RH}}, \quad (11)$$

where oxi represents oxidants other than $\cdot\text{OH}$ that may be present, such as ferryl, hydroxyl radical which is usually regarded as the sole or most important reactive species. Then

$$\frac{-dC_{\text{MAG}}}{dt} = k_{\text{HO}}k_{\text{OH}}k_{\text{MAG}}. \quad (12)$$

And, by integration, the rate law of first-order reaction can be written as follows:

$$\ln C_{\text{MAG}} = \ln C_{(\text{MAG})0} - k_{\text{app}}t, \quad (13)$$

where C_{MAG} and $C_{(\text{MAG})0}$ are initial concentration of MAG and concentration of MAG at any time. A plot of $\ln C_{\text{MAG}}$ versus time generated a straight line with a negative slope. The slope of this line corresponds to the apparent rate constant value for the degradation of the organic target compound. In our case, we follow the rate of decolourization of the MAG dye. Consequently, (13) was converted to

$$\frac{\ln C_{\text{MAG}}}{\ln C_{(\text{MAG})0}} = -k_{\text{app}}t. \quad (14)$$

Figure 8 shows the plot of first-order Fenton reaction. Rate law of the second-order reaction can be written as follows:

$$\frac{1}{[C_{\text{MAG}}]} - \frac{1}{[C_{(\text{MAG})0}]} = kt. \quad (15)$$

The plot of $1/[C]$ against k shows the rate constant of second-order Fenton reaction (Figure 9). The results from R^2 of Figures 8 and 9 show that the kinetic of Fenton-like reaction for degradation of MAG was second-order reaction [41].

FIGURE 8: Pseudo-first-order model for Fenton-like oxidation of MAG.

FIGURE 9: Pseudo-second-order model for Fenton-like oxidation of MAG.

3.10. Thermodynamic of Fenton Reaction. Thermodynamic parameters including Gibbs free energy ΔG° , standard enthalpy ΔH° , and standard entropy ΔS° are the parameters to better understand the temperature effect on degradation of dye which was studied. Gibbs free energy ΔG° by using equilibrium constant K_C is calculated:

$$\Delta G^\circ = -RT \ln K_C. \quad (16)$$

K_C value is calculated from the following formula:

$$K_C = \frac{C_{\text{Ae}}}{C_{\text{Se}}}. \quad (17)$$

C_{Ae} is amount of degradation dye at equilibrium and C_{Se} equilibrium concentration of dye at the solution.

Standard enthalpy ΔH° and standard entropy ΔS° are as van't Hoff equation:

$$\ln K_C = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (18)$$

In this equation R is the gas constant equal to the public ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The amounts of degradation dye at equilibrium at different temperatures $25\text{--}55^\circ\text{C}$ have been examined to obtain thermodynamic parameters for Fenton-like reaction of MAG. ΔH° and ΔS° were calculated as the slope and intercept of van't Hoff plots of $\ln K_C$ versus

TABLE 1: Thermodynamic parameters for Fenton oxidation of MAG ([MAG] = 3.0×10^{-5} M, $[\text{Fe}^{3+}] = 1.0 \times 10^{-4}$ M, $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2}$ M).

ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (J mol ⁻¹)	ΔG° (KJ mol ⁻¹)	K_C	T (K)	
43.2823	9.610	-3.255	3.80	293	Fenton like oxidation
		-3.408	3.870	303	
		-4.213	4.80	323	
		-5.680	7.33	333	

$1/T$. The results of thermodynamic parameters are given in Table 1. As observed in Table 1, negative value of ΔG° at different temperatures shows the oxidation process to be spontaneous. The ΔH° positive value indicates that the uptake is endothermic [42].

4. Conclusion

The results of Fenton-like oxidation process of MAG showed the following.

- (1) The optimal parameters for Fenton-like process are

$$[\text{MAG}] = 3 \times 10^{-5} \text{ M}, \quad [\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M},$$

$$[\text{H}_2\text{O}_2] = 5 \times 10^{-2} \text{ M}, \quad \text{pH} = 3. \quad (19)$$

- (2) Fenton-like process not only completes decolorization of MAG dye (95%) but also mineralizes it (70%).
- (3) The oxidation process of MAG follows pseudo-second-order kinetic model.
- (4) The negative values of ΔG° and positive value of ΔH° obtained indicated that the MAG dye oxidation by Fenton reaction processes is spontaneous and endothermic.
- (5) The overall equation of MAG degradation and production of carbon dioxide and nitrate ion is as follows:

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