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Degradation of methyl violet by Fenton's reagent: kinetic modeling and effects of parameters

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ABSTRACT

The degradation of methyl violet by Fenton treatment was modeled. A mathematical model was tested by fitting experimental data and was compared with first-order and second-order models. The results indicated that this mathematical model could better describe the kinetics of methyl violet degradation by Fenton in the experimental research scope. In addition, the effects of initial molar ratios of the Fenton reagents ($[Fe(II)]_0$:$[H_2O_2]_0$), pH, and some anions (e.g. Cl^-, SO_4^{2-}, and CO_3^{2-}) on the Fenton degradation of methyl violet were discussed. The results implicated that the greatest decolorization rate of methyl violet could be obtained when the initial molar ratios of $[Fe(II)]_0$ and $[H_2O_2]_0$ was 1:3 and the optimum pH was 3.0. The degradation of methyl violet was inhibited in the presence of anions, which can be attributed to the fact that they were scavengers of $^{\bullet}OH$. And the negative impact of these anions on the degradation rate followed the order $CO_3^{2-} > Cl^- > SO_4^{2-}$.

Keywords: Model; Hydroxyl radicals; Methyl violet; Removal

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1. Introduction

Nowadays, dyes are widely used in many industrial fields, such as textiles, plastics, paper, coatings, and rubber [1], therefore existing widely in the effluent wastewater. Some of the dyes are stable to light and oxidant and are resistant to biodegradation for their complex structure [2,3]. Thus, the treatment of dye wastewater has received global concern. Advanced oxidation processes (AOPs) which are based on the generation of the highly reactive hydroxyl radicals ($^{\bullet}OH$) have been proposed as an alternative method for treating refractory wastewaters [4,5]. $^{\bullet}OH$ is a nonselective oxidant which can react with most of the organic contaminants at near diffusion-limited rates [6]. The Fenton system, comprised of aqueous mixtures of ferrous iron (Fe(II)) and hydrogen peroxide (H_2O_2), represents one of the most attractive AOPs [7]. Fenton's regents are normally innocuous to the environment with no by-products dangerous to human and environmental health, and Fenton's processes are often related to the simple equipment, mild operating conditions (atmospheric pressure and room temperature), easy operation and maintenance [8–10].

More recently, a number of studies have presented chemical kinetic models to accurately predict the species behavior, process performance, and efficiency as well as to optimize operating conditions, and the simulations can help to confirm the mechanism and rates governing the Fenton reaction [11–14]. However,

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no model describes well the overall rate of the degradation of organics over a wide range of experimental conditions (pH, Fe(II), and H_2O_2 concentrations) for the complexity of the degradation pathway of organics and the considerable uncertainties on the various equilibrium and kinetic constants of individual reactions [15].

Triphenylmethane dyes are widespread used as colorants in industry and as antimicrobial agents in medical and related biological sciences [16,17]. Methyl violet, a basic triphenylmethane-type dye, is usually used for textiles and gives deep violet colors in paint and ink. This kind of dye in wastewater is toxic and they present a health hazard to humans [16], and great concern has arisen about the degradation of methyl violet in wastewater. The number and variety of studies for the removal of methyl violet were undertaken including adsorption [18,19], photocatalysis by TiO_2 [20] and $K_3PW_{12}O_{40}$ [21], and biodegradation [22]. Nevertheless, few works have applied the basic Fenton's models to methyl violet oxidation for a wide range of initial reagent concentrations. In this paper, the mathematical model proposed by Chan and Chu [14] was applied due to the fact that the reaction mechanism and degradation trends of methyl violet showed in the pre-experiments were consistent with their results. In addition, the most common and the simplest first-/second-order model [23–25] was also used.

Some anions affected the degradation of organics in wastewater. For example, halide ions (X^-) are significant $\cdot OH$ scavengers, for their forming of reactive halogen species ($X^\cdot$, $X_2^{\cdot -}$) [26,27]. El-Fass et al. [28] have reported that the "common ion effect" due to the presence of inorganic anions led to decreased π-electron (electrostatic) repulsion between two ionic dyes hence increasing the degree of aggregation.

The primary objective of this work was to test a mathematical model by fitting the experimental data using this model and the first-/second-order model over a wide range of experimental conditions. Initial molar ratios of the Fenton reagents ($[Fe(II)]_0$:$[H_2O_2]_0$) were varied from 1:0.33 to 1:3 at pH 4.0. Methyl violet was chosen as the target organic compound. The effects of initial molar ratios of the Fenton reagents ($[Fe(II)]_0$:$[H_2O_2]_0$), pH, and some anions (e.g. Cl^-, SO_4^{2-}, and CO_3^{2-}) on the Fenton degradation of methyl violet were discussed in this paper.

2. Materials and methods

2.1. Materials

All chemicals were reagent grade and used as received. Methyl violet ($C_{24}H_{28}N_3Cl$, MW: 393.96 g/mol, CAS: 800-87-3) was purchased from Shanghai Chemical Reagent Co. Ltd, and the stock solution was prepared as 40 mg/L in distilled water. $FeSO_4 \cdot 7H_2O$ (CAS: 7782-63-0) was purchased from Tianjin Kemio Chemical Reagent Co. Ltd and was dissolved in an aqueous solution of 0.1 mol/L H_2SO_4 as Fe(II) stock solution. H_2O_2 (30%, CAS: 7722-84-1) was obtained from Tianjin Damao Chemical Co. Ltd. All stock solutions were stored in a refrigerator at 4℃ in the dark and used within one week. Milli-Q water (resistivity ≥ 18 MΩ cm) was used in all experiments.

2.2. Procedures and analyses

Experiments were carried out in a glass cylindrical reactor of *ca*. 7 cm diameter and *ca*. 9 cm height, and the reaction volume was 100 mL. Reaction mixtures were prepared by taking an appropriate amount of methyl violet and Fe(II) stock solutions. The reaction was initiated when the known amount of H_2O_2 was added to the mixtures. The initial pH value of reaction system was adjusted by HCl or NaOH solutions (1 mol/L) before adding H_2O_2 solution.

In Fenton experiments, samples were taken out at the reaction time of 0, 1, 3, 5, 10, 15, 20, and 25 min. Because methyl violet shows the maximum absorption peak at 575 nm, a UV–Vis spectrophotometer (WFJ2100, Unico Co., Shanghai) was used to determine the absorbance of methyl violet at a wavelength of 575 nm. The reaction solutions were always magnetically stirred during 30 min. In all the above experiments, the temperature of the solution was maintained at 25.0 ± 1℃. All experiments were run in duplicate. Because the reaction in the sample taken from the reactor continued, the sampling and the measurement of the absorbance should be completed within 10 s.

The reaction rate and efficiency of methyl violet in Fenton system is characterized by degradation rate (%).

$$\text{degradation rate} = \left(1 - \frac{A}{A_0}\right) \times 100\%$$

where A and A_0 are the absorbance of methyl violet in reaction solution at time t (min) and zero, respectively.

2.3. Kinetic modeling

Modeling results were generated using a mathematical equation (Eq. (1)) proposed by Chan and Chu [14], and straight lines with intercept ρ and slope σ were obtained by plotting $t/(1 - C/C_0)$ vs. t (Eq. (2)).

$$\frac{C}{C_0} = 1 - \frac{t}{\rho + \sigma t} \tag{1}$$

$$\frac{t}{1 - C/C_0} = \sigma t + \rho \tag{2}$$

where C is the concentration of the probe (i.e. methyl violet) remaining in the system after a reaction time of t (min), and C_0 is the initial concentration of the probe. The ρ (min) and σ (dimensionless) are two characteristic constants relating to the initial degradation rate and the final oxidation capacity of Fenton reaction. $1/\rho$ represents the initial methyl violet removal rate in the process and $1/\sigma$ represents the maximum oxidation capacity of Fenton's reagent.

The first-order model (Eq. (3)) and the second-order model (Eq. (4)) can be expressed as:

$$\ln\left(\frac{C_0}{C}\right) = k_1 t \tag{3}$$

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \tag{4}$$

where C and C_0 are the same as above, k_1 is the first-order rate constant and k_2 is the second-order rate constant.

3. Results and discussion

3.1. Kinetic modeling on experimental data

In an effort to verify the applicability of the models, experiments were performed at different concentrations of $[\mathrm{Fe(II)}]_0$ and $[H_2O_2]_0$ in solutions containing 10 mg/L methyl violet at pH 4.0. The concentration of Fe(II) was 0.01, 0.05, 0.1, 0.15, and 0.2 mmol/L, respectively. The experimental data were fitted using the mathematical model, the first-order model, and the second-order model, respectively. Fig. 1 shows the results with the 1:3 initial mole ratio of $[\mathrm{Fe(II)}]_0$ and $[H_2O_2]_0$ fittings in linear forms of the mathematical model of $t/(1 - C/C_0)$ vs. t (Eqs. (1)–(2)) and the first-/second-order models (Eqs. (3)–(4)). From Fig. 1, the correlation coefficients (R^2) ranging from 0.99 to 1.00 for fitting by the mathematical model were much higher than those by the two simple order models. And similar fitting tendency were observed in fitting other experimental data in this work. The conformity of the fittings demonstrated that the mathematical model could better fit the experimental data than the other two models; therefore, this mathematical model could better describe the kinetics of methyl violet degradation by Fenton reaction in this experimental research scope. The good fitting could be related to the facts that the reaction mechanism of methyl violet removal is $^{\bullet}$OH attack and the degradation trends include a rapid decay at the commencement of the reactions and a much slower decay rate followed, which are the two keys of the mathematical model.

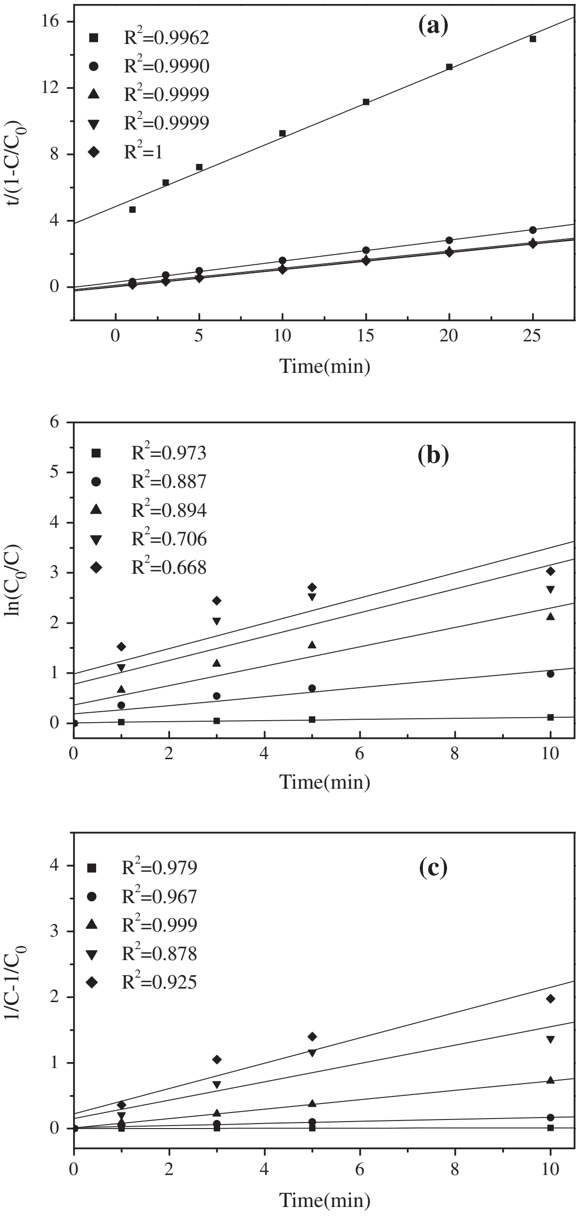

Fig. 1. The linear relationship of the methyl violet degradation by Fenton reaction using the mathematical model (a), the first-order model (b), and the second-order model (c) ($[\mathrm{Fe(II)}]_0 = 0.01$ mmol/L (■), 0.05 mmol/L (●), 0.1 mmol/L (▲), 0.15 mmol/L (▼), 0.2 mmol/L (◆); pH 4.0; $[\mathrm{Fe(II)}]_0$:$[H_2O_2]_0 = 1:3$; [methyl violet]$_0$ = 10 mg/L; $\lambda_{\max} = 575$ nm).

3.2. Effect of initial molar ratios of the Fenton reagents ($[Fe(II)]_0$:$[H_2O_2]_0$)

Fig. 2 shows the effects of different initial molar ratios of $[Fe(II)]_0$ and $[H_2O_2]_0$ on the degradation of methyl violet by Fenton's reagents, which were varied from 1:0.33 to 1:3 for fixed initial concentrations of methyl violet of 10 mg/L and pH 4.0. The results indicated that the greatest decolorization rate was obtained in the system when the initial molar ratios of $[Fe(II)]_0$ and $[H_2O_2]_0$ was 1:3, regardless of the initial concentration of Fe(II). And it can be seen from Fig. 2 that all the curves showed a rapid degradation in the first few minutes and then reached a plateau. Hence, the decolorization rate of methyl violet was greatly influenced by the initial degradation rate. In addition, the increasing initial Fe(II) concentration from 0.01 to 0.2 mmol/L promoted ·OH formation and enhanced the removal of methyl violet.

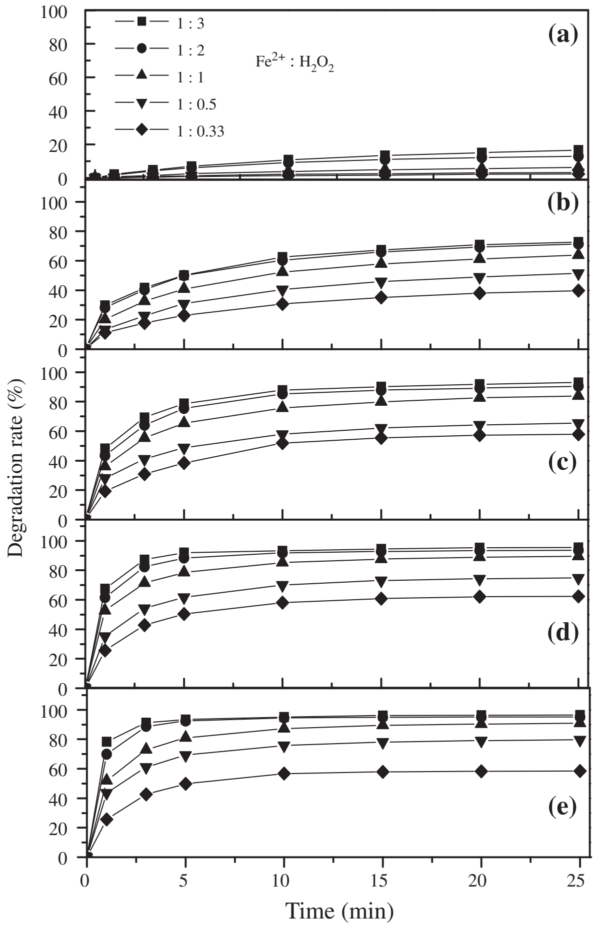

Fig. 2. Degradation rates of methyl violet with Fe(II) dosages of 0.01 (a), 0.05 (b), 0.10 (c), 0.15 (d), and 0.20 mmol/L (e) at different ratios of $[Fe(II)]_0$ and $[H_2O_2]_0$. (pH 4.0; $[\text{methyl violet}]_0 = 10$ mg/L; $\lambda_{max} = 575$ nm).

Table 1 presents the fitting parameters of the model for Fenton degradation of methyl violet. $1/\rho$ and $1/\sigma$ at different initial Fe(II) concentration of 0.01, 0.1, and 0.2 mmol/L and at constant ratio of 1:3 ($[Fe(II)]_0$:$[H_2O_2]_0$) corresponded to the values of 0.02, 0.87, and 4.35, and 0.24, 0.97, and 0.97, respectively. Simulation results showed that $1/\rho$ and $1/\sigma$ increased with increasing Fe(II) dosage at fixed molar ratios of the Fenton reagents. As expected, increasing both concentrations of $[Fe(II)]_0$ and $[H_2O_2]_0$ resulted in higher initial degradation rate and higher oxidation capacity. It can be seen that the mathematical model was better in explaining the conclusions from experiments.

3.3. Effect of initial pH value of solution

The solution pH plays a very important part in the degradation of organic compounds in Fenton system. Fig. 3 shows the effect of initial pH in a range of 2–5.5 on the degradation of methyl violet for fixed initial concentrations of 10 mg/L methyl violet, 0.2 mmol/L H_2O_2, and 0.1 mmol/L Fe(II). It can be seen clearly from Fig. 3(b), the degradation rate quickly increased when the initial pH increased from 2.0 to 3.0, subsequently it decreased when the initial pH increased from 3.0 to 4.0 and then dropped off sharply at pH values between 5.0 and 5.5. Below pH 3, Fenton reactions (5) and (6) slowed down because of the forming of iron complexes as $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_5OH]^{2+}$ which react more slowly with H_2O_2 [29]. In addition, this behavior was also attributed to the enhancement of $^{\bullet}OH$ scavenging by H^+ (Eq. (7)) at pH 2.0 [30,31]. When the initial pH was raised above 5.0, the coagulation of Fe(III) complex molecules (Eq. (8)) inhibited the catalytic reaction of redox cycling of Fe(II) [31]. Moreover, it can be seen in Table 2, the mathematical model can well describe the variation of the initial degradation rate and maximum oxidation capacity at various initial pH by $1/\rho$ and $1/\sigma$. At pH 3.0, the degradation efficiency of methyl violet was 96.5%, corresponding to the highest $1/\rho$ of 0.917 and $1/\sigma$ of 1.01.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{5}$$

$$Fe^{3+} + H_2O_2 \rightarrow O_2^{\cdot-} + Fe^{2+} + 2H^+ \tag{6}$$

$$^{\cdot}OH + H^+ \rightarrow H_2O \tag{7}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{8}$$

Table 1
The parameters of the model for Fenton degradation of methyl violet at different dosage of Fe(II) and H_2O_2

Related coefficients	$0.01\,mmol/L[Fe^{2+}]_0$					$0.1\,mmol/L[Fe^{2+}]_0$					$0.2\,mmol/L[Fe^{2+}]_0$				
	$[H_2O_2]_0$ (mmol/L)					$[H_2O_2]_0$ (mmol/L)					$[H_2O_2]_0$ (mmol/L)				
	0.0033	0.005	0.01	0.02	0.03	0.033	0.05	0.1	0.2	0.3	0.067	0.1	0.2	0.4	0.6
ρ	513.71	303.8	154.27	52.8	48.68	4.46	2.8	1.95	1.35	1.15	1.99	1.16	0.86	0.28	0.23
σ	20.93	17.94	9.92	5.6	4.14	1.53	1.42	1.12	1.05	1.03	1.61	1.21	1.06	1.04	1.03
$1/\rho$	0.0019	0.0033	0.0065	0.019	0.02	0.22	0.36	0.51	0.74	0.87	0.5	0.86	1.16	3.57	4.35
$1/\sigma$	0.048	0.056	0.1	0.18	0.24	0.65	0.7	0.89	0.95	0.97	0.62	0.83	0.94	0.96	0.97
R^2	0.9956	0.9929	0.9949	0.9995	0.9924	0.9978	0.9993	0.9998	0.9999	0.9999	0.9995	1	1	0.9999	1

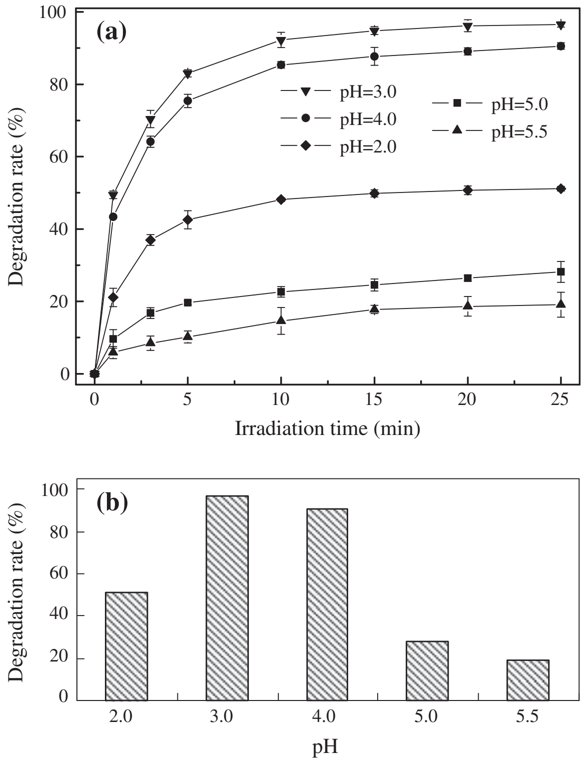

Fig. 3. The effect of initial pH on Fenton degradation of methyl violet. ([methyl violet]$_0$ = 10 mg/L; $[H_2O_2]_0 = 0.2$ mmol/L; $[Fe(II)]_0 = 0.1$ mmol/L; $\lambda_{max} = 575$ nm).

3.4. Effect of different anions and ionic strength

Inorganic anions (e.g. Cl^-, CO_3^{2-}, and SO_4^{2-}) occur naturally in wastewater or may be added to facilitate the dyeing process [32]. Fig. 4 shows the effect of different anions including chloride, carbonate, and sulfate ions on Fenton degradation of methyl violet for fixed initial concentrations of 10 mg/L methyl violet, 0.4 mmol/L H_2O_2, and 0.2 mmol/L Fe(II). As can be seen from Fig. 4, the degradation of methyl violet was inhibited differently in the presence of different anions. It was attributed to the fact that these anions were scavengers of $^{\cdot}OH$ (Eqs. (9)–(11)). Production of radicals such as $OHCl^{\cdot-}$, $CO_3^{\cdot-}$, and $SO_4^{\cdot-}$ which may be less reactive for methyl violet removal than $^{\cdot}OH$ lowered the amount of $^{\cdot}OH$ during the course of the reaction hence decreasing the decolorization rate. The inhibited impact of these anions on the degradation rate followed the order $CO_3^{2-} > Cl^- > SO_4^{2-}$ (see Fig. 4). Grebel et al. [26] came to a similar conclusion when examining the effects of Cl^-, Br^-, and carbonates by UV/H_2O_2 treatment, that the impact of these constituents on contaminant destruction rate suppression at circumneutral pH followed the order carbonates > Cl^-.

Table 2
The fitting parameters of the model for Fenton degradation of methyl violet at different pH values

Related coefficients	pH				
	5.5	5	4	3	2
ρ	20.59	8.89	1.35	1.09	2.6
σ	4.42	3.31	1.05	0.99	1.84
$1/\rho$	0.049	0.112	0.74	0.917	0.385
$1/\sigma$	0.226	0.302	0.952	1.01	0.543
R^2	0.9933	0.9977	0.9999	0.9999	0.9999

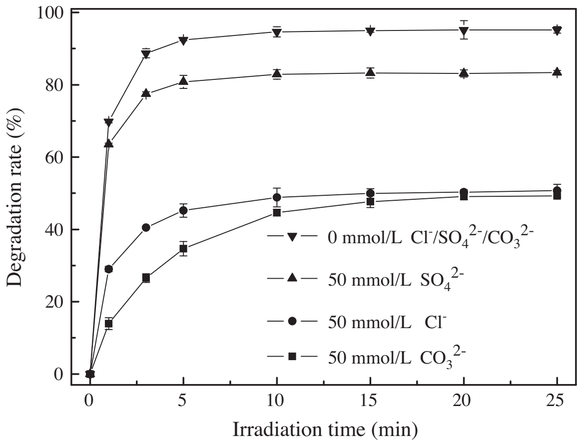

Fig. 4. The effect of different anions on Fenton degradation of methyl violet. ([methyl violet]$_0$ = 10 mg/L; [H_2O_2]$_0$ = 0.4 mmol/L; [Fe(II)]$_0$ = 0.2 mmol/L; pH = 4.0; λ_{max} = 575 nm).

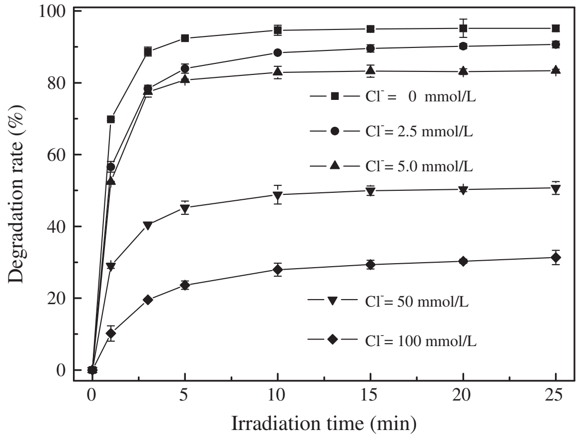

Fig. 5. The effect of chloride ions in different ionic strength on Fenton degradation of methyl violet. ([methyl violet]$_0$ = 10 mg/L; [H_2O_2]$_0$ = 0.4 mmol/L; [Fe(II)]$_0$ = 0.2 mmol/L; pH = 4.0; λ_{max} = 575 nm).

$$Cl^- + {}^{\cdot}OH \rightarrow OHCl^{\cdot -} \tag{9}$$

$$CO_3^{2-} + {}^{\cdot}OH \rightarrow CO_3^{\cdot -} + OH^- \tag{10}$$

$$SO_4^{2-} + {}^{\cdot}OH \rightarrow SO_4^{\cdot -} + OH^- \tag{11}$$

Fig. 5 shows the effect of chloride ions in different ionic strength on Fenton degradation of methyl violet for fixed initial concentrations 10 mg/L methyl violet, 0.4 mmol/L H_2O_2, and 0.2 mmol/L Fe(II). The degradation rate decreased slightly with an increase in initial Cl^- concentration from 0 to 5 mmol/L and then decreased sharply when the initial Cl^- concentration varied from 5 to 100 mmol/L. It was attributed to both the consuming of ·OH by Cl^- and the formation of chlorinated hydrocarbons (RCl) in Fenton processes in the presence of Cl^- [27]. Meanwhile, higher Cl^- concentration led to a decrease in the amount of ·OH and an increase in the generation of RCl. Therefore, the increasing Cl^- concentration promoted ·OH consumption and inhibited the degradation of methyl violet.

4. Conclusion

The experimental data were fitted using the mathematical model, the first-order model and the second-order model, respectively. The goodness of fittings of the mathematical model demonstrated that it could better describe the kinetics of Fenton reaction in this experimental research scope. Meanwhile, the experimental results indicated that the optimum initial molar ratios of [Fe(II)]$_0$ and [H_2O_2]$_0$ was 1:3 and the optimal reaction condition of pH was 3.0. The degradation of methyl violet was inhibited differently in the presence of CO_3^{2-}, Cl^-, or SO_4^{2-}, and it followed the order $CO_3^{2-} > Cl^- > SO_4^{2-}$. And the degradation rate decreased with an increase in initial Cl^- concentration in the presence of chloride ions in different concentration.

Acknowledgments

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