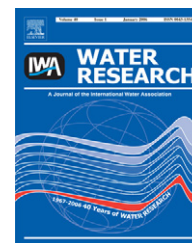


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Kinetic modeling of electro-Fenton reaction in aqueous solution

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ARTICLE INFO

Article history:

Received 2 June 2006

Received in revised form

2 December 2006

Accepted 5 December 2006

Available online 26 January 2007

Keywords:

E-Fenton

H₂O₂

Kinetic Model

Phenol

ABSTRACT

To well describe the electro-Fenton (E-Fenton) reaction in aqueous solution, a new kinetic model was established according to the generally accepted mechanism of E-Fenton reaction. The model has special consideration on the rates of hydrogen peroxide (H₂O₂) generation and consumption in the reaction solution. The model also embraces three key operating factors affecting the organic degradation in the E-Fenton reaction, including current density, dissolved oxygen concentration and initial ferrous ion concentration. This analytical model was then validated by the experiments of phenol degradation in aqueous solution. The experiments demonstrated that the H₂O₂ gradually built up with time and eventually approached its maximum value in the reaction solution. The experiments also showed that phenol was degraded at a slow rate at the early stage of the reaction, a faster rate during the middle stage, and a slow rate again at the final stage. It was confirmed in all experiments that the curves of phenol degradation (concentration vs. time) appeared to be an inverted “S” shape. The experimental data were fitted using both the normal first-order model and our new model, respectively. The goodness of fittings demonstrated that the new model could better fit the experimental data than the first-order model appreciably, which indicates that this analytical model can better describe the kinetics of the E-Fenton reaction mathematically and also chemically.

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1. Introduction

It has been well proven that a variety of refractory organics can be effectively degraded by the Fenton reaction without producing any toxic substances in water environment (Joseph, 1992; Oliveros et al., 1997; Lunar et al., 2000; Kawabe et al., 2004). Recent development of electro-Fenton (E-Fenton) reaction by generating H₂O₂ from dissolved oxygen in aqueous solution electrically provides fresh H₂O₂ in a continuous mode, which is more efficient and cost-effective than conventional chemical dosing methods (Brillas et al.,

1998, 2000, 2003; Brillas and Casado, 2002; Qiang et al., 2002; Gözmen et al., 2003).

It should be noted that like most chemical reactions, the H₂O₂ concentration in a conventional Fenton reaction is gradually reduced after a batch chemical dosing along with reaction time (Malato et al., 2001; Li et al., 2003). It has been reported that adding H₂O₂ in a single batch leaves much of it available to attack by hydroxyl radicals, whereas continuously feeding smaller quantities of the reagent to the system would allow the majority of radicals generated to target the organic contaminant (Duesterberg and Waite, 2006). In an E-Fenton

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doi:10.1016/j.watres.2006.12.006

reaction process, H_2O_2 is continuously generated on the cathode throughout the reaction and its accumulative concentration in aqueous solution depends on a competition between its generation rate and consumption rate (Oturán, 2000; Oturan et al., 2000; Boye et al., 2002). Particularly, at the beginning of the reaction such as the first 5 min, the H_2O_2 concentration rises from zero and the rate of organic degradation in aqueous solution is quite slow, although H_2O_2 concentration builds up at a maximum rate. When the reaction further proceeds, the rate of organic degradation is gradually increased with the increased H_2O_2 concentration and then eventually decreased again. Therefore, the most commonly used first-order reaction model has a difficulty to well describe the kinetics with a continuous H_2O_2 supply, particularly during the initial reaction period of the E-Fenton reaction (Malato et al., 2001; Gözmen et al., 2003). Wang and Lemley (2001) developed a second-order kinetic model to describe the E-Fenton reaction (anodic Fenton reaction) for degradation of 2,4-dichlorophenoxyacetic acid in aqueous solution as a more accurate kinetic model than the first-order model. Moreover, a recent work by Anota et al. (2006) compared the kinetics of aniline degradation by Fenton and E-Fenton reactions. It was found that the overall rate equation for aniline degradation by Fenton reaction followed a reaction order of 1.1 (almost a first-order reaction), but that by E-Fenton reaction demonstrated a reaction order of 0.46 (about a half-order reaction). Alternatively, other researchers still applied the first-order model to describe the E-Fenton reaction but either in terms of total organic carbon (Brillas et al., 1998, 2000) or by subdividing the overall reaction period into two or three phases with different values of kinetic constant representing different reaction rates (Chu et al., 2005). It should be indicated that a good kinetic model to well describe the E-Fenton reaction should consider some other key factors including current density, dissolved oxygen concentration and ferrous ion concentration jointly.

In this work, a new kinetic model for the E-Fenton reaction in aqueous solution was established according to the generally accepted mechanism of the E-Fenton reaction. Phenol was used as a model pollutant and a series of phenol degradation experiments in an E-Fenton reaction system were carried out. The new model was then validated by the experimental data and evaluated in this study.

2. Experimental section

2.1. Chemicals

Phenol, hydrogen peroxide (H_2O_2 , 30% w/v), sodium sulfate (Na_2SO_4), potassium titanium (IV) oxalate [$\text{K}_2\text{Ti}(\text{C}_2\text{O}_4)_3$] and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) chemicals were obtained from Aldrich, USA with analytical grade and used without further purification.

2.2. Experimental setup

All experiments were conducted in an E-Fenton reactor consisting of two electrochemical cells connected with a glass frit. A Pt flake (20×20 mm) from Superior Chemicals &

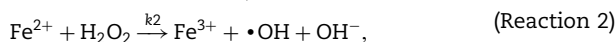
Instruments, China was used as the anode and a commercially available carbon rod ($\Phi = 5$ mm and $L = 80$ mm) from Shanghai, China was employed as the cathode to generate H_2O_2 . In addition, a saturated calomel electrode was applied as the reference electrode. Both the cathode and the reference electrode are placed in one compartment, while the anode is placed in another compartment. A potentiostat/galvanostat (ZF-9) from Zhenfang Electronic Ltd., China was employed to apply an electrical current between the anode and cathode. This E-Fenton reactor has an effective volume of 150 mL. Phenol solution was prepared in aqueous 0.01 M Na_2SO_4 electrolyte solution. The pH of reaction solution was adjusted to be 2.5 using 0.1 M H_2SO_4 before reaction. A mixture gas of oxygen and air was continuously bubbled through a sintered-glass diffuser to supply dissolved oxygen and also to provide mixing, in which the concentrations of dissolved oxygen in the reaction solution were maintained at 0.26, 0.40 and 0.57 mM, respectively in three sets of experiments, when different ratios between oxygen and air gases were controlled. During the reaction, water samples were collected at different time intervals for analyses. To quench any further reaction with radicals in the samples, 10 μL of methanol was injected into the 2.0 mL of sample as soon as the sample taking.

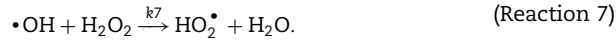
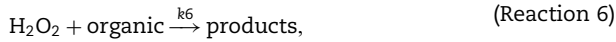
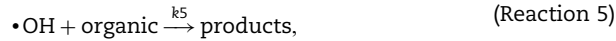
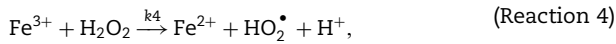
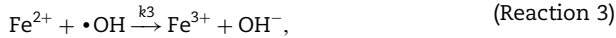
2.3. Analytical methods

Phenol concentration was analyzed by HPLC (Waters 486) equipped with a reverse-phase column (Waters, XTerra™ MS C-18) and a UV detector. A mobile phase consists of acetonitrile and water (20%:80%) with 0.5% acetic acid. Under these conditions, phenol was determined at the wavelength of 269 nm with a retention time of 5.8 min. The ferrous ion (Fe^{2+}) concentration was determined using a UV-VIS spectrophotometer (Spectronic, GENISIS-2), according to the light absorption at 510 nm of a colored complex solution formed from Fe^{2+} and 1,10-phenanthroline (APHA, 1995). H_2O_2 solution was prepared with 30% H_2O_2 chemical and calibrated by KMnO_4 titration, which had been calibrated by $\text{Na}_2\text{C}_2\text{O}_4$ titration (Vogel, 1978). Whereas, the H_2O_2 concentration during the E-Fenton reaction was determined using the UV-VIS spectrophotometer, according to the light absorption at 407 nm of a yellow complex solution formed from the H_2O_2 and $\text{K}_2\text{Ti}(\text{C}_2\text{O}_4)_3$ in 2 M H_2SO_4 solution to prevent any interference caused by the organic disturbance (Sellers, 1980).

3. Kinetic modeling of E-Fenton reaction

It is generally believed that a typical E-Fenton reaction should involve three key reactions: (1) the generation of H_2O_2 from dissolved oxygen on the surface of the cathode (Reaction 1), (2) the generation of hydroxyl radicals ($\cdot\text{OH}$) between H_2O_2 and Fe^{2+} (Reaction 2), and (3) the degradation of organic substance by the $\cdot\text{OH}$ (Reaction 5). In the meantime, some reversed reactions and side reactions (Reactions 3, 4, 6 and 7) coexist along with the key reactions as summarized below (Walling, 1975; Buvet et al., 1987; Neyens and Baeyens, 2003):





To establish a new kinetic model for describing the E-Fenton reaction, we may assume that organic substance (S) is primarily degraded by the $\bullet\text{OH}$ and its reaction rate ($d[S]/dt$) can be expressed by Eq. (1)

$$-\frac{d[S]}{dt} = k_5[\bullet\text{OH}][S]. \quad (1)$$

From the reactions 2, 3, 5, and 7, the change of $\bullet\text{OH}$ concentration ($d[\bullet\text{OH}]/dt$) relies on its generation rate from H_2O_2 and Fe^{2+} , and its consumption rate reacting with Fe^{2+} , organic substance and H_2O_2 as shown below

$$\begin{aligned} \frac{d[\bullet\text{OH}]}{dt} = & k_2[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_3[\text{Fe}^{2+}][\bullet\text{OH}] \\ & - k_5[\bullet\text{OH}][S] - k_7[\bullet\text{OH}][\text{H}_2\text{O}_2]. \end{aligned} \quad (1a)$$

Since k_7 (3.30×10^7) is about one order smaller than k_3 (3.20×10^8) at pH 3–4 according to the data in the literature (Duesterberg and Waite, 2006) and also $[\text{H}_2\text{O}_2]$ is much lower than $[\text{Fe}^{2+}]$ in our E-Fenton reaction system, it is fair enough to remove the item of $k_7[\bullet\text{OH}][\text{H}_2\text{O}_2]$ from Eq. (1a) in order to simplify the model.

Also, since $\bullet\text{OH}$ is a highly reactive free radical with an extremely short lifetime of nanoseconds (Liu et al., 1999), its concentration is normally considered to be constant but at a low level and the $d[\bullet\text{OH}]/dt$ will approach zero according to a steady state approximation. Then Eq. (1) can be rearranged as Eq. (2) and the rate of organic degradation becomes a function of $[\text{H}_2\text{O}_2]$ and $[S]$ mainly.

$$-\frac{d[S]}{dt} = k_5 \frac{k_2[\text{Fe}^{2+}][S]}{k_3[\text{Fe}^{2+}] + k_5[S]} [\text{H}_2\text{O}_2]. \quad (2)$$

On the other hand, the variation of H_2O_2 concentration in the reaction solution depends on its generation rate (Reaction 1) and decomposition rate (Reactions 2, 4, 6 and 7). If it is assumed that the rate of H_2O_2 generation is proportional to the applied current density (I/A) and the oxygen coverage (θ) on the cathode, it can be expressed by Eq. (3).

$$\begin{aligned} \frac{d[\text{H}_2\text{O}_2]}{dt} = & k_1 \frac{I\theta}{A} - (k_2[\text{Fe}^{2+}] + k_4[\text{Fe}^{3+}])[\text{H}_2\text{O}_2] \\ & - k_6[\text{H}_2\text{O}_2][S] - k_7[\bullet\text{OH}][\text{H}_2\text{O}_2]. \end{aligned} \quad (3)$$

By considering that the adsorption of dissolved oxygen on the cathode surface obeys the Langmuir adsorption model, a relationship between oxygen coverage (θ) and dissolved oxygen concentration $[\text{O}_2]$ can be expressed by the following equation, where K_{ad} is the adsorption equilibrium constant.

$$\theta = \frac{K_{ad}[\text{O}_2]}{1 + K_{ad}[\text{O}_2]}.$$

Since $k_2 \gg k_4$, k_6 and k_7 , Eq. (3) can be simplified into Eq. (4). After integration, the $[\text{H}_2\text{O}_2]$ becomes a function of experimental time (t). According to the initial condition when $t = 0$, $[\text{H}_2\text{O}_2] = 0$, and also assuming that the $[\text{Fe}^{2+}]$ during the

reaction is proportional to its initial concentration $[\text{Fe}^{2+}]_0$ with a fixed ratio of λ , $[\text{H}_2\text{O}_2]$ can be eventually expressed as Eq. (5).

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_1 \frac{IK_{ad}[\text{O}_2]}{A(1 + K_{ad}[\text{O}_2])} - k_2[\text{Fe}^{2+}][\text{H}_2\text{O}_2], \quad (4)$$

$$[\text{H}_2\text{O}_2] = \frac{k_1 K_{ad} I [\text{O}_2]}{k_2 \lambda A [\text{Fe}^{2+}]_0 (1 + K_{ad} [\text{O}_2])} (1 - e^{-k_2 \lambda [\text{Fe}^{2+}]_0 t}). \quad (5)$$

The above equation indicates that the $[\text{H}_2\text{O}_2]$ is a function of experimental time, increasing from zero at the beginning of reaction ($t = 0$) toward its maximum value after sufficient reaction time as shown below

$$[\text{H}_2\text{O}_2]_{\max} = \frac{k_1 K_{ad} I [\text{O}_2]}{k_2 \lambda A [\text{Fe}^{2+}]_0 (1 + K_{ad} [\text{O}_2])}. \quad (5a)$$

This equation demonstrates that $[\text{H}_2\text{O}_2]_{\max}$ in the E-Fenton reaction depends on few factors of I/A , $[\text{Fe}^{2+}]_0$ and $[\text{O}_2]$. Alternatively Eq. (5) has a simplified form as shown below

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_{\max} (1 - e^{-k_2 \lambda [\text{Fe}^{2+}]_0 t}). \quad (5b)$$

Once we use Eq. (5) to replace the $[\text{H}_2\text{O}_2]$ in Eq. (2), the rate of organic degradation can be further expressed as follows:

$$-\frac{d[S]}{dt} = \frac{k_5}{k_3 \lambda [\text{Fe}^{2+}]_0 + k_5 [S]} \frac{k_1 K_{ad} I [\text{O}_2]}{(1 + K_{ad} [\text{O}_2])} (1 - e^{-(k_2 \lambda [\text{Fe}^{2+}]_0 t)}) [S]. \quad (2a)$$

After integration, the organic concentration $[S]$ becomes a function of experimental time, decreasing from its initial concentration $[S]_0$ at the beginning of reaction ($t = 0$) gradually as described by Eq. (6)

$$\begin{aligned} \ln \left(\frac{[S]_0}{[S]} \right) + \frac{k_5}{k_3 \lambda [\text{Fe}^{2+}]_0} ([S]_0 - [S]) \\ = \frac{k_1 k_5 K_{ad} I [\text{O}_2]}{k_3 \lambda A [\text{Fe}^{2+}]_0 (1 + K_{ad} [\text{O}_2])} \left(t - \frac{1 - e^{-(k_2 \lambda [\text{Fe}^{2+}]_0 t)}}{k_2 \lambda [\text{Fe}^{2+}]_0} \right), \end{aligned} \quad (6)$$

To simplify Eq. (6), let $a = k_5/k_3 \lambda [\text{Fe}^{2+}]_0$, $b = k_1 k_5 K_{ad} I [\text{O}_2]/k_3 \lambda A [\text{Fe}^{2+}]_0 (1 + K_{ad} [\text{O}_2])$ and $c = k_2 \lambda [\text{Fe}^{2+}]_0$, the above equation can be re-arranged in a simplified form as shown below

$$\ln \frac{[S]_0}{[S]} + a([S]_0 - [S]) = b \left(t - \frac{1 - e^{-ct}}{c} \right). \quad (6a)$$

It can be concluded that the above pair of equations (Eqs. (5) and (6)) has been established as the main kinetic model for the E-Fenton reaction to describe H_2O_2 accumulation and organic degradation in aqueous solution against reaction time.

4. Validation of the new kinetic model by experiments

To validate the new model for its application in an E-Fenton reaction system, three sets of experiments were carried out in aqueous phenol solution by varying three key factors of current density (I/A), dissolved oxygen concentration $[\text{O}_2]$ and ferrous ion concentration $[\text{Fe}^{2+}]$, respectively. Each experiment with an initial phenol concentration of 1.5×10^{-4} M and initial pH 2.5 lasted for up to 90 min, in which the concentrations of H_2O_2 and phenol were determined at different reaction intervals.

The H_2O_2 model (Eq. (5b)) was first validated by the above experimental data of H_2O_2 concentration. The fitting results are presented in Fig. 1. It can be seen clearly that the new H_2O_2 model can well describe the H_2O_2 variation in all experiments. Both the experimental data and the model simulation showed that H_2O_2 concentration increased quickly at the initial stage of the reaction and gradually approached to the maximum values. The experimental results in Fig. 1A and B indicate that the higher I/A and $[\text{O}_2]$ would be beneficial to enhance the H_2O_2 generation rate, while the results in Fig. 1C show that the higher $[\text{Fe}^{2+}]$ could decompose H_2O_2 faster. These experimental data were also fitted using Eq. (5) to demonstrate the relationship between $[\text{H}_2\text{O}_2]_{\text{max}}$ and three factors of current density, dissolved oxygen concentration and initial ferrous ion concentration, respectively as shown in Fig. 2. The fitting results demonstrated a good agreement between simulation and experimental data with three correlation coefficients of $R = 0.9998, 0.9973$, and 0.9647 .

The new organic degradation model (Eq. (6)) was also validated by the above first set of experiments of phenol degradation at $[\text{O}_2] = 0.57 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.20 \text{ mM}$ and $\text{pH } 2.5$, but three different current density ($I/A = 0.04, 0.16$ and 0.32 mA cm^{-2}). The experimental data were fitted using both the first-order model and our new model, respectively. Fig. 3 presents the results of fittings in linear forms of the first-order model (Fig. 3A) and our new model of $[\ln([S_0]/[S]) + a([S_0] - [S])] \text{ vs. } (t - (1 - e^{-ct}/c))$ (Fig. 3B). It can be seen that the correlation coefficients for fitting by our new model are much higher than those by the first-order model. Furthermore, Fig. 4 shows variation of phenol concentration $[S]$ against reaction time (t) fitted by our new model (Eq. (6a)). The experiments demonstrated that a trend of all experimental data between phenol concentration and reaction time appeared as an inverted 'S' shape curve, which means that the rate of phenol

degradation was quite slow during the initial stage of the reaction due to a low H_2O_2 concentration, then significantly increased during the middle stage of the reaction due to a quick growth of H_2O_2 concentration in the reaction solution, and eventually slowed down again during the later stage of the reaction after phenol had been reduced to a low level. It is obvious that our new model well fitted the experimental data, since the model considers both variables of phenol concentration and H_2O_2 concentration simultaneously. Actually many reactions cannot be simply fitted by the first-order model. Some researchers would rather subdivide the reaction period into two or three phases to fit the experimental data using the first-order model separately with different values of kinetic constant (k) (Chu et al., 2005). This approach may well simulate the experimental data mathematically, but not chemically. Our model can satisfy the kinetic description of such an E-Fenton reaction in both ways.

It has been identified that three parameters of current density (I/A), dissolved oxygen concentration $[\text{O}_2]$, and initial ferrous ion concentration $[\text{Fe}^{2+}]_0$ are the key factors affecting both the H_2O_2 generation and also the phenol degradation. The experimental results shown in Fig. 4 demonstrated that the increase of the applied current density up to 0.32 mA cm^{-2} in the E-Fenton reaction could enhance the phenol degradation significantly, since the higher rate of H_2O_2 generation was achieved at the higher current density. It is believed that at the lower side of current density ($I/A \leq 0.32 \text{ mA cm}^{-2}$), phenol is mainly degraded by the typical E-Fenton reaction, but at the higher side of current density ($I/A > 0.32 \text{ mA cm}^{-2}$), the H_2O_2 reduction to water on the cathode would be involved.

The experimental data from the second set of experiments with different dissolved oxygen concentration were fitted using the new model and the results are presented in Fig. 5. It can be seen that the three curves of phenol degradation at

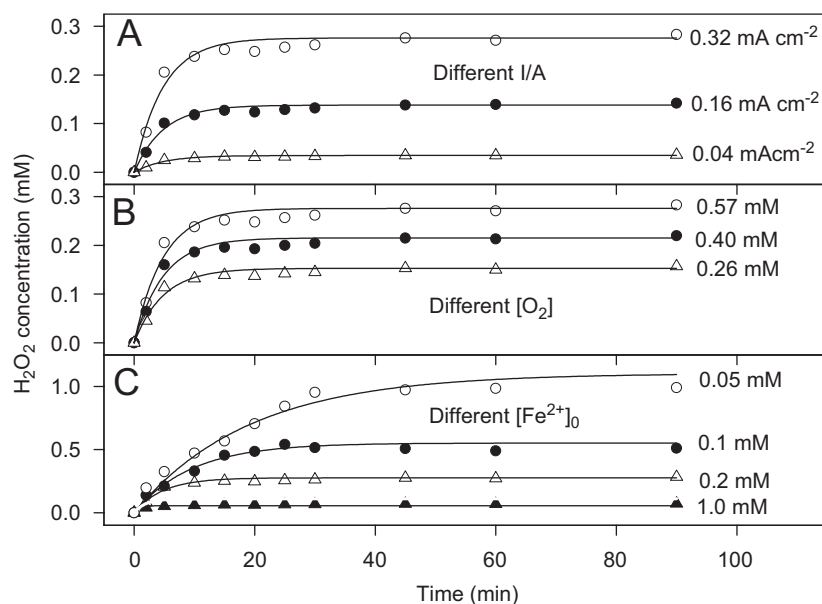


Fig. 1 – H_2O_2 accumulation in the reaction solution with initial phenol concentration of $1.5 \times 10^{-4} \text{ M}$ (A) different I/A , when $[\text{O}_2] = 0.57 \text{ mM}$ and $[\text{Fe}]_0 = 0.20 \text{ mM}$; (B) different $[\text{Fe}^{2+}]_0$, when $I/A = 0.32 \text{ mA cm}^{-2}$ and $[\text{O}_2] = 0.57 \text{ mM}$; and (C) different $[\text{O}_2]$, when $I/A = 0.32 \text{ mA cm}^{-2}$ and $[\text{Fe}]_0 = 0.20 \text{ mM}$.

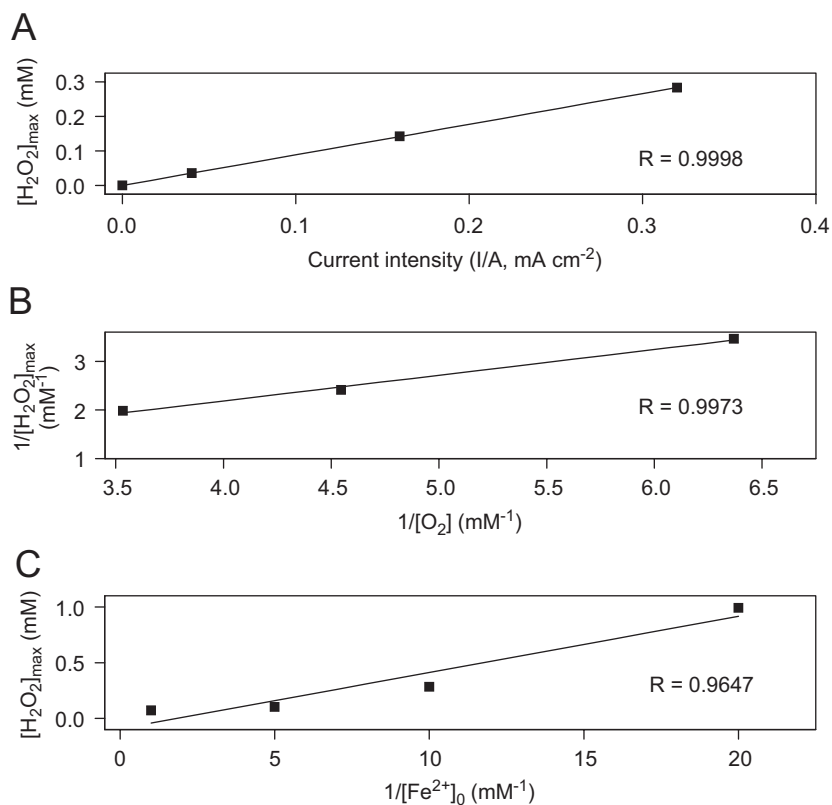


Fig. 2 – Linear fittings of $[H_2O_2]_{max}$ at different (A): I/A , (B): $[Fe^{2+}]_0$ and (C): $[O_2]$, respectively.

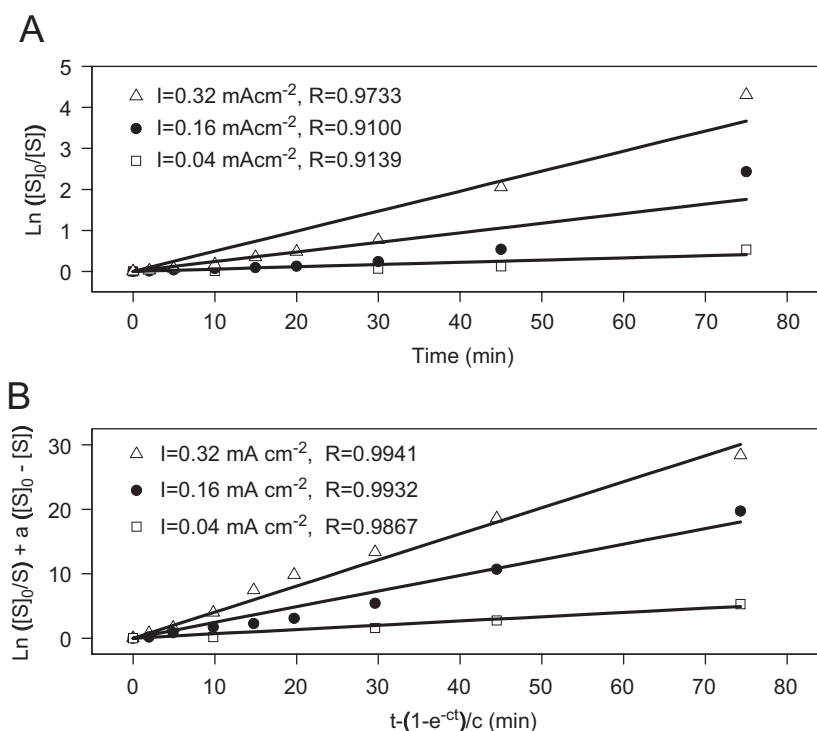


Fig. 3 – Linear relationship of phenol degradation during the E-Fenton reaction at different I/A fitted by (A) the first-order model and (B) the new kinetic model, when $[O_2] = 0.57\ mM$, $[Fe]_0 = 0.2\ mM$ and pH 2.5.

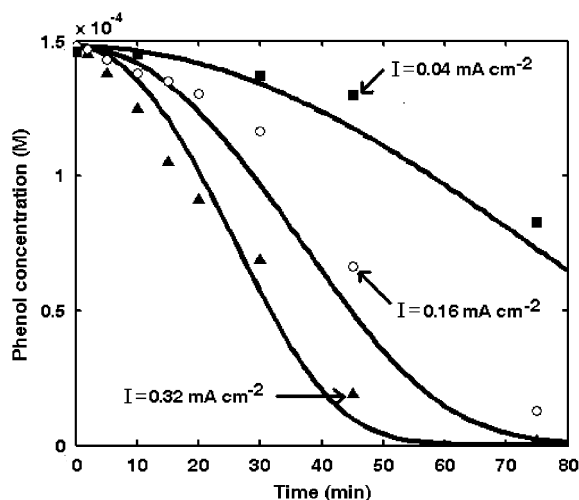


Fig. 4 – Phenol degradation during the E-Fenton reaction at different I/A fitted by the new kinetic model ($[O_2] = 0.57 \text{ mM}$, $[Fe^{2+}]_0 = 0.2 \text{ mM}$ and $pH 2.5$).

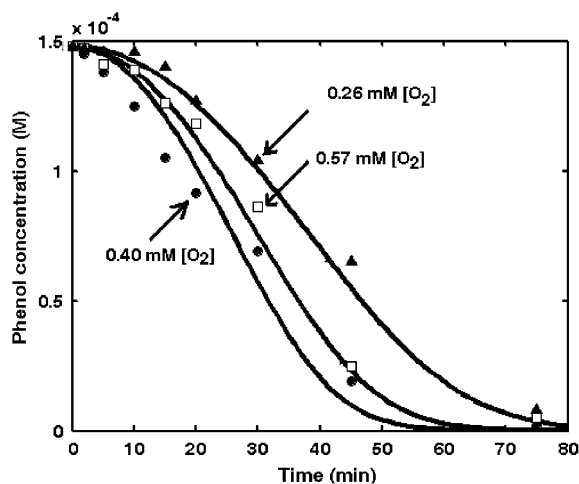


Fig. 5 – Phenol degradation during the E-Fenton reaction at different $[O_2]_0$ fitted by the new kinetic model ($K_{ad} = 1.1 \text{ L mM}^{-1}$, $k_1 = 6.6 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 81 \text{ M}^{-1} \text{ s}^{-1}$, $k_5/k_3 = 0.31$, $\lambda = 0.2$, $pH 2.5$, $I/A = 0.32 \text{ mA cm}^{-2}$ and $[Fe^{2+}]_0 = 0.2 \text{ mM}$).

different dissolved oxygen concentration showed the same pattern of the inverted 'S' shape and good fittings were achieved by our new model. Also the results showed that the higher $[O_2]$ up to 0.57 mM accelerated the phenol degradation significantly, but not as much as the effect of current density. These results further confirmed that the rate of substance degradation can be enhanced by increasing I/A as the first-order reaction, but by increasing $[O_2]$ at the order between 0 and 1 as indicated by Eq. (6). From an engineering point of view, the application of such an E-Fenton reaction in water and wastewater treatment should adopt a dissolved oxygen level below 9 mg l^{-1} (equivalent to 0.28 mM), which can be simply realized by aeration under normal atmosphere pressure.

It should be noted that the overall efficiency of phenol degradation in such an E-Fenton reaction depends on both rates of H_2O_2 generation and Fenton reaction in the solution. When the current density and dissolved oxygen concentration mainly affect the rate of H_2O_2 generation, the ferrous ion concentration would affect both rates of H_2O_2 decomposition and $\cdot OH$ formation in the reaction solution simultaneously. The third set of experiment of phenol degradation with different initial concentrations of ferrous ion was conducted. The results presented in Fig. 6 showed that the phenol degradation reaction increased with the increased initial concentrations of ferrous ion $[Fe^{2+}]_0$ from 0.05 to 0.2 mM significantly, and further enhanced from 0.2 to 1.0 mM slightly. Without surprise, the inverted "S" shape curves of phenol concentration vs. reaction time were confirmed and the goodness of the fittings at different $[Fe^{2+}]_0$ by our new model is presented in Fig. 6.

In our study, it was further found that a turning point for the enhancement of phenol degradation reaction from high to low by $[Fe^{2+}]_0$ was around 1.0 mM under our experimental condition. At a higher $[Fe^{2+}]_0$ of 2.0 mM , no significant increase in phenol degradation was observed. At much higher $[Fe^{2+}]_0$, the rate of phenol degradation could be reduced (not shown here). These results indicate clearly that there must be an optimum ferrous ion concentration in such an E-Fenton reaction. In this study, $[Fe^{2+}]_0 = 0.2 \text{ mM}$ was determined to be a suitable concentration to achieve an efficient rate of phenol degradation under our experimental condition.

Although the conventional first-order kinetic model is the simplest model to describe a variety of chemical reactions and has been widely applied in various processes relevant to water and wastewater treatment, it is difficult to well describe the kinetics of the E-Fenton reaction precisely. It should be noted that the cathodic E-Fenton reaction has a few particular characters that: (i) H_2O_2 is continuously generated throughout the reaction; (ii) the initial H_2O_2 concentration in the reaction

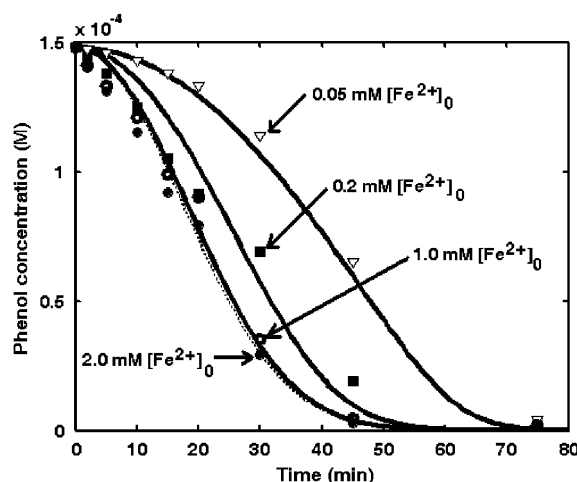


Fig. 6 – Phenol degradation during the E-Fenton reaction at different $[Fe^{2+}]_0$ fitted by the new kinetic model ($K_{ad} = 1.1 \text{ L mM}^{-1}$, $k_1 = 6.6 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 81 \text{ M}^{-1} \text{ s}^{-1}$, $k_5/k_3 = 0.31$, $\lambda = 0.2$, $pH 2.5$, $I/A = 0.32 \text{ mA cm}^{-2}$ and $[O_2]_0 = 0.57 \text{ mM}$).

solution is zero and gradually increases along with the reaction time toward a maximum value, depending on the applied current density, the dissolved oxygen concentration and the ferrous iron concentration; and (iii) the variation of substrate concentration vs. reaction time has a typical inverted “S” shape curve, indicating a low reaction rate during the initial stage of the reaction, a high reaction rate during the middle stage, and a low reaction rate again during the final stage.

5. Conclusion

In this study, a new kinetic model for the E-Fenton reaction in aqueous solution was established mathematically as an analytical solution by considering both the H_2O_2 generation rate and the H_2O_2 consumption rate. In addition, it also includes the three key factors of current density, dissolved oxygen concentration and ferrous ion concentration. Therefore, this model with its inverted “S” shape curve can describe the cathodic E-Fenton reaction much better than the first-order model more accurately than other kinetics by subdividing the reaction period into two or three phases. However, the new model was only validated by the experiments of phenol degradation so far. Further studies to apply this kinetic model in degradation of other organics become necessary.

Acknowledgments

This work was financially supported by the RGC grant of Hong Kong Government (RGC Grant no. PolyU5148/03E). The project is also partially supported by Natural Science Foundation of China (Project no: 20577071) and Natural Science Foundation of China Guangdong Province, China (Project no: 04009709). The authors would thank Mr. Zhang Guangchi for his help in the modeling work.

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