KINETIC MODELING OF ELECTRO-FENTON REACTION IN AQUEOUS SOLUTION

H. Liu[1], X. Z. LI[*2], Y. J. Leng[3], C. Wang[1]

[1]*School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China.*

[2]*Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China*

[3]*School of Mechanical and Aerospace Engineering, Nanyang Technological University,50 Nanyang Ave, Singapore 639798*

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 (H_2O_2) 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 H_2O_2 was 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 in all experiments 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.

Keywords: E-Fenton; H_2O_2; Kinetic Model; Phenol

[*] *Corresponding author, Tel:: (852) 2766 6016; Fax: (852) 2334 6389; Email address: cexzli@polyu.edu.hk*

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; Wang et al., 2004). Recent development of electro-Fenton (E-Fenton) reaction by generating H_2O_2 from dissolved oxygen in aqueous solution electrically provides fresh H_2O_2 in a continuous mode, which is more efficient and cost-effective than conventional chemical dosing methods (Brillas et al., 1998; Brillas et al., 2000; Brillas and Casado, 2002; Brillas et al., 2003; Gözmen et al., 2003).

It should be noted that like most chemical reactions, the H_2O_2 concentration in a conventional Fenton reaction is gradually reduced after a batch chemical dosing along with reaction time (Malato et al., 2001; Liu et al., 2003). It has been reported that adding H_2O_2 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 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 (Oturan, 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 in 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. in 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; Brillas et al., 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 [$K_2Ti(C_2O_4)_3$] and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) 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 mm × 20 mm) from Superior Chemicals & Instruments, China was used as the anode and a commercially-available carbon rod (Φ = 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 mM, 0.40 mM 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, XT erra^{TM} 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 spectrosphotometer (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 $Na_2C_2O_4$ titration (Vogel, 1978). Whereas, the H_2O_2 concentration during the E-Fenton reaction was determined using the UV-VIS spectrosphotometer, according to the light absorption at 407 nm of a yellow complex solution formed from the H_2O_2 and $K_2Ti(C_2O_4)_3$ 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 (·OH) between H_2O_2 and Fe^{2+} (Reaction 2), and (3) the degradation of organic substance by the ·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;):

$$O_2 + 2H^+ + 2e \xrightarrow{k1} H_2O_2 \qquad \text{(Reaction 1)}$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k2} Fe^{3+} + \cdot OH + OH^- \qquad \text{(Reaction 2)}$$

$$Fe^{2+} + \cdot OH \xrightarrow{k3} Fe^{3+} + OH^- \qquad \text{(Reaction 3)}$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k4} Fe^{2+} + HO_2^{\cdot} + H^+ \qquad \text{(Reaction 4)}$$

$$\cdot OH + organic \xrightarrow{k5} products \qquad \text{(Reaction 5)}$$

$$H_2O_2 + organic \xrightarrow{k6} products \qquad \text{(Reaction 6)}$$

$$\cdot OH + H_2O_2 \xrightarrow{k7} HO_2^{\cdot} + H_2O \qquad \text{(Reaction 7)}$$

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

$$-\frac{d[S]}{dt} = k_5[\cdot OH]\cdot[S] \qquad (1)$$

From the reactions 2, 3, 5, and 7, the change of ·OH concentration ($\frac{d[\cdot OH]}{dt}$) 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:

$$\frac{d[\cdot OH]}{dt} = k_2[Fe^{2+}]\cdot[H_2O_2] - k_3[Fe^{2+}]\cdot[\cdot OH] - k_5[\cdot OH][S] - k_7[\cdot OH][H_2O_2] \qquad (1a)$$

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 $[H_2O_2]$ is much lower than $[Fe^{2+}]$ in our E-Fenton reaction system, it is fair enough to remove the item of $k_7[\cdot OH][H_2O_2]$ from Eq. 1a in order to simplify the model.

Also, since ·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 $\frac{d[^{\cdot}OH]}{dt}$ 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 $[H_2O_2]$ and [S] mainly.

$$-\frac{d[S]}{dt} = k_5 \cdot \frac{k_2[Fe^{2+}]\cdot[S]}{k_3[Fe^{2+}]+k_5[S]}\cdot[H_2O_2] \quad (2)$$

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.

$$\frac{d[H_2O_2]}{dt} = k_1 \cdot \frac{I\cdot\theta}{A} - (k_2[Fe^{2+}]+k_4[Fe^{3+}])\cdot[H_2O_2] - k_6[H_2O_2]\cdot[S] - k_7[^{\cdot}OH]\cdot[H_2O_2] \quad (3)$$

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 ($[O_2]$) can be expressed by the following equation, where K_{ad} is the adsorption equilibrium constant.

$$\theta = \frac{K_{ad}[O_2]}{1+K_{ad}[O_2]}$$

Since $k_2 >> k_4$, k_6 and k_7, Eq. 3 can be simplified into Eq. 4. After integration, the $[H_2O_2]$ becomes a function of experimental time (t). According to the initial condition when t = 0, $[H_2O_2]$ = 0, and also assuming that the $[Fe^{2+}]$ during the reaction is proportional to its initial concentration ($[Fe^{2+}]_0$) with a fixed ratio of λ, $[H_2O_2]$ can be eventually expressed as Eq. 5.

$$\frac{d[H_2O_2]}{dt} = k_1 \cdot \frac{Ik_{ad}[O_2]}{A(1+k_{ad}[O_2])} - k_2[Fe^{2+}]\cdot[H_2O_2] \quad (4)$$

$$[H_2O_2] = \frac{k_1 K_{ad} I[O_2]}{k_2 \lambda A[Fe^{2+}]_0 (1 + K_{ad}[O_2])} (1 - e^{-k_2 \lambda [Fe^{2+}]_0 t}) \quad (5)$$

The above equation indicates that the $[H_2O_2]$ 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:

$$[H_2O_2]_{max} = \frac{k_1 K_{ad} I[O_2]}{k_2 \lambda A[Fe^{2+}]_0 (1 + K_{ad}[O_2])} \quad (5a)$$

This equation demonstrates that $[H_2O_2]_{max}$ in the E-Fenton reaction depends on few factors of I/A, $[Fe^{2+}]_0$ and $[O_2]$. Alternatively Eq. 5 has a simplified form as shown below:

$$[H_2O_2] = [H_2O_2]_{max} (1 - e^{-k_2 \lambda [Fe^{2+}]_0 t}) \quad (5b)$$

Once we use Eq. 5 to replace the $[H_2O_2]$ in Eq. 2, the rate of organic degradation can be further expressed as follows:

$$-\frac{d[S]}{dt} = \frac{k_5}{k_3 \lambda [Fe^{2+}]_0 + k_5 [S]} \cdot \frac{k_1 K_{ad} I[O_2]}{(1 + K_{ad}[O_2])} (1 - e^{-(k_2 \lambda [Fe^{2+}]_0) t}) \cdot [S] \quad (2a)$$

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:

$$Ln(\frac{[S_0]}{[S]}) + \frac{k_5}{k_3 \lambda [Fe^{2+}]_0} ([S_0] - [S]) = \frac{k_1 k_5 K_{ad} I[O_2]}{k_3 \lambda A[Fe^{2+}]_0 (1 + K_{ad}[O_2])} \left(t - \frac{1 - e^{-(k_2 \lambda [Fe^{2+}]_0) t}}{k_2 \lambda [Fe^{2+}]_0} \right) \quad (6)$$

196 To simplify Eq. 6, let $a = \frac{k_5}{k_3 \lambda [Fe^{2+}]_0}$, $b = \frac{k_1 k_5 K_{ad} I[O_2]}{k_3 \lambda A [Fe^{2+}]_0 (1 + K_{ad}[O_2])}$ and $c = k_2 \lambda [Fe^{2+}]_0$, the above equation

197 can be re-arranged in a simplified form as shown below:

198

199 $$Ln\frac{[S_0]}{[S]} + a([S_0] - [S]) = b(t - \frac{1 - e^{-ct}}{c}) \quad (6a)$$

200

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

204

205 **4. Validation of the New Kinetic Model by Experiments**

206

207 To validate the new model for its application in an E-Fenton reaction system, three sets of
208 experiments were carried out in aqueous phenol solution by varying three key factors of current
209 density (I/A), dissolved oxygen concentration ($[O_2]$) and ferrous ion concentration ($[Fe^{2+}]$),
210 respectively. Each experiment with an initial phenol concentration of 1.5×10^{-4} M and initial pH 2.5
211 lasted for up to 90 min, in which the concentrations of H_2O_2 and phenol were determined at
212 different reaction intervals.

213 The H_2O_2 model (Eq. 5b) was first validated by the above experimental data of H_2O_2
214 concentration. The fitting results are presented in Fig. 1. It can be seen clearly that the new H_2O_2
215 model can well describe the H_2O_2 variation in all experiments. Both the experimental data and the
216 model simulation showed that H_2O_2 concentration increased quickly at the initial stage of the
217 reaction and gradually approached to the maximum values. The experimental results in Fig. 1A and
218 B indicate that the higher I/A and $[O_2]$ would be beneficial to enhance the H_2O_2 generation rate,
219 while the results in Fig. 1C show that the higher $[Fe^{2+}]$ could decompose H_2O_2 faster. These
220 experimental data were also fitted using Eq. 5 to demonstrate the relationship between $[H_2O_2]_{max}$
221 and three factors of current density, dissolved oxygen concentration and initial ferrous ion
222 concentration, respectively as shown in Fig. 2. The fitting results demonstrated a good agreement
223 between simulation and experimental data with three correlation coefficients of R = 0.9978, 0.9973,

224 and 0.9647.

225

226 [Fig. 1]

227 [Fig. 2]

228

229 The new organic degradation model (Eq. 6) was also validated by the above first set of
230 experiments of phenol degradation at $[O_2]$ = 0.57 mM, $[Fe^{2+}]_0$ = 0.20 mM and pH 2.5, but three
231 different current density (I/A = 0.04, 0.16 and 0.32 mA cm^{-2}). The experimental data were fitted
232 using both the first-order model and our new model, respectively. Fig. 3 presents the results of
233 fittings in linear forms of the first-order model (Fig. 3A) and our new model of
234 $[Ln\frac{[S_0]}{[S]}+a([S_0]-[S])]$ vs. $(t-\frac{1-e^{-ct}}{c})$ (Fig. 3B). It can be seen that the correlation coefficients
235 for fitting by our new model are much higher than those by the first-order model. Furthermore, Fig.
236 4 shows variation of phenol concentration [S] against reaction time (t) fitted by our new model (Eq.
237 6a). The experiments demonstrated that a trend of all experimental data between phenol
238 concentration and reaction time appeared as an inverted "S" shape curve, which means that the rate
239 of phenol degradation was quite slow during the initial stage of the reaction due to a low H_2O_2
240 concentration, then significantly increased during the middle stage of the reaction due to a quick
241 growth of H_2O_2 concentration in the reaction solution, and eventually slowed down again during the
242 later stage of the reaction after phenol had been reduced to a low level. It is obvious that our new
243 model well fitted the experimental data, since the model considers both variables of phenol
244 concentration and also H_2O_2 concentration simultaneously. Actually many reactions can not be
245 simply fitted by the first-order model. Some researchers would rather subdivide the reaction period
246 into two or three phases to fit the experimental data using the first-order model separately with
247 different values of kinetic constant (k) (Chu et al., 2005). This approach may well simulate the
248 experimental data mathematically, but not chemically. Our model can satisfy the kinetic description
249 of such an E-Fenton reaction in both ways.

250

251 [Fig. 3]

252 [Fig. 4]

It has been identified that three parameters of current density (I/A), dissolved oxygen concentration ($[O_2]$), and initial ferrous ion concentration $[Fe^{2+}]_0$ 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 ($I/A \leq 0.32$ mA cm^{-2}), phenol is mainly degraded by the typical E-Fenton reaction, but at the higher side of current density ($I/A > 0.32$ 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 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.

[Fig. 5]

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 ·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.

[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 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 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.

Acknowledgements

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.

References

Anota, J., Lu M.C., Chewpreech, P., 2006. Kinetics of aniline degradation by Fenton and electro-Fenton Processes. Wat. Res. 40, 1841-1847.

APHA, 1995. Standard methods for the examination of water and wastewater, 19th edition.

Boye, B., Dieng, M. M., Brillas, E., 2002. Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation. Environ. Sci. Technol. 36, 3030-3035.

Brillas, E., Baños, M. Ă., Garrido, J. A., 2003. Mineralization of herbicide 3,6-dichloro-2-methoxybezoic acid in aqueous medium by anodic oxidation, electro-Fenton and photoelectron-Fenton. Electrochim. Acta. 48, 1697-1705.

Brillas, E., Calpe, J. C., Casado, J., 2000. Minerallization of 2,4-D by advanced electrochemical oxidation process. Wat. Res. 34, 2253-2262.

Brillas, E., Casado, J., 2002. Aniline degradation by Electro-Fenton® and peroxy-coagulation processes using a flow reactor and for waste water treatment. Chemosphere 47, 241-248.

Brillas, E., Sauleda, R., Casado, J., 1998. Degradation of 4-chlorophenol by anodic oxidation, electro-Fenton, photo-electro-Fenton and peroxi-coagulation processes. J. Electrochem. Soc. 145, 759-765.

344 Buvet, R, Sechaud, P., Darolles, J., Leport., Sechaud, F., 1987. Electrochemical and chemical
345 reductions of oxygen dissolved in aqueous solutions. Bioelectrochem. Bioenerg. 18, 13-19.
346 Chu W., Kwan C. Y., Chan K. H., Kam S. K., 2005. A study of kinetic modelling and reaction
347 pathway of 2,4-dichlorophenol transformation by photo-fenton-like oxidation. J. Hazard. Mat.
348 121, 119-126.
349 Duesterberg, C. and Waite, T. D., 2006. Process optimization of Fenton oxidation using kinetic
350 modeling. Environ. Sci. Technol. 40, 4189-4195
351 Gözmen, B., Oturan, M. A., Oturan, N. O., Erbatur, O., 2003. Indirect electrochemical treatment of
352 bisphenol in water via electrochemically generated Fenton reagent. Environ. Sci. Technol. 37,
353 3716-3723.
354 Joseph J. P., 1992. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides
355 by hydrogen peroxide. Environ. Sci. Technol. 26, 944-951.
356 Kawabe, S., Kaneco, S., Suzuki, T., Ohta, K., 2004. Degradation of bisphenol A in water by the
357 photo-Fenton reaction. J. Photochem. Photobiol. A: Chem. 162, 297-305.
358 Liu D. X., Liu J., Wen J., 1999. Elevation of hydrogen peroxide after spinal cord injury detected by
359 using the Fenton reaction. Free Radical Biology and Medicine. 27, 478-482.
360 Liu, H., Li, F. B., Li, X. Z., 2003. Photocatalytic oxidation using a new catalyst-titanium dioxide
361 microsphere for water and waste water treatment. Abstr. Pap. Am Chem. S225, PP 104.
362 Lunar, A., Sicilia, D., Rubio S., Pérez-Bendito D., Nickel, U., 2000. Degradation of photographic
363 developers by Fenton reagent: condition optimization and kinetics for metol oxidation. Wat.
364 Res., 34, 1791-1802.
365 Malato, S., Caceres, J., Aguera, A., Mezcua, M., Hernando, D., Vial, J., Fernandez-Alba, A. R.,
366 2001. Degradation of imidacloprid in water by photo-Fenton and TiO_2 photocatalysis at a solar
367 pilot plant: A comparative study. Environ. Sci. Technol. 35, 4359-4366.
368 Malato, S., Caceres, J., Aguera, A., Mezcua, M., Hernando, D., Vial, J., Fernandez-Alba, A. R.,
369 2001. Degradation of imidacloprid in water by photo-Fenton and TiO_2 photocatalysis at a solar
370 pilot plant: A comparative study. Environ. Sci. Technol. 35, 4359-4366.
371 Neyens, E., Baeyens, J., 2003. A review of classic Fenton peroxidation as an advanced oxidation
372 technique. J. Haz. Mat. 98, 33–50.
373 Oliveros, E., Legrini, O., Hohl, M., Müller, T., Braun, A. M., 1997. Industrial waste water treatment:
374 large scale development of a light-enhanced Fenton reaction Esther. Chem. Eng. Proc. 36,
375 397-405.
376 Oturan, M. A., 2000. An ecologically effective water treatment technique using electrochemically

generated hydroxyl radicals for in situ destruction of organic pollutants: Application to herbicide 2,4-D. J. Appl. Eelectrochem. 30, 475-482.

Oturan, M. A., Peiroten, J., Chartrin. P., Acher., A. J., 2000. Complete destruction of p-nitrophenol in aqueous medium by electro-Fenton method. Environ. Sci. Technol. 34, 3474-3479.

Qiang, Z. M., Chang, J. H., Huang, C. P., 2002. Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions. Wat. Res. 36, 85-94.

Sellers, R.M., 1980. Spectrophotometric determination of hydrogen-peroxide using potassium titanium(IV) oxalate. Analyst 105**,** 950–954.

Vogel, A., 1978. A Textbook of Quantitative Inorganic Analysis, fourth ed. Longman Scientific and Technical, England.

Walling, C., 1975. Fenton Reagent Revisited. Acc. Chem. Res. 8, 125-131.

Wang, Q.Q., Lemley, A.T., 2001. Kinetic model and optimization of 2,4-D degradation by anodic Fenton treatment. Environ. Sci. Technol. 35, 4509-4514**.**

391 **LIST OF FIGURE CAPTIONS**

392

393 Fig. 1. H_2O_2 accumulation in the reaction solution with initial phenol concentration of 1.5 x 10^{-4} M
394 (A) different I/A, when $[O_2]$ = 0.57 mM and $[Fe]_0$ = 0.20 mM; (B) different $[Fe^{2+}]_0$, when I/A =
395 0.32 mA cm^{-2} and $[O_2]$ = 0.57 mM; and (C) different $[O_2]$, when I/A = 0.32 mA cm^{-2} and $[Fe]_0$
396 = 0.20 mM.

397

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

399

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

403

404 Fig. 4. Phenol degradation during the E-Fenton reaction at different I/A fitted by the new kinetic
405 model ($[O_2]$ = 0.57 mM, $[Fe]_0$ = 0.2 mM and pH 2.5).

406

407 Fig. 5. Phenol degradation during the E-Fenton reaction at different $[O_2]_0$, fitted by the new kinetic
408 model (K_{ad} = 1.1 L mM^{-1}, k_1 = 6.6 M^{-1} S^{-1}, k_2 = 81 M^{-1} S^{-1}, k_5/k_3 = 0.31, λ = 0.2, pH 2.5, I/A =
409 0.32 mA cm^{-2} and $[Fe^{2+}]_0$ = 0.2 mM).

410

411 Fig. 6. Phenol degradation during the E-Fenton reaction at different $[Fe^{2+}]_0$ fitted by the new kinetic
412 model (K_{ad} = 1.1 L mM^{-1}, k_1 = 6.6 M^{-1} S^{-1}, k_2 = 81 M^{-1} S^{-1}, k_5/k_3 = 0.31, λ = 0.2, pH 2.5, I/A =
413 0.32 mA cm^{-2} and $[O_2]_0$ = 0.57 mM).

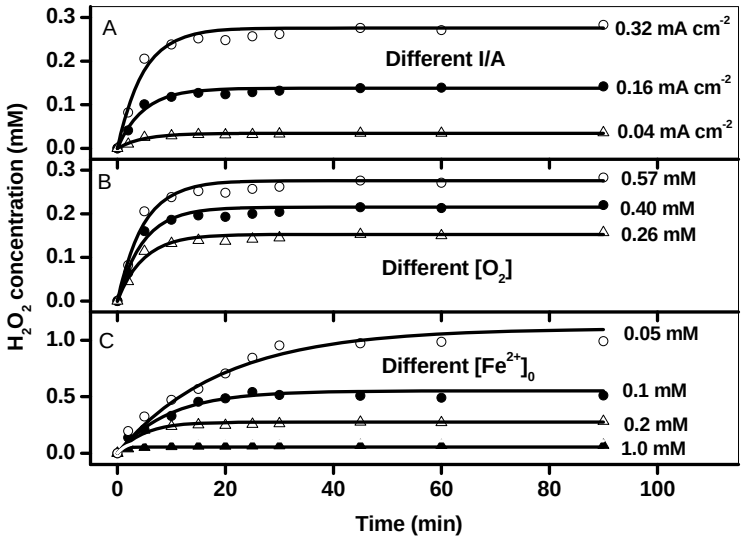
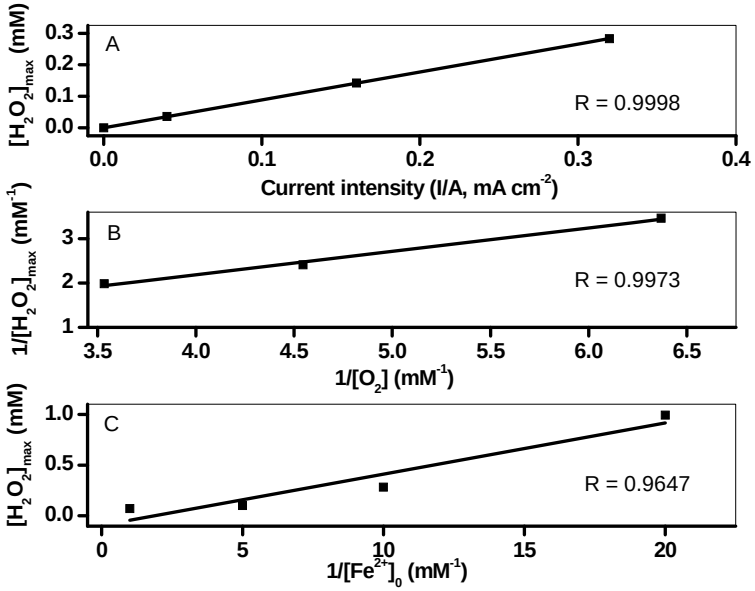

A
Different I/A
0.32 mA cm-2
0.16 mA cm-2
0.04 mA cm-2
B
Different [O2]
0.57 mM
0.40 mM
0.26 mM
C
Different [Fe2+]0
0.05 mM
0.1 mM
0.2 mM
1.0 mM
H2O2 concentration (mM)
Time (min)

Fig. 1.

422



423

424

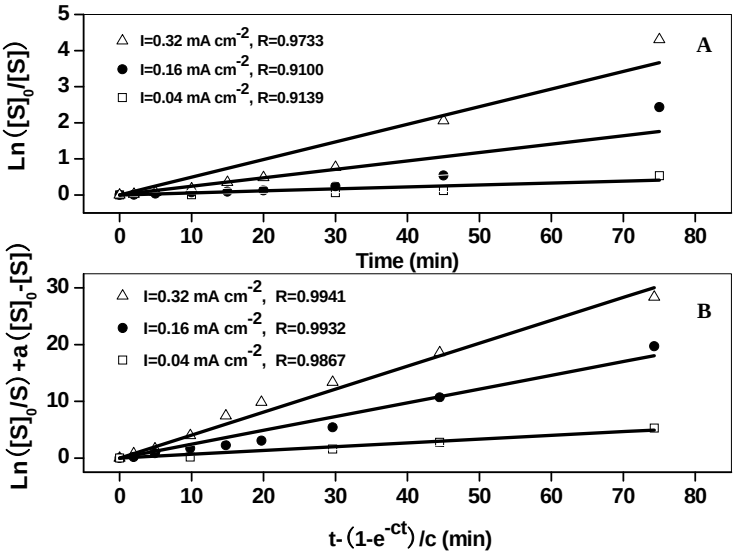
425

426

427 **Fig. 2.**

428

429



430

431

432

433

434 **Fig. 3.**

435

436

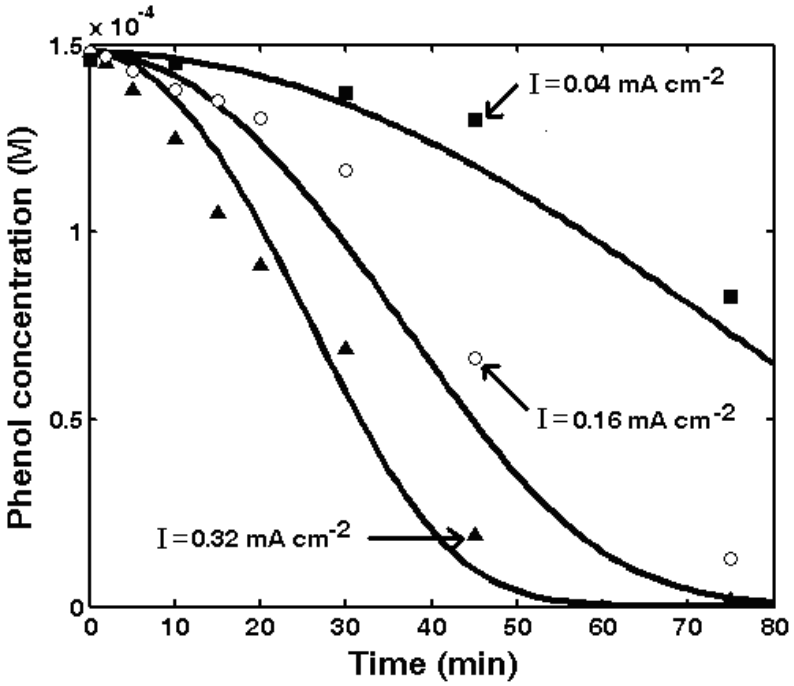
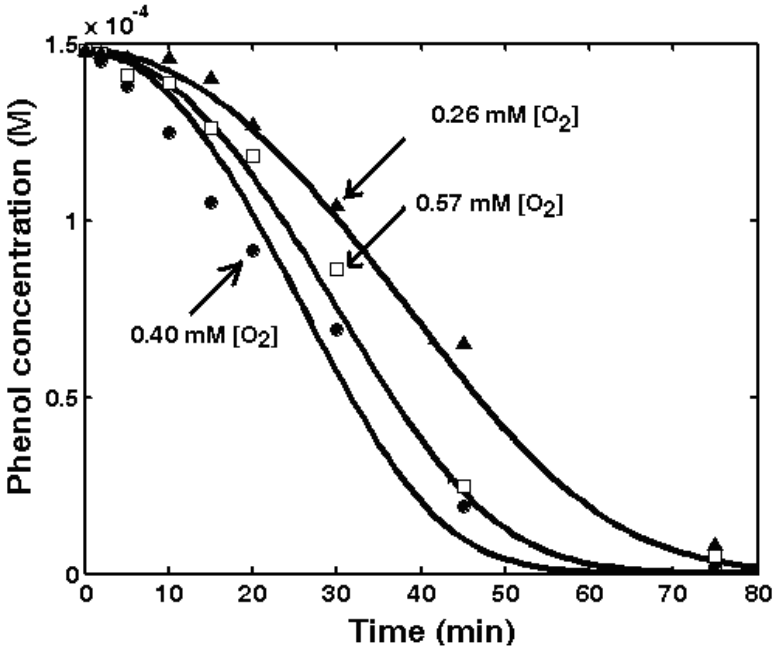

x 10^-4
1.5
1
0.5
0
Phenol concentration (M)
I = 0.04 mA cm^-2
I = 0.16 mA cm^-2
I = 0.32 mA cm^-2
0
10
20
30
40
50
60
70
80
Time (min)

Fig. 4.



447

448

449

450

451

452

453

454

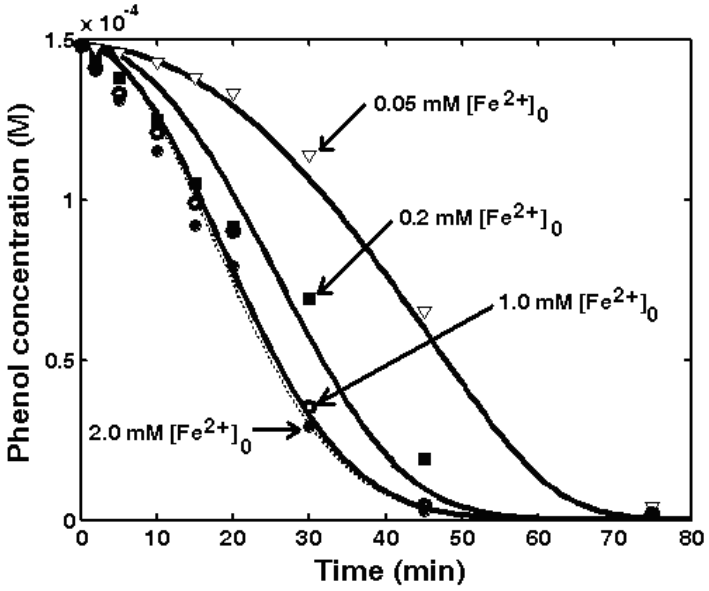
455

456 **Fig. 5**.

457

458

459



460

461

462

463

464 **Fig. 6**.