

Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid

Yanyu Wu^{a,c}, Shaoqi Zhou^{a,b,c,*}, Fanghui Qin^{a,c}, Ke Zheng^{a,c}, Xiuya Ye^{a,c}

^a College of Environmental Science and Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, 510006, PR China

^b State Key Laboratory of Subtropical Building Science, South China University of Technology, Guangzhou, 510641, PR China

^c Key Laboratory of Environmental Protection and Eco-remediation of Guangdong Regular Higher Education Institutions, South China University of Technology, Guangzhou Higher Education Mega Center, 510006, PR China

ARTICLE INFO

Article history:

Received 9 December 2009

Received in revised form 7 February 2010

Accepted 8 March 2010

Available online 12 March 2010

Keywords:

Kinetic model

Fenton

Humic acid

Oxidation

ABSTRACT

The degradation of humic acid (HA) was carried out in the presence of the Fenton reagent. The experiments demonstrated that HA was removed by oxidation and coagulation. Moreover, the oxidation occurred mainly at the first 60 min and predominated the HA removal efficiency. A new kinetic model was established according to the generally accepted mechanism of high active $\cdot\text{OH}$ oxidation in order to well describe the Fenton oxidation reaction in HA aqueous solution. The model embraced two key operating factors affecting the HA degradation in Fenton process, including the dosages of hydrogen peroxide and ferrous ion. The experimental data were fitted by using the most commonly used first- and the second-order reaction models and the new model, respectively. The goodness of fittings demonstrated that the new model could better fit the experimental data than the other two models, which indicated that this analytical model could better describe the kinetics of Fenton reaction mathematically and chemically. Results indicated that the oxidation rate and removal efficiency were strongly dependent on initial pH, initial concentration of Fenton reagents, initial HA concentration and reaction temperature. The experiments demonstrated that hydrogen peroxide and ferrous ion would approach their saturated value with increasing dosage.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Humic substances are a naturally occurring mixture of organic compounds, ubiquitous in nature, which play an important role in both pollutant chemistry and biogeochemistry in aquatic systems [1]. They can generally be subdivided into three fractions: humin, which represents insoluble components in aqueous solutions at all pH values; humic acid (HA), which is soluble in alkaline solution to weakly acidic solutions, but deposits at or below pH 2.0; fulvic acid (FA), which is soluble in aqueous solutions at all pH values [2]. They impart a brown/yellow colour to water, and they are able to bind heavy metals by complexation [3,4]. Moreover, humic substances can interact with low molecular weight pollutants by absorbing them or by forming covalent linkages like ether or ester bonds [1,5]. The most significantly, humic substances are the precursors of mutagenic halogenated compounds in water formed after chlorination [6–8]. Hence, the degradation techniques of humic substances need to be established.

In common water treatment processes, the removal of humic substances has been accomplished by physical separation, such as

coagulation followed by subsequent floc separation, ion exchange, adsorption of activity carbon, and membrane filtration [3,9]. However, the phase transference of pollutants, instead of their elimination, is the main disadvantage associated with those techniques. In the last decades, it has been well proven that Fenton process is one of suitable advanced oxidation processes (AOPs) techniques for refractory HA degradation because of the lack of toxicity of reagents, eventually leaving no residues and the simplicity of the technology [10–12]. During Fenton process, hydrogen peroxide is catalyzed by ferrous ion to produce hydroxyl radicals. The hydroxyl radicals can oxidize HA by abstraction of protons producing highly reactive organic radicals ($\text{R}\cdot$), and the organic radicals can be further oxidized and degraded. However, early works on HA degradation by Fenton oxidation were typically limited in their scopes to the investigation of the influences of process parameters, such as chemical oxygen demand (COD), the amount and the ratio of hydrogen peroxide and iron salt, and pH. In-depth understanding of the degradation kinetics of the process has remained relatively limited until recently.

As we know, the effect of reaction factors should be tested for implementation of Fenton oxidation at a practical level. Moreover, knowledge of the kinetics, reaction rate-law and rate constants obtained are crucial for predicting the performance of factors. Generally, the first-order and second-order reaction models were the

* Corresponding author. Tel.: +86 20 39380579; fax: +86 20 85511266.

E-mail address: fesqzhou@scut.edu.cn (S. Zhou).

most commonly used to describe Fenton reaction [13,14]. However, actually many reactions cannot be simply fitted by the simple order models such as the first- and the second- order models [15]. 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) [16]. This approach may well simulate the experimental data mathematically, but not chemically. In addition, these results have sometimes been controversial. For instance, a number of researchers have suggested that Fenton process is a second-order reaction [17], while others have suggested that it should be a first-order reaction [18]. The reasons for this might be the complexity of the decomposition pathway of hydrogen peroxide by ferrous ion, and of considerable uncertainties concerning various equilibrium and kinetic constants of individual sub-reactions [15,16]. It is necessary to build up a new model which can satisfy the Fenton reaction kinetic description in both ways.

Hence, in this study, a new kinetic model for HA degradation by Fenton oxidation in aqueous solution was established mathematically and chemically according to the generally accepted mechanism of high active $\bullet\text{OH}$ oxidation. The new model was validated and evaluated by the experimental data. Effects of operating parameters such as initial pH, dosages of Fenton's reagents, initial HA concentration and temperature on the degradation of HA have been quantitatively discussed.

2. Experiments

2.1. Reagents

Commercial HA (CAS No. 308067-45-0) was purchased from Shanghai, China and was used as received. The chemical components of HA indicated that the H/C atomic ratio and the O/C atomic ratio were 0.956 and 0.412, respectively. HA was dissolved in 0.1 M sodium hydroxide solution (NaOH, CAS No. 1310-73-2) and then it was separated by 0.45 μm membrane. The filtrate was diluted to a desired concentration ranging from 250 to 1000 mg/L. Analytical grade hydrogen peroxide solution (H_2O_2 , CAS No. 7722-84-1, 30%, w/w) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, CAS No. 7782-63-0) were purchased from Tianjin Chemical Reagents Co., China and were used as received. All other chemicals and solvents were analytical grade and used without further purification.

2.2. Experimental procedure

Fenton reactor was a 2.0-L beaker equipped with a variable mixer and a water jacket for temperature control. Temperature was maintained at pre-determined temperature by circulating the water through the jacket around the reactor. The initial pH value of the HA sample was adjusted to given levels by adding concentrated sulfuric acid (H_2SO_4 , 96%, CAS No. 7664-93-9) or sodium hydroxide solutions (NaOH, 10 M, CAS No. 1310-73-2). After granular ferrous sulfate addition, the reactions were initiated by adding hydrogen peroxide to the solution under vigorous magnetic stirring. At selected time interval, two aliquot of 5 mL reaction mixture were taken and immediately 10 M sodium hydroxide solution were added dropwise to increase the pH over 8.0 to terminate Fenton reaction. Then they were heated in a 55 $^\circ\text{C}$ water bath for 30 min to remove any residual hydrogen peroxide in solution. Subsequently an aliquot sample was brought to room temperature for a 60 min sedimentation period and another aliquot sample was taken to mix uniformly by vigorous magnetic stirring. The precipitated supernatant and the uniformly mixed sample were filtered with 0.45 μm membrane and for analyses. All experiments were repeated at least

three times and averages were reported, while reproducibility of the experiments was within 5%.

2.3. Analyses

UV-HA and TOC methods were used for the measurement of HA concentration [9,19]. Specific UV absorbance of filtered samples was monitored at 254 nm with UV-vis spectrophotometer (Unico UV-2800A, China), which was used to represent aromatic moieties. Additionally, UV/Vis spectrum was recorded from 200 to 650 nm. The progress of mineralization of HA was monitored by measuring the TOC with TOC analyzer (Liquid TOC, Germany). COD was analyzed following the standard method with potassium dichromate [20].

Generally, Fenton's process is composed of following stages: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation [21]. The refractory organic substances are removed at two stages of oxidation and coagulation. It is necessary to isolate and separate that oxidation process from coagulation process, in order to evaluate and quantify the oxidation process respectively. A slight modification of the methods of Kang and Hwang [21] and Deng [22] was used to measure and analyze the parameters of overall removal, removal by oxidation and coagulation. The supernatant was taken to measure as the overall decontamination process—Fenton's oxidation plus coagulation [as $(\text{COD}/\text{TOC}/\text{HA})_{\text{overall}}$]. An aliquot of uniformly solution mixed by continuous stirring with a magnetic stirrer was taken to measure as oxidation removal [as $(\text{COD}/\text{TOC}/\text{HA})_{\text{oxid}}$]. The coagulation removal [as $(\text{COD}/\text{TOC}/\text{HA})_{\text{coag}}$] was the difference between the overall removal value and the oxidation removal value:

$$[(\text{COD}/\text{TOC}/\text{HA})_{\text{coag}} = (\text{COD}/\text{TOC}/\text{HA})_{\text{overall}} - (\text{COD}/\text{TOC}/\text{HA})_{\text{oxid}}]$$

3. Results and discussion

3.1. Degradation performance

Spectroscopic data were compared with those before reaction to clarify the degradation characteristics of HA. The UV-vis absorbance values of HA exhibited a featureless increase with decreasing wavelength (Fig. 1). The absorbance at 200–650 nm decreased with the increase of reaction time as a result of Fenton process. Consequently, it was confirmed that HA could be degraded effectively by Fenton process. Since HA was removed by

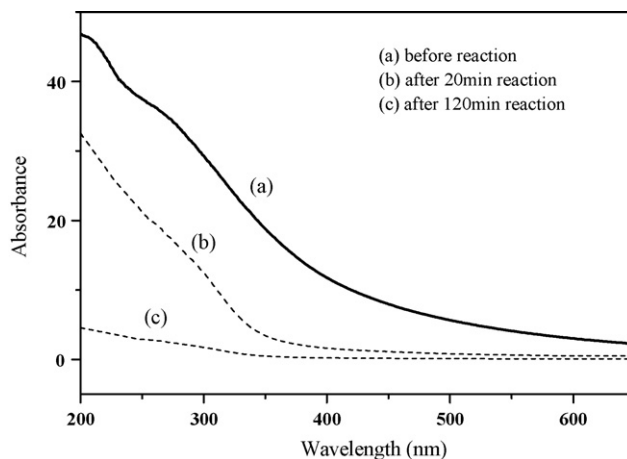


Fig. 1. UV-vis absorption spectra of commercial HA before and after Fenton process. (a) Before reaction; (b) after 20 min and (c) after 120 min (conditions: $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 160 \text{ mM}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$; temperature = 30 $^\circ\text{C}$).

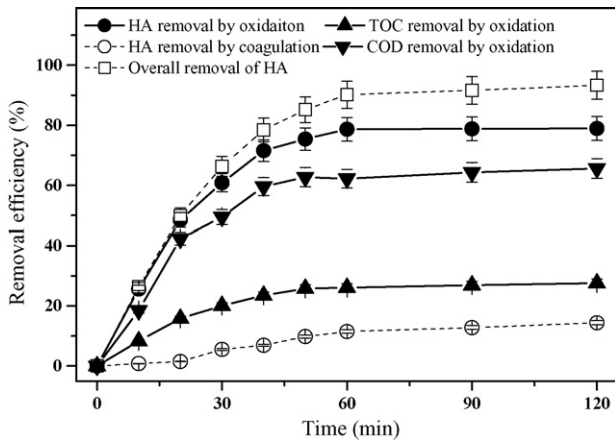


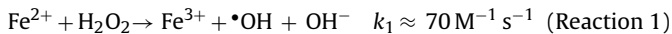
Fig. 2. Removal performance of humic acid (conditions: $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 160 \text{ mM}$; $\text{COD}_0 = 512 \text{ mgO}_2/\text{L}$; $\text{TOC}_0 = 445 \text{ mgC/L}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$; temperature = 30°C). Error bars represent the $\pm\text{SD}$ ($n=5$) for measurements made in triplicate.

both oxidation and coagulation, it was very interesting to observe from Fig. 2 that the oxidation removal of HA was retarded after 60 min, but the overall removal of HA increased due to the coagulation removal increased gradually with extending reaction time. In addition, the results that HA removal by oxidation was greatly four times higher than that by coagulation, which indicated that the oxidation dominated the overall removal. A decrease of TOC indicated that approximately 27.6% of the carbon in HA was mineralized to CO_2 after 2 h of reaction time. It can be seen clearly that the reduction of TOC was approximately three times lower than the reduction of HA, and the reduction of COD was about 20% lower than the HA reduction. Moreover, the COD and TOC oxidation removal kept steady around 24% and 60%, respectively, after 40 min of reaction time, even though HA was still being oxidized. The results implied that HA was not completely oxidized to carbon dioxide during Fenton oxidation but rather transformed to some intermediates which no significant decrease of TOC and COD.

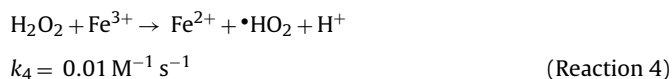
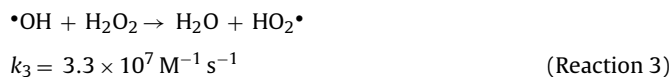
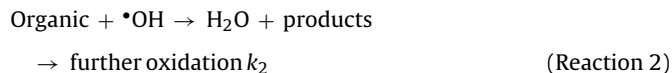
3.2. Kinetic modeling

The reactivity of Fenton system was first observed in 1894 by its inventor H.J.H. Fenton, but its utility was not recognized until the 1930s when a mechanism based on hydroxyl radicals was proposed [23]. It is generally believed that a typical Fenton reaction should involve these key reactions:

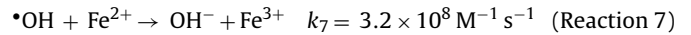
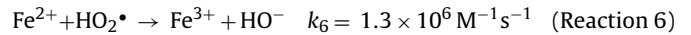
Chain initiation



Chain propagation



Chain termination



Therefore, to establish a new kinetic model for describing Fenton reaction, we may assume that HA is primarily degraded by the $\cdot\text{OH}$. Accordingly, the degradation rate of HA can be expressed:

$$r_{\text{HA}} = -\frac{d[\text{HA}]}{dt} = k_2[\text{HA}][\cdot\text{OH}] \quad (1)$$

Since k_4 , k_5 and k_6 are about one or two order smaller than k_3 and k_7 according to the data in the literature [10], Reactions (4)–(6) can be made unimportant. From Reactions (1)–(3) and (7), the change of $\cdot\text{OH}$ concentration can be shown below:

$$\frac{d[\cdot\text{OH}]}{dt} = k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_2[\text{HA}][\cdot\text{OH}] - k_3[\text{H}_2\text{O}_2][\cdot\text{OH}] - k_7[\cdot\text{OH}][\text{Fe}^{2+}] \quad (2)$$

Based on the pseudo steady state assumption, at a certain time, the concentration of reactive $\cdot\text{OH}$ radical will not vary with reaction time and its change rate was normally considered to approach zero, Eq. (2) can be re-arranged as Eq. (3):

$$[\cdot\text{OH}] = \frac{k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_2[\text{HA}] + k_3[\text{H}_2\text{O}_2] + k_7[\text{Fe}^{2+}]} \quad (3)$$

Substituting Eq. (3) into Eq. (1), we obtain:

$$r_{\text{HA}} = -\frac{d[\text{HA}]}{dt} = k_2[\text{HA}][\cdot\text{OH}] = \frac{k_1 k_2 [\text{HA}][\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_2[\text{HA}] + k_3[\text{H}_2\text{O}_2] + k_7[\text{Fe}^{2+}]} \quad (4)$$

On the other hand, the consumption of H_2O_2 and Fe^{2+} concentration can be expressed by Eqs. (5) and (6):

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_3[\cdot\text{OH}][\text{H}_2\text{O}_2] - k_4[\text{H}_2\text{O}_2][\text{Fe}^{3+}] \quad (5)$$

$$\frac{d[\text{Fe}^{2+}]}{dt} = -k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] + k_4[\text{Fe}^{3+}][\text{H}_2\text{O}_2] + k_5[\text{Fe}^{3+}][\text{HO}_2\cdot] - k_6[\text{Fe}^{2+}][\text{HO}_2\cdot] - k_7[\text{Fe}^{2+}][\cdot\text{OH}] \quad (6)$$

Since k_1 , $k_4 \ll k_3$ and k_6 , $k_5 \ll k_7$ [10,13], Eqs. (5) and (6) can be simplified as Eqs. (7) and (8).

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_3[\cdot\text{OH}][\text{H}_2\text{O}_2] \quad (7)$$

$$\frac{d[\text{Fe}^{2+}]}{dt} = -k_7[\cdot\text{OH}][\text{Fe}^{2+}] \quad (8)$$

Since $\cdot\text{OH}$ is a highly reactive free radical with an extremely short lifetime of nanoseconds [24], its concentration is normally considered to be constant but at a low level, the residual concentration of hydrogen peroxide and ferrous ion in the reaction solution depends on its initial concentration and consumption rate. They can be eventually expressed as Eqs. (9) and (10).

$$[\text{H}_2\text{O}_2] = e^{-\lambda_1 t} [\text{H}_2\text{O}_2]_0 \quad (9)$$

$$[\text{Fe}^{2+}] = e^{-\lambda_2 t} [\text{Fe}^{2+}]_0 \quad (10)$$

where $\lambda_1 = k_3[\cdot\text{OH}]$, $\lambda_2 = k_7[\cdot\text{OH}]$, $[\text{H}_2\text{O}_2]_0$, $[\text{Fe}^{2+}]_0$ and $[\text{H}_2\text{O}_2]$, $[\text{Fe}^{2+}]$ represent the initial concentration ($t=0$) and the residual concentration ($t=t$) of hydrogen peroxide and ferrous ion, respectively. According to k_3 , $k_7 > 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, assuming that

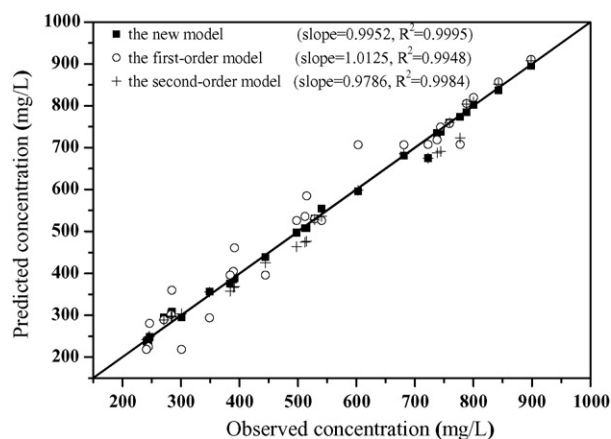


Fig. 3. Relationship between observed and predicted residual HA concentration of the first-order model, the second-order model and the new model.

$(k_3 e^{-\lambda_1 t} [\text{H}_2\text{O}_2]_0 + k_7 e^{-\lambda_2 t} [\text{Fe}^{2+}]_0)$ can keep constant, and using Eqs. (9) and (10) to replace the $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$ in Eq. (4), the rate of HA can be further expressed as follows:

$$r_{\text{HA}} = -\frac{d[\text{HA}]}{dt} = k_2 [\text{HA}] [\cdot\text{OH}]$$

$$= \frac{k_1 k_2 e^{-\lambda_1 t} e^{-\lambda_2 t} [\text{Fe}^{2+}]_0 [\text{H}_2\text{O}_2]_0}{k_2 [\text{HA}] + k_3 [\text{H}_2\text{O}_2]_0 + k_7 [\text{Fe}^{2+}]_0} \cdot [\text{HA}] \quad (11)$$

After integration, the $[\text{HA}]$ becomes a function of experimental time, decreasing from $[\text{HA}]_0$ at the beginning of reaction ($t=0$) gradually as described by Eq. (12):

$$\left(\frac{k_3 [\text{H}_2\text{O}_2]_0 + k_7 [\text{Fe}^{2+}]_0}{k_1 k_2 [\text{H}_2\text{O}_2]_0} \right) \ln \frac{[\text{HA}]_0}{[\text{HA}]} + \frac{1}{k_1 [\text{H}_2\text{O}_2]_0} ([\text{HA}]_0 - [\text{HA}])$$

$$= \frac{1}{(\lambda_1 + \lambda_2)} (1 - e^{-(\lambda_1 + \lambda_2)t}) \quad (12)$$

This equation demonstrates that $[\text{HA}]$ in Fenton reaction depends on two factors of $[\text{H}_2\text{O}_2]_0$ and $[\text{Fe}^{2+}]_0$. Eq. (12) can be re-arranged in a simplified form as follows:

$$b \ln \frac{[\text{HA}]_0}{[\text{HA}]} + a([\text{HA}]_0 - [\text{HA}]) = \frac{1}{c} (1 - e^{-ct}) \quad (13)$$

where $a = 1/(k_1 [\text{H}_2\text{O}_2]_0)$, $b = (k_3 [\text{H}_2\text{O}_2]_0 + k_7 [\text{Fe}^{2+}]_0)/k_1 k_2 [\text{H}_2\text{O}_2]_0$, $c = \lambda_1 + \lambda_2$.

Eqs. (12) and (13) show that the main kinetic model for Fenton reaction to describe the degradation of HA in aqueous solution against reaction time has been established.

3.3. Validation of the new kinetic model

A set of experiments were carried out in aqueous HA solution to validate the new model for its application in Fenton reaction system by varying hydrogen peroxide and ferrous ion dosages, as well as initial HA concentration, respectively. Each experiment with initial pH 4.0 lasted for up to 120 min at 30 °C temperature. Fig. 3 depicts the comparisons between the observed and predicted residual concentration of HA by using the first-order model, the second-order model and the new model, respectively. The linear regression for the first-order model, the second-order model and the new model with the slope of 1.0125, 0.9786, 0.9952 and R^2 of 0.9948, 0.9984, 0.9995, respectively, indicated that the new model was the most justified.

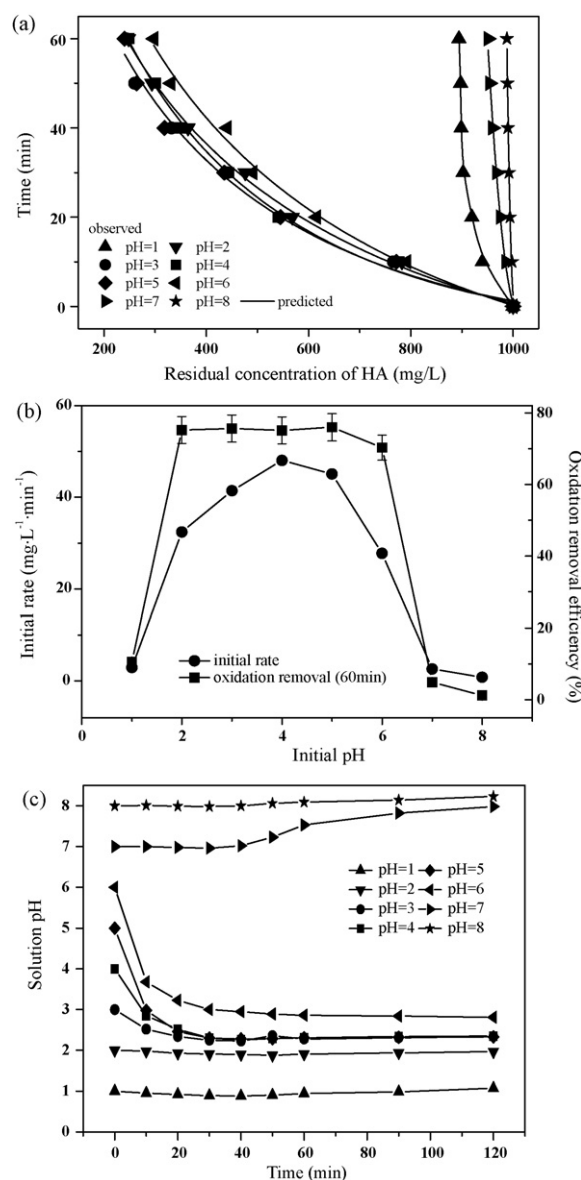


Fig. 4. The effect of initial pH (a) HA degradation during Fenton reaction fitted by the new kinetic model; symbols and lines represent the measured data and the fit of the hypothetical reaction model, respectively; (b) initial rate and oxidation removal efficiency; (c) solution pH (conditions: $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 120 \text{ mM}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$; temperature = 30 °C). Error bars represent the $\pm\text{SD}$ ($n=5$) for measurements made in triplicate.

3.4. Kinetic studies

In this study, oxidation degradation kinetic of HA in Fenton process was performed by using an initial rate technique in order to eliminate any interferences from intermediate competition.

3.4.1. The role of initial pH

The experiments were performed in the initial pH range of 1.0–8.0. It can be seen clearly in Fig. 4(a) that the new model can well describe the variation of residual HA concentration at various initial pH. Both the experimental data and the model simulation showed that initial pH significantly influenced the HA degradation. As shown in Fig. 4(b), the oxidation degradation rate quickly increased when the initial pH increased from 1.0 to 3.0, subsequently it kept constant when the initial pH was raised from 3.0 to 5.0, and then dropped off sharply with the increase of pH higher

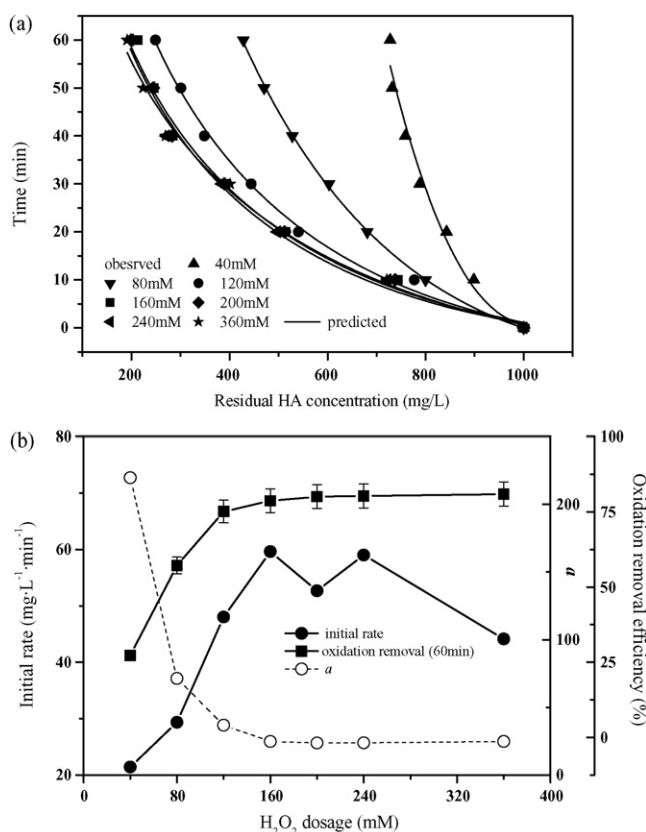


Fig. 5. The effect of H₂O₂ dosage on (a) HA degradation during Fenton reaction fitted by the new kinetic model; (b) initial rate and model parameter *b* (conditions: initial pH 4.0; [Fe²⁺]₀ = 40 mM; [H₂O₂]₀ = 120 mM; [HA]₀ = 1000 mg/L; temperature = 30 °C). Error bars represent the ±SD (*n* = 5) for measurements made in triplicate.

than 5.0. Such an initial pH range is clearly in accordance with that suggested in the literature as being the ideal initial pH for Fenton oxidation of many chemicals [25]. In addition, the oxidation removal efficiency progressed at a higher value at initial pH 2.0–5.0. As the initial pH was raised above 7.0, HA showed resistance to degradation due to the coagulation of Fe³⁺ complex molecules inhibited the catalytic reaction of Fe²⁺ ions with the oxidants. At a pH below 2, the contributing factors for the low reaction rate may be due to the formation of oxonium ion (i.e. H₃O₂⁺) [26], complex species [Fe(H₂O)₆]²⁺ and [Fe(H₂O)₆]³⁺ [27], as well the enhancement of •OH scavenging by H⁺ [28]. The changes of solution pH values during Fenton oxidation process are presented in Fig. 4(c). The solution pH dropped rapidly to around 2.5 under initial pH values 3.0–6.0, and then pH reached a steady state for the remaining time. The changes of pH could be explained by two reasons: firstly, the hydrolysis of ferrous sulfate caused the pH to drop; secondly, low-molecule weight organic acids produced by decomposition of organic pollutants and other organic compounds could lead to the rapid pH fluctuation. Some similar results have been proved in other researchs on Fenton oxidation [29,30]. The initial pH of 4.0 was selected for further experiments.

3.4.2. The role of H₂O₂ dosage

The dosage of hydrogen peroxide plays a very important role in the degradation of HA wastewater in Fenton process. Fig. 5 presents the effect of hydrogen peroxide dosage from 40 to 360 mM on the HA degradation for fixed initial concentrations of HA and ferrous ion of 1000 mg/L and 40 mM, respectively. The HA degradation profiles in the presence of different concentrations of hydrogen peroxide followed the new kinetic model with *R*² value higher than

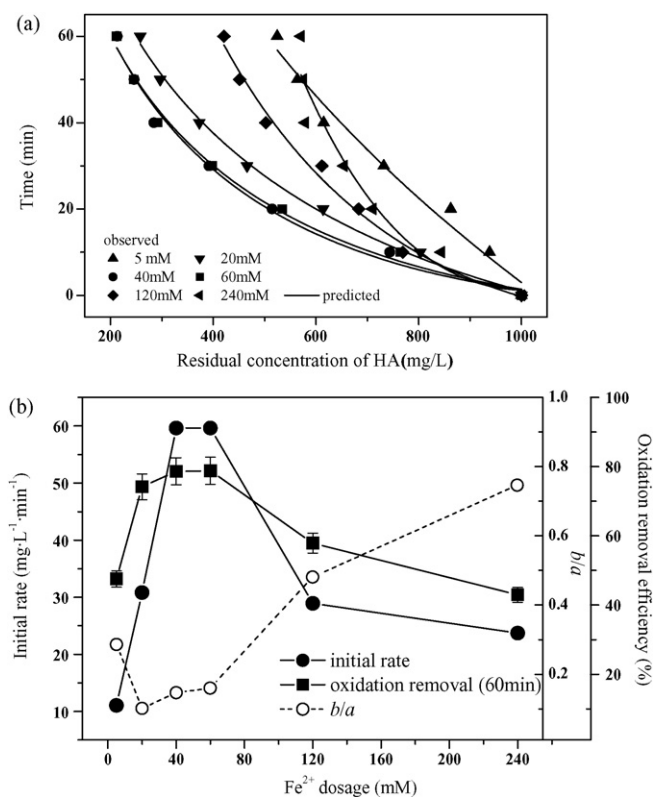


Fig. 6. Effect of Fe²⁺ on (a) HA degradation during Fenton reaction fitted by the new kinetic model; (b) initial rate, model parameter *b/a* and oxidation removal efficiency (condition: initial pH 4.0; [H₂O₂]₀ = 160 mM; [HA]₀ = 1000 mg/L; temperature = 30 °C). Error bars represent the ±SD (*n* = 5) for measurements made in triplicate.

0.99 (Fig. 5(a)). Judging from Fig. 5(b), at a fixed ferrous dosage, generally the higher the hydrogen peroxide dosage, the faster and higher the HA degradation. The enhancement of degradation is due to the addition of hydrogen peroxide increased the production of •OH radicals by Reaction (1). However, when the value of hydrogen peroxide dosage was over 160 mM, the degradation rate was almost unchanged or even decreased. The results implied that hydrogen peroxide was present in excess in the system with hydrogen peroxide dosage above 160 mM. This is possibly due to hydrogen peroxide in high concentration acted as a scavenger of the •OH radicals to produce perhydroxyl radicals (•OOH), which had much lower oxidation capabilities than hydroxyl radicals (•OH) (Reaction (3)). Almost no degradation of HA occurred without ferrous ion.

The lumped parameter *a* is defined as $a = 1/(k_1[\text{H}_2\text{O}_2]_0)$. In this lumped parameter, *k*₁ is invariant under the evaluated experimental conditions, so the variables in *a* are [H₂O₂]₀. It could be observed in Fig. 5(b) that *a* value decreased with the increase of hydrogen peroxide dosage up to 160 mM. Increasing hydrogen peroxide dosage from 160 to 360 mM did not show significantly the change of the *a* value. The 160 mM dosage of hydrogen peroxide corresponding to the minimum *a* value was consistent with its critical excess hydrogen peroxide concentration in system as had been discussed above. Therefore, the trend of *a* value as a function of hydrogen peroxide concentration was most likely responsible for the saturation of hydrogen peroxide.

3.4.3. The role of Fe²⁺ dosage

The amount of catalysts is one of the main parameters for the HA degradation process. An increase of Fe²⁺ supplement was supposed to accelerate the •OH generation rate and should consequently

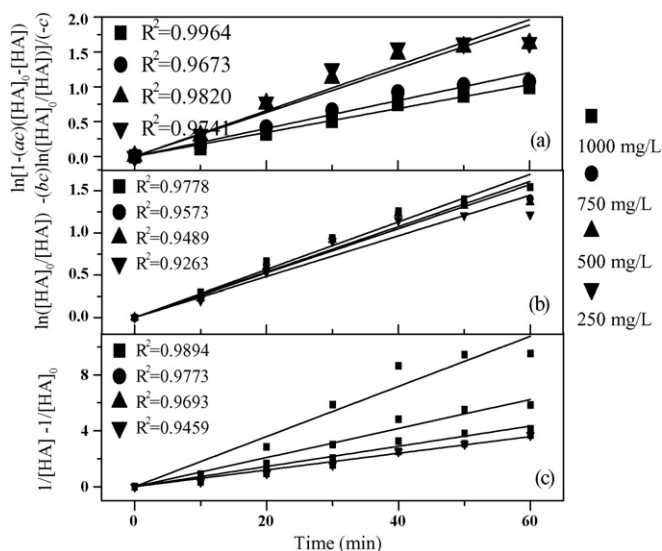


Fig. 7. Effect of initial HA concentration on the linear relationship of oxidation degradation during Fenton reaction (a) the new kinetics model; (b) the first-order model; and (c) the second-order model (condition: initial pH 4.0; $[\text{H}_2\text{O}_2]_0 = 160 \text{ mM}$; $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$; temperature = 30°C).

enhance the oxidation rate of HA. As can be seen in Fig. 6, the higher the Fe^{2+} dosage, the faster the HA degradation rate until the limiting Fe^{2+} concentration of 60 mM while other constituents remained constant. The efficiency of oxidation removal was drastically improved from 47.5% to 74.2% after 60 min reaction, while the Fe^{2+} dosage increased from 5 to 20 mM. It was noted that the limiting Fe^{2+} concentration of 60 mM was found to be a turning point for the enhancement of HA degradation reaction under our experimental condition. Above the concentration of 60 mM, an abrupt decrease of degradation was observed, i.e., the oxidation rate decreased almost one half and the oxidation removal efficiency reduced 30%. These were due to higher Fe^{2+} concentrations favoured the occurrence of the scavenging reaction (Reactions (6) and (7)). These results indicated clearly that there must be an optimum ferrous ion concentration in Fenton reaction. The fitting parameter $b/a = (k_3[\text{H}_2\text{O}_2]_0 + k_7[\text{Fe}^{2+}]_0)/k_2$ was a function only of $[\text{Fe}^{2+}]_0$ if the $[\text{H}_2\text{O}_2]_0$ concentration was fixed. As shown in Fig. 6 (b), b/a decreases with the increase of $[\text{Fe}^{2+}]_0$ from 5 to 40 mM significantly, and changes slightly while further enhanced $[\text{Fe}^{2+}]_0$ up to 60 mM. These results further confirmed that there was a critical concentration of $[\text{Fe}^{2+}]_0$ around 40–60 mM. The 40 mM Fe^{2+} was thought to be a suitable concentration to achieve an efficient rate of HA degradation under our experimental condition considering two adverse factors: the corresponding disposal costs increased according to the amount of $\text{Fe}(\text{OH})_3$ sludge, as well as the initial investment costs increased according to the increasing reaction time.

3.4.4. The role of initial HA concentration

The effect of initial HA concentration on the oxidation rate was studied at various HA concentration of 250, 500, 750 and 1000 mg/L of HA with fixed 160 mM of hydrogen peroxide and 40 mM of ferrous ion. The experimental data were fitted using the first-order model, the second-order model and the new model, respectively. Fig. 7 presents the results of fittings in a linear form of the two simple order models and our new model of $\ln[1 - (ac)([\text{HA}]_0 - [\text{HA}]) - (bc)\ln([\text{HA}]_0/[\text{HA}])]/(-c)$ vs. time. The correlation coefficients for fitting by the new model were much higher than those by the two simple order models. Furthermore, it was seen from Fig. 8 that the initial oxidation degradation rate was accelerated as the initial HA concentration increased. Possible

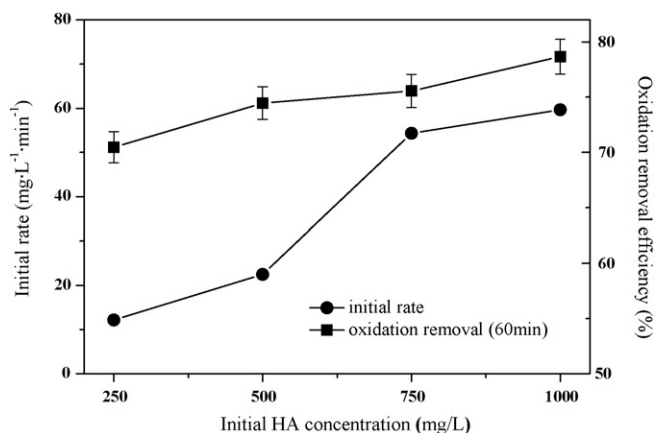


Fig. 8. Effect of initial HA at the initial rate and the oxidation removal efficiency (condition: initial pH 4.0; $[\text{H}_2\text{O}_2]_0 = 160 \text{ mM}$; $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$; temperature = 30°C). Error bars represent the $\pm\text{SD}$ ($n = 5$) for measurements made in triplicate.

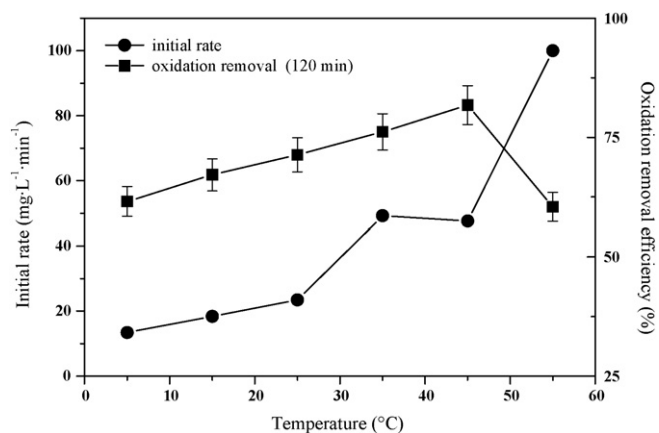


Fig. 9. Effect of temperature on the initial rate and oxidation removal efficiency (condition: initial pH 4.0; $[\text{H}_2\text{O}_2]_0 = 120 \text{ mM}$; $[\text{Fe}^{2+}]_0 = 40 \text{ mM}$; $[\text{HA}]_0 = 1000 \text{ mg/L}$). Error bars represent the $\pm\text{SD}$ ($n = 5$) for measurements made in triplicate.

explanation for this observation was that higher HA concentration increased the ability of HA to compete with Fe^{2+} for $\bullet\text{OH}$. A similar trend was found by Ntampeliotis et al. [31]. However, the initial rate increased slightly at extremely high initial HA. As the initial HA concentration increased from 500 to 750 mg/L, the initial rate increased 141.7%; whereas only 9.8% of initial rate increment was achieved as the initial HA concentration enhanced from 750 to 1000 mg/L. This was due to the fact that a relative lower concentration of $\bullet\text{OH}$ resulted from the increasing concentration of HA but the same dosage of hydrogen peroxide and ferrous ion, which slowed down the oxidation rate of HA.

3.4.5. The role of temperature

Temperature is one of the important factors influencing oxidation reaction. A series of experiments were conducted at 5, 15, 25, 35, 45 and 55°C at 4.0 of initial pH, 120 mM of hydrogen peroxide dosage and 40 mM ferrous ion dosage. The results are shown in Fig. 9. As can be seen, temperature has a positive impact on the oxidation degradation rate of HA. The oxidation removal efficiency increased from 61% to 81% linearly when the temperature increased up to 45°C . Increasing the temperature from 45 to 55°C reduced the yield of the process. This could be explained that increasing temperature had two opposite effects on the reaction yield. On one hand, higher temperature enhanced the generation rate of $\bullet\text{OH}$ and therefore enhanced the oxidation efficiency of HA. On the other

hand, extremely high temperature over 55 °C started to accelerate the hydrogen peroxide decomposition into oxygen and water significantly, so the HA oxidation efficiency declined.

4. Conclusions

In this study, a new model could satisfy the kinetic description of the degradation of HA in Fenton process in both mathematical and chemical ways according to the generally accepted oxidation mechanism of hydroxyl radicals. In addition, it could be suggested that the fitting parameter a was most likely related to the effect of $[H_2O_2]_0$, and b/a reflected the effect of $[Fe^{2+}]_0$. The rate equations for HA degradation by Fenton process, which account for the •OH scavenging effects, matched experimental results at wider Fenton reagent's dosages, initial HA concentration and reaction temperature comparing with the first- and second- order models. However, the new model was only validated by the experiments of HA degradation so far. Further studies to apply this kinetic model in degradation of other organics become necessary.

Acknowledgements

The authors are grateful to Professor Yingyuan Li from School of Foreign Languages, South China University of Technology for his help and would like to acknowledge assistance from staffs that provided full support to this study. The Ministry of Science and Technology of China is also acknowledged for their financial support (2008BAE64B05). In addition, the kind suggestions from the anonymous reviewers are greatly acknowledged.

References

- [1] F.J. Gobbels, W. Puttmann, Structural investigation of isolated aquatic fulvic and humic acids in seepage water of waste deposits by pyrolysis gas chromatography mass spectrometry, *Water Res.* 31 (1997) 1609–1618.
- [2] L.E. Bennett, M. Drikas, The evaluation of colour in natural waters, *Water Res.* 27 (1993) 1209–1218.
- [3] H. Katsumata, M. Sada, S. Kaneco, T. Suzuki, K. Ohta, Y. Yobiko, Humic acid degradation in aqueous solution by the photo-Fenton process, *Chem. Eng. J.* 137 (2008) 225–230.
- [4] D. Imai, A.H.A. Dabwan, S. Kaneco, H. Katsumata, T. Suzuki, T. Kato, K. Ohta, Degradation of marine humic acids by ozone-initiated radical reactions, *Chem. Eng. J.* 148 (2009) 336–341.
- [5] F.D. Kopinke, J. Pfrschermann, U. Stottmeister, Sorption of organic pollutants on anthropogenic humic matter, *Environ. Sci. Technol.* 29 (1995) 941–950.
- [6] J.J. Rook, Chlorination reactions of fulvic acids in natural waters, *Environ. Sci. Technol.* 11 (1977) 478–482.
- [7] J. Hemming, B. Holmborn, M. Reunanen, L. Kronberg, Determination of strong mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H) furanone in chlorinated drinking and humic water, *Chemosphere* 15 (1986) 549–556.
- [8] H. Zhang, J.H. Qu, H.J. Liu, X. Zhao, Characterization of isolated fractions of dissolved organic matter from sewage treatment plant and the related disinfection by-products formation potential, *J. Hazard. Mater.* 164 (2009) 1433–1438.
- [9] S. Park, T.I. Yoon, The effects of iron species and mineral particles on advanced oxidation processes for the removal of humic acids, *Desalination* 208 (2007) 181–191.
- [10] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [11] F.L. Palmer, B.R. Eggins, H.M. Coleman, The effect of operational parameters on the photocatalytic degradation of humic acid, *J. Photochem. Photobiol. A—Chem.* 148 (2002) 137–143.
- [12] M.J. Farre, X. Domenech, J. Peral, Combined photo-Fenton and biological treatment for Diuron and Linuron removal from water containing humic acid, *J. Hazard. Mater.* 147 (2007) 167–174.
- [13] F. Fu, Q. Wang, B. Tang, Effective degradation of C.I. Acid Red 73 by advanced Fenton process, *J. Hazard. Mater.* 174 (2010) 17–22.
- [14] T.M. Elmorsi, Y.M. Riyad, Z.H. Mohamad, H.M.H. Abd El Bary, Decolorization of Mordant red 73 azo dye in water using H_2O_2/UV and photo-Fenton treatment, *J. Hazard. Mater.* 174 (2010) 352–358.
- [15] H. Liu, X.Z. Li, Y.J. Leng, C. Wang, Kinetic modeling of electro-Fenton reaction in aqueous solution, *Water Res.* 41 (2007) 1161–1167.
- [16] W. Chu, K.H. Chan, C.Y. Kwan, K.Y. Choi, Degradation of atrazine by modified stepwise-Fenton's processes, *Chemosphere* 67 (2007) 755–761.
- [17] J. De Laat, H. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling, *Environ. Sci. Technol.* 33 (1999) 2726–2732.
- [18] H. Gallard, J. De Laat, Kinetics of oxidation of chlorobenzenes and phenyl-ureas by Fe(II)/ H_2O_2 and Fe(III)/ H_2O_2 . Evidence of reduction and oxidation reactions of intermediates by Fe(II) or Fe(III), *Chemosphere* 42 (2001) 405–413.
- [19] G.S. Wang, S.T. Hsieh, Monitoring natural organic matter in water with scanning spectrophotometer, *Environ. Int.* 26 (2001) 205–212.
- [20] APHA, Standard Methods for the Examination of Water and Wastewater, 21th ed., American Public Health Association, Washington, DC, 2005.
- [21] Y.W. Kang, K.Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res.* 34 (2000) 2786–2790.
- [22] Y. Deng, Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate, *J. Hazard. Mater.* 146 (2007) 334–340.
- [23] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [24] D.X. Liu, J. Liu, J. Wen, Elevation of hydrogen peroxide after spinal cord injury detected by using the Fenton reaction, *Free Radical Biol. Med.* 27 (1999) 478–482.
- [25] A. Guedes, L.M.P. Madeira, R.A.R. Boaventura, C.A.V. Costa, Fenton oxidation of cork cooking wastewater—overall kinetic analysis, *Water Res.* 37 (2003) 3061–3069.
- [26] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of p-chlorophenol oxidation by Fenton's reagent, *Water Res.* 33 (1999) 2110–2118.
- [27] S.H. Bossmann, E. Oliveros, S. Gob, S. Siegwart, E.P. Dahlen, L. Payawan, M. Straub, M. Worner, A.M. Braun, New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced fenton reactions, *J. Phys. Chem. A* 102 (1998) 5542–5550.
- [28] J.Y. Feng, X.J. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Degradation of azo-dye Orange II by a photoassisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst, *Ind. Eng. Chem. Res.* 42 (2003) 2058–2066.
- [29] Y. Zhong, X. Jin, R. Qiao, X. Qi, Y. Zhuang, Destruction of microcystin-RR by Fenton oxidation, *J. Hazard. Mater.* 167 (2009) 1114–1118.
- [30] A.A. Burbano, D.D. Dionysiou, M.T. Suidan, T.L. Richardson, Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent, *Water Res.* 39 (2005) 107–118.
- [31] L. Nunez, J.A. Garcia-Hortal, F. Torrades, Study of kinetic parameters related to the decolorization and mineralization of reactive dyes from textile dyeing using Fenton and photo-Fenton processes, *Dyes Pigments* 75 (2007) 647–652.