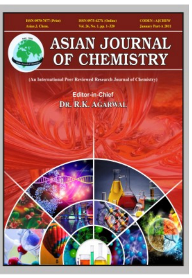
Asian Journal of Chemistry; Vol. 26, No. 3 (2014), 860-864

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15901



Kinetics of Degradation of 4-Chlorophenol by Fenton Oxidation

SHUANGXI NIE, ZHENGMEI WU, SHUANGQUAN YAO, XINLIANG LIU,
HAINONG SONG, ZHEN FANG, XINYU WANG and SHUANGFEI WANG*

College of Light Industry and Food Engineering, Guangxi University, Guangxi, P.R. China

*Corresponding author: E-mail: wangsf@gxu.edu.cn

Received: 12 June 2013; *Accepted*: 29 August 2013; *Published online*: 30 January 2014; AJC-14654

In this paper, the degradation of 4-chlorophenol contaminated water by Fenton process was investigated. It was found that 4-chlorophenol could be removed efficiently by Fenton process, and rapidly be degraded into low molecular weight organics under an optimum concentration of hydrogen peroxide to ferrous sulfate ($[H_2O_2]/[FeSO_4]$) molar ratio of 20:1.Based on the reaction characteristics of the contaminant oxidized by Fenton, degradation kinetics model of 4-chlorophenol was constructed, kinetics equation of 4-chlorophenol degradation was eventually obtained through experiments, which could be expressed as: $dW/dt = kC_{H_2O_2}^{0.282} W^{-0.273}$, where: dW/dt is the reaction rate, k is the rate constant, $C_{H_2O_2}$ is the concentration of H_2O_2, W is the concentration decrease of 4-chlorophenol. The results showed that the reaction rate could be significantly increased when the concentration of H_2O_2 increased, and temperature increased in favor of the degradation of 4-chlorophenol. The reaction mechanisms of degradation of 4-chlorophenol were analyzed based on the kinetics equation, and the entire degradation process could be divided into two stages of rapid reaction and slow reaction.

Keywords: 4-Chlorophenol, Fenton, Kinetics model, Reaction mechanism.

INTRODUCTION

Phenolic compounds is highly toxic material in papermaking wastewater and is potential toxicity of carcinogenic, teratogenesis and mutagenic. The growth and reproduction of aquatic life will be seriously affected by the phenolic compounds, as well as the drinking water sources[1,2], so strict rules must exist for the discharging of phenolic compounds industrial wastewater[3]. Standards of global pulp and paper industry wastewater discharging increasingly strict and the traditional physico-chemical and biochemical secondary treatment process has been difficult to meet the new emission standards[4]. Fenton as a new advanced oxidation technology, have advantages of simple operation, rapid response and flocculation automatically generate and is efficient for the treatment of high concentration, biodegradable, toxic and hazardous wastewater, such as phenol, chlorophenol, chlorobenzene, nitrobenzene and aniline[3,5] and has been widely used in the treatment of industrial wastewater.

The core of the Fenton advanced oxidation technology is the strong oxidant hydroxyl radical (·OH) that generate during the reaction by chemical or physical methods[6,7], the ·OH is provided with high electronegativity and electron affinity (569.3 kJ) and the attack of ·OH in a certain degree of selectivity, which makes it easy to attack the high intensive electron cloud[8]. Furthermore, addition reaction can be also easy to happen when ·OH exists and addition reaction will be occurred when double bond exists, unless there are highly reactive C-H bond in the attack molecules[9], then the pollutants are mineralized completely or conversion to low toxicity and readily biodegradable products.

To provide guidance to the adhibition of sewage water oxidation by Fenton system, developing a kinetic model, containing the key reactions of Fenton oxidation is apparently important. The kinetic models of 4-chlorophenol by Fenton system have been presented. Early studies[10,11] had established the relationship between the concentration of Fenton reagent and the apparent kinetic rate constants in a given context, but most of them were based on the reaction equation and assuming the initial reactant mathematical model was established with the first order reaction.

The objective of this paper is to establish a macro-kinetics model that describes the reactions relevant in the degradation of 4-chlorophenol by the Fenton process. The experimental method used in Pontes and Pinto[12] is applied to present research work. First, a model containing some unknown variables is developed to describe the reactions relevant in the degradation of 4-chlorophenol by the Fenton process, then unknown parameters are solved out through experiments and the kinetics model is employed to determine how fast these reactions occur.

EXPERIMENTAL

4-Chlorophenol with a purity of 99 % was supplied by Sigma Aldrich Chemicals, Germany and used without further purification. Hydrogen peroxide with a concentration of 30 % was provided by Chuandong chemical, China. Ferrous sulfate was purchased from Kelong chemical, China and was employed as a source of ferrous ion. All other chemicals used in this study were analytical grade.

Experimental setup: One liter sewage water containing 40 mg 4-chlorophenol was added into a flask, which was put in a thermostatic bath (T = 298 K)[13]. Ferrous sulfate was added into the flask first, the pH value of solution was adjusted by concentrated sulfuric acid, when it was stabled at around 4.0, hydrogen peroxide was added to initiate the reaction. At predetermined time intervals, samples were taken from the beaker for analysis[14].

Analysis methods: Analyses of residual 4-chlorophenol was carried out by HPLC using a Agilent system (America). It was equipped with an UV detector setting at a wavelength of 275 nm for the analysis of 4-chlorophenol. A Supelco C-18 reversed phase column (L: 25 cm, ID: 4.6 mm, particle size: 5 μm) was used. The mobile phase was a mixture of methanol (60 %) and deionized water (40 %). The flow rate of mobile phase was set at 1 mL/min. Under the analytical conditions, the retention time of 4-chlorophenol was 12.5 ± 0.1 min[1]. 1.0 mL 1.0 M *tert*-butyl alcohol was added to the sample to prevent the potential reaction of 4-chlorophenol and the aromatic intermediates with hydroxyl radical[13].

RESULTS AND DISCUSSION

Kinetics of 4-chlorophenol degradation

Mathematical model of kinetics equation: Chemical kinetics is employed to study the reaction rate and impacts of various factors of the reaction system to it. By means of the determination of the kinetics equation, the reaction mechanism are understood and then a realistic process of the reaction is proposed, in order to achieve the purpose of degradation process controlling. The parameters that affect the reaction rate of reaction temperature, concentration of 4-chlorophenol, hydrogen peroxide and ferrous sulfate in the degradation of 4-chlorophenol by Fenton. Studying of Fenton oxidizer indicates that, concentration of hydrogen peroxide and ferrous sulfate effect on the reaction rate needn't to be considered in isolation when $[H_2O_2]/[Fe^{2+}]$ participated in a given value in the reaction[15]. Effect of Fenton reagent on the reaction rate are considered only and the experimental is designed according to the process conditions above. Thus, the kinetics equation mathematical model of 4-chlorophenol oxidized by Fenton can be expressed as follows:

$$\frac{dW}{dt} = kC^{a}_{H_2O_2} W^{b} \tag{1}$$

where dW is the concentration difference value of 4-chlorophenol to the initial concentration, dt is the reaction time, dW/dt is the reaction rate, a and b are the reactant orders determined from experiment, $C_{H_2O_2}$ is the concentration of H_2O_2, W is the concentration decrease of 4-chlorophenol, k is the rate constant and $k = Ae^{-E/RT}$ (where in A is known the frequency or pre pre-exponential factor, E is the activation energy, R is the ideal-gas constant (8.314 J/mol), T is the temperature in K)

Constant determination of the kinetics equation

Determination of the constant b: Fenton reagent constantly added was employed to maintain a constant value of the concentration of each chemical during the degradation, where the initial concentration of 4-chlorophenol of 40 mg/L, initial concentration of H_2O_2 of 20 mmol/L and $FeSO_4$ of 1 mmol/L and then each unknown constant were found out. Under the conditions of the reaction temperature, pH, initial concentration of H_2O_2, $FeSO_4$ and 4-chlorophenol remained unchanged, relationship between concentration decrease of 4-chlorophenol and reaction time are shown in Table-1.

At this moment, in eqn. 1, suppose that $k_1 = kC^{a}_{H_2O_2}$, the reaction rate can be determined by eqn. 2 in the above conditions.

$$\frac{dW}{dt} = k_1 W^{b} \tag{2}$$

For convenience of calculation and expression, logarithm are taken at the both sides of eqn. 2 at the same time, which is shown as following

$$\log\left(\frac{dW}{dt}\right) = b \log W + \log k_1 \tag{3}$$

A linear regression is taken when log (dW/dt) as the y-coordinate and log W as the x-coordinatethe line relationship between log (dW/dt) and log W as shown in Fig. 1, from the slope of the line fitted, the value of constant 'b' can be obtained as -0.273.

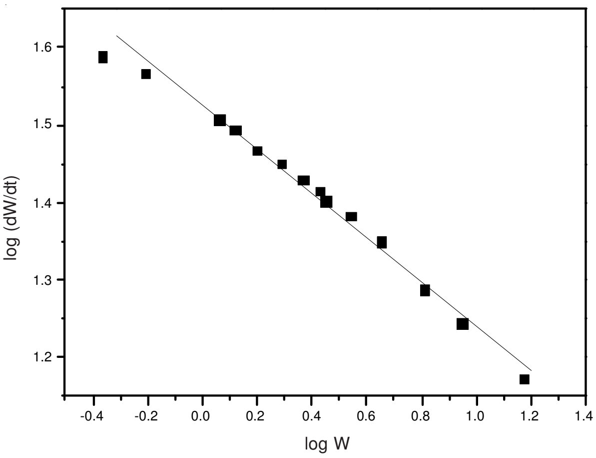


Fig. 1. Line relationship between log (dW/dt) and log W

TABLE-1
RELATIONSHIP BETWEEN CONCENTRATION DECREASE OF 4-CHLOROPHENOL AND REACTION TIME

Reaction time (min)		1	2	3	5	7	9	10	12	15	20	25	30	60	90
Concentration decrease of 4-chlorophenol (mg/L)	1	15.04	17.82	19.15	22.49	23.83	24.98	26.27	27.07	27.87	29.28	30.61	32.39	37.12	37.99
	2	14.95	17.19	19.36	22.66	23.97	24.95	26.44	26.81	27.99	29.42	31.6	32.34	37.23	38.38
	3	14.9	17.58	19.39	22.4	24.14	25.26	26.01	27.04	28.26	29.36	31.24	32.16	36.98	38.79

Determination of the constant a: Similarly, when concentration of 4-chlorophenol was kept at 40 mg/L by continually adding and the other conditions were remained unchanged, the dosage of Fenton was changed only, the value of constant 'a' can be determined. At this moment, suppose that $k_2 = kW^b$, the reaction rate can be determined by eqn. 4

$$\frac{dW}{dt} = k_2 C_{H_2O_2}^{a} \tag{4}$$

Logarithm are taken at the both sides of eqn. 4 at the same time, which is shown as following

$$\log\left(\frac{dW}{dt}\right) = a \log C_{H_2O_2} + \log k_2 \tag{5}$$

A linear regression is taken when log (dW/dt) as the y-coordinate and log $C_{H_2O_2}$ as the x-coordinatethe line relationship between log (dW/dt) (Fig. 2), from the slope of the line fitted, the value of constant a can be obtained as following, where $a_1 = 0.2889$, $a_2 = 0.2837$, $a_3 = 0.2973$, $a_4 = 0.2718$, $a_5 = 0.2677$, so the value of 'a' can be taken as 0.282.

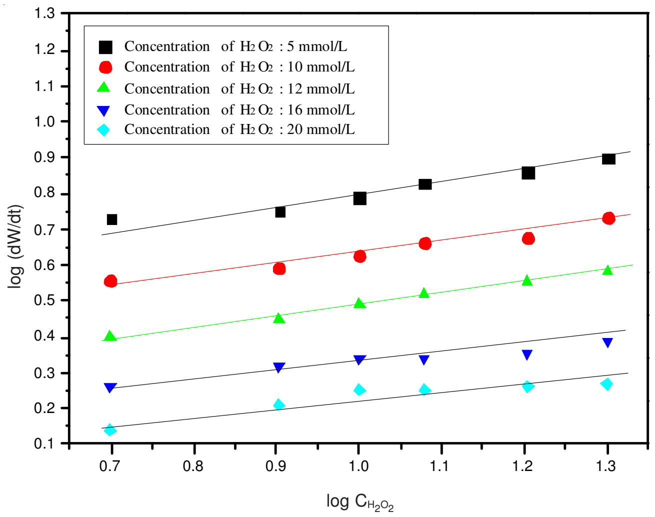


Fig. 2. Line relationship between log (dW/dt) and log $C_{H_2O_2}$

Determination of the reaction activation energy: Concentration of various chemicals were maintained at a constant value, where the initial concentration of 4-chlorophenol of 40 mg/L, initial concentration of H_2O_2 of 20 mmol/L and $FeSO_4$ of 1 mmol/L. Relationship between concentration decrease of 4-chlorophenol and reaction time in five different temperatures are shown in Fig. 3. Eqn. 1 can be transformed as following

$$\ln k = \ln\left(\frac{dW}{dt}\right) - a \ln C_{H_2O_2} - b \ln W \tag{6}$$

The constants 'a' and 'b' determined are substituted into the formula 6 and the W values are substituted at different times of each temperature, thus the ln K can be obtained. The results is shown in Fig. 4, -E/R is the slope of the line in Fig. 6 and that is -11248, that is to say -E/R of -11248, where the constant R of 8.314 J/mol, so the activation energy E of 93.515 kJ/mol, At this point, the formula 1 can be determined as follows:

$$\frac{dW}{dt} = kC_{H_2O_2}^{0.282} W^{-0.273} \tag{7}$$

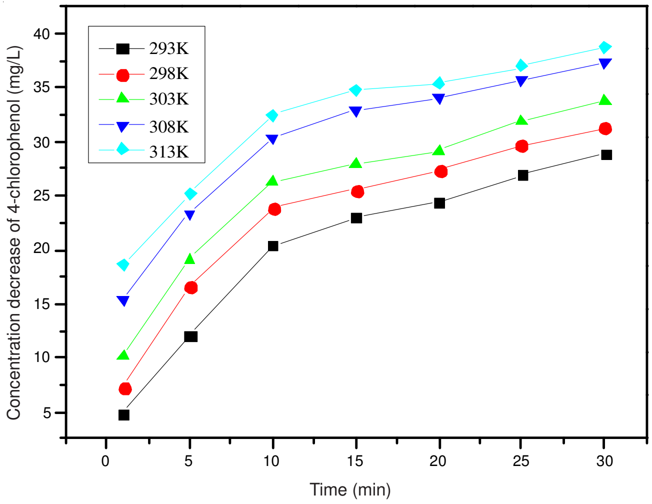


Fig. 3. Relationship between concentration decrease of 4-chlorophenol and reaction time in different temperature

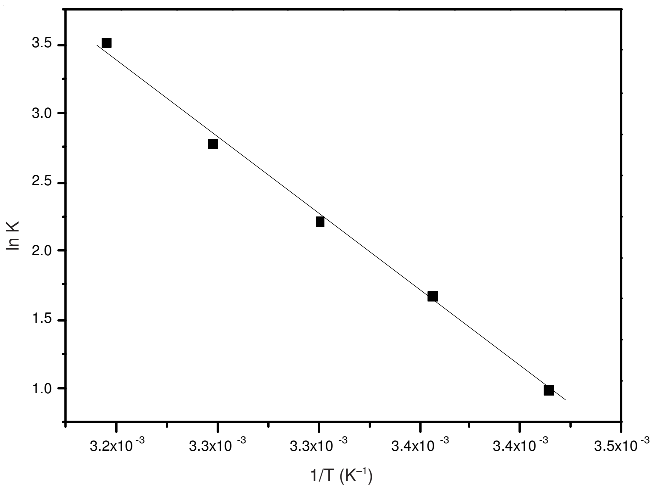


Fig. 4. Line relationship between ln K and 1/T

Relationship between reaction rate and reactant concentration: It can be seen from the reaction order and kinetics equation of degradation of 4-chlorophenol deduced above, reaction of 4-chlorophenol oxidized by Fenton was complex and multi-stage, when the reaction temperature, pH and concentration of the chemicalswere remained unchanged, where the initial concentration of 4-chlorophenol of 40 mg/L, initial concentration of H_2O_2 of 20 mmol/L and $FeSO_4$ of 1 mmol/L. Concentration of residual 4-chlorophenoldecreases to 2 mg/L from 10 mg/L after the treatment of Fenton, the ratio of the reaction rate is shown as follows

$$\gamma_{10}/\gamma_2 = \frac{kC_{H_2O_2}^{0.282}\, 30^{-0.273}}{kC_{H_2O_2}^{0.282}\, 38^{-0.273}} = \frac{30^{-0.273}}{38^{-0.273}} = 1.067$$

It is thus clear that, the reaction rate is gradually dropped with the process of the reaction, but not much decreases.

When the same reaction temperature and pH, concentration of H_2O_2 changes from 5 to 20 mmol/L, the ratio of the reaction rate is shown as follows

$$\gamma_{20}/\gamma_5 = \frac{k \times 20^{0.282}\, W^{-0.273}}{k \times 5^{0.282}\, W^{-0.273}} = \frac{20^{0.282}}{5^{0.282}} = 1.478$$

Thus, the reaction rate significantly increases when the concentration of H_2O_2 increases.

Effect of reaction temperature on the degradation rate: It can be found from the activation energy of the degradation process of 4-chlorophenol, the reaction situated in the lowest level of conventional chemical reaction activation energy, which mean that the reaction should be completed in the twinkling of an eye as fast reaction. But the degradation process completes needed about 1.5 h in fact, it follows that the degradation process is the coexistence of a multi-stage reaction. According to the activation energy of the degradation and derivative of the Arrhenius equation, formula 8 is shown as follows

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \tag{8}$$

Formula 8 shows that large activation energy means temperature increasing can substantially improve the reaction rate, in other words, the degradation reaction of 4-chlorophenol is sensitive to temperature. When the reaction temperature improves from 298-308 K, the ratio of the two reaction rates is as follows.

$$\frac{K_{308}}{K_{298}} = \frac{A\times e^{-E/RT_2}}{A\times e^{-E/RT_1}} = e^{-\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} = e^{-\frac{E}{R}\left(\frac{1}{308}-\frac{1}{298}\right)} = 3.406$$

This shows that changes of temperature vastly influence on the degradation rate of 4-chlorophenol and temperature increasing is conducive to the reaction.

Reaction mechanism of degradation of 4-chlorophenol by Fenton oxidation: The rate equation of 4-chlorophenol oxidative by Fenton is shown above,when the initial concentration of 4-chlorophenol of 40 mg/L, temperature of 298 K, pH of 4.0 and concentration of H_2O_2 of 5 mmol/L, the relationship between concentration decrease of 4-chlorophenol and reaction time is shown in Fig. 5 and the relationship between reaction rate and concentration decrease of 4-chlorophenol is shown in Fig. 6.

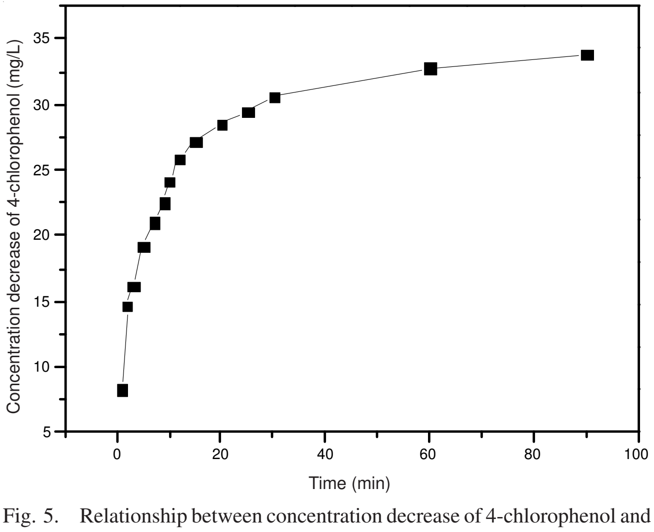


Fig. 5. Relationship between concentration decrease of 4-chlorophenol and reaction time

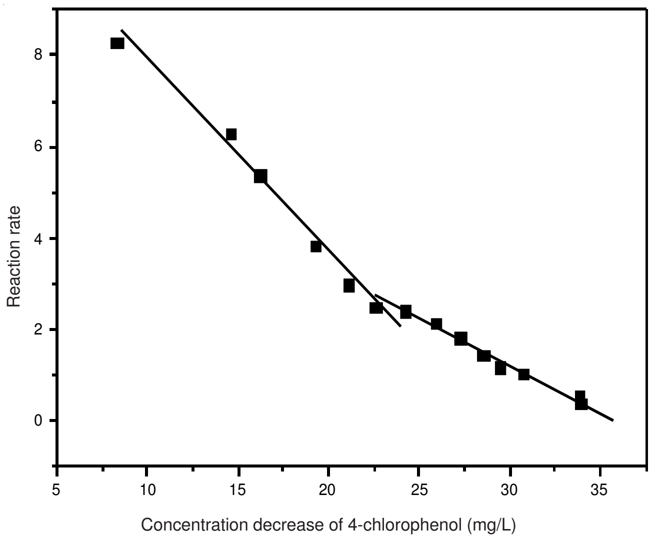


Fig. 6. Relationship between reaction rate and concentration decrease of 4-chlorophenol

As can be seen from Fig. 5, the concentration decrease of 4-chlorophenol increased rapidly in the first 15 min of the degradation reaction, the concentration decrease of 4-chlorophenol of 27.2 mg/L, subsequently, concentration decrease of 4-chlorophenol increased gently. Fig. 6 showed that the reaction rate decreases sharply in the range of concentration decrease of 4-chlorophenol less than 22.5 mg/L and the downward trend tends to be gentle when the concentration decrease of 4-chlorophenol is greater than 22.5 mg/L.

In advanced oxidation processes, the aromatic ring of 4-chlorophenol was attacked by hydroxyl radical (·OH) produced, electrophilic addition occurs between the ·OH and chlorine atomic of the aromatic ring, then the chloride atomic is taken off and benzene quinones intermediate material form. It can be seen that, the degradation of 4-chlorophenol can be roughly divided into two stages within the range of time of the study. The initial 15 min is the first stage of the reaction, the benzenoid hydroxy compound (benzene quinones intermediate material) forms during the initial stage of this period, then the structure of the benzene ring is destroyed and organic acids forms; after reacting for 15 min and till the end of the reaction. It is the advanced oxidation stage, the intermediate product is dropped in this period and carbon dioxide is the main product.

Conclusion

The degradation of 4-chlorophenol contaminated water by Fenton was designed in this study. Based on the reaction characteristics of the contaminant oxidized by Fenton, degradation kinetics model of 4-chlorophenol was constructed and kinetics equation of 4-chlorophenol degradation was eventually obtained through experiments, which could be expressed as: $dW/dt = kC_{H_2O_2}^{0.282} W^{-0.273}$, where the activation energy of the reactions of 93.515 kJ/mol. The reaction mechanisms of 4-chlorophenol degradation were preliminary based on the kinetics equation and it could be found that, the oxidation rate of 4-chlorophenol by Fenton was rapid in the first 15 min and then become relatively slow, thus the entire degradation process could be divided into two stages of rapid reaction and slow reaction.

ACKNOWLEDGEMENTS

This work was supported by the Innovation Project of Guangxi Graduate Education (YCBZ2012003), National High Technology Research and Development Program (863 Program) (2009AA06A416), Guangxi Natural Fund (2012GXNSFAA053023) and (2013GXNSFFA019005). Gratitude is also expressed to Dr. Xinliang Liu of Guangxi University, China, who helped during the whole experiment and publication of this paper.

REFERENCES

1. W.S. Kuo and L.N. Wu, *Sol. Energy,* **84**, 59 (2010).
2. R.F. Pontes, J.E. Moraes, A. Machulek Jr. and J.M. Pinto, *J. Hazard. Mater.*, **176**, 402 (2010).
3. X.Y. Duan, F. Ma and L.M. Chang, *Water Sci. Technol.*, **66**, 2468 (2012).
4. M. Ugurlu and M.H. Karaoglu, *Environ. Sci. Pollut. Res. Int.*, **16**, 265 (2009).
5. E. Sahinkaya and F.B. Dilek, *J. Hazard. Mater.*, **137**, 282 (2006).
6. S. Sahinkaya, M. Onüçyildiz and C. Özdemir, *Asian J. Chem.*, **20**, 3795 (2008).
7. Z. Djilali, A.H. Altaiar and A.Y. Mounia, *Asian J. Chem.*, **21**, 4793 (2009).
8. G.H. Èrtel, M.Y. Ghaly, R. Mayer and R. Haseneder, *Waste Manage*., **21**, 41 (2001).
9. N. Kulik M. Trapido, A. Goi, Y. Veressinina and R. Munter, *Water Sci. Technol.*, **60**, 1795 (2009).
10. X.F. Zhu, S.L. Xi and X.H. Xu, *J. Zhejiang Univ. (Sci. Ed.)*, **31**, 669 (2004).
11. B.H. Kwon, S.H. Hong, J.K. Lee and I.K. Kim, *Korean J. Chem. Eng.*, **25**, 6 (2008).
12. J.M. Pinto and R.F. Pontes, *Chem. Eng. J.*, **122**, 65 (2006).
13. Y. Du, M. Zhou and L. Lei, *Water Res.*, **41**, 1121 (2007).
14. W.S. Kuo and I.T. Lin, *Water Sci. Technol.*, **59**, 973 (2009).
15. A. Bach, H. Shemer and R. Semiat, *Desalination*, **264**, 188 (2010).