Kinetic modeling of electrochemical degradation of phenol in a three-dimension electrode process

Lizhang Wang [a,*], Jianfeng Fu [b], Qicheng Qiao [a], Yuemin Zhao [c,**]

[a] *College of Environment and Spatial Informatics, China University of Mining and Technology, Xuzhou City, Jiangsu 221008, PR China*
[b] *Department of Environmental Engineering, Southeast University, Nanjing City, Jiangsu 210096, PR China*
[c] *School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou City, Jiangsu 221008, PR China*

Abstract

For giving a reasonable design method of electro-chemistry reactor, based on law of conservation of energy and law of conservation of charge, using a series of assumption, theoretical energy model was proposed in this study. By proper mathematics simplification method for the new model which demonstrats the relation between energy demanding and providing of the three-dimension electrode (TDE) reactor, the most important characteristic parameters (K_1, K_2) which are constant for a certain matter during electro-oxidation process were obtained. Experiments about phenol degradation using TDE reactor filling with granular activated carbon (GAC) were conducted to examine the fitness of new energy equation and experimental data. Results from experiments revealed that the oxidation behavior could be reasonably described using new model and the energy providing can be calculated by following equation: $W = 1.56 \times 10^{14} \eta(d^2/V)C_0 E Q^2 (1 + \sqrt{1 + (V \ln K)/(3.63 \times 10^{13} \eta^2 d^2 Q^2 C_0 E)})$. The calculated results obtained from above equation were in good agreement with experimental data especially at higher phenol removal efficiency. The new energy equation illustrates energy could be easily obtained through the solution of the value of characteristic parameters by simple lab-scale experiments.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Kinetic modeling; Three-dimension electrode (TDE); Energy demanding; Energy providing; Characteristic parameters

1. Introduction

Phenolic compounds are common pollutants in the effluents of several industries [1–3]. Removal of these refractory compounds becomes difficult and expensive when it is dealt with at a very low level of pollutants [4]. Effective electrochemical methods were also developed for the treatment of wastewater polluted by toxic and stable organic compounds [5–10]. Direct electrochemical techniques for water purification involve anodic or cathodic decomposition; however, these are commonly associated with anodic oxidation of water (release of O_2). Therefore, only low current yields can be achieved this way. Additional problems, which are related to the low miscibility of most organics in water and to the hindered mass transfer to the anode, are responsible for rather low space-time yields. Considerably better results may be achieved using indirect electrochemical oxidation, where the pollutants are oxidized in the bulk by a mediator in a high oxidation state.

Three-dimension electrode (TDE) process is frequently used to oxidize phenolic compounds because of the high efficiency of generation of hydroxyl radicals (OH•) [11–12], especially with the following privileges [13]: fewer or no reagents, simple later disposal, less acreage, running conveniently and less sludge, etc. Although focused on this field, effective kinetics modeling for TDE process has not been proposed yet. Many concepts including instantaneous current efficiency (ICE), average current efficiency (ACE), electric oxidation index (EOI) and electric oxygen demand (EOD) were presented to describe the relation between current and phenol removal [14–16]. Model for calculation of effectiveness factor [17], non-Tafel kinetics of anodic electrochemical reaction [18], equation for evaluation of the effect with the addition of metal catalysts [19], reaction

* Corresponding author. Tel.: +86 138 13295455; fax: +86 516 83893414.
** Corresponding author. Tel.: +86 516 83590092; fax: +86 516 83885455.
E-mail addresses: wlzh0731@126.com (L. Wang), ymzhao@cumt.edu.cn (Y. Zhao).

mechanism of electrochemical dissolution of aluminum in an alkaline solution [20] and kinetics described multiple ion electrolyte system [21] were also proposed. Given all the kinetics modeling an evaluation, they still could not describe the relationship between the inner energy demanding and the energy providing outside. As is important for the cost of technical process, before the application of the TDE method, the electric energy demanding is difficult to be estimated based on previous works.

In this paper, phenolic pollutant was oxidized by TDE process and kinetics modeling for phenol oxidation was proposed based on law of conservation of energy and law of conservation of charge. Experimental data were rational fit using the new energy model and energy demanding of phenol oxidation was easily calculated using the characteristic parameters obtained from data analysis.

2. Experimental

2.1. Materials

Distilled water was used for the preparation of synthetic wastewater and phenol was obtained from Merck (99.5% pure). All reagents used for the analysis were also obtained in extra pure condition. SnO_2 electrodes with high congregation of $OH^\bullet$ [22] have an area of 20 cm × 20 cm coated Ti which thickness was 3 μm [23] used in the runs were manufactured by Flag Corporation, China. The DC electric motor from Huatai Company, China, with type of WWL-LDX could provide direct current ranged from 0 to 30 A and voltage ranged between 0 and 30 V separately. The granular activated carbon (GAC) used in this study with iodine adsorption value of 1000 mg/g which has an average particle size of approximately 2 mm, a specific surface of 1028 m^2/g according to the BET method and a specific weight of 0.375 kg/L was provided by Huaxin Company, China. The 5.25 kg GAC was cleaned several times using distilled water until the impurity was removed completely.

2.2. TDE reactor

A continuous electrochemical quadrangular reactor as shown in Fig. 1(A) was designed in our laboratory with working volume of 14 L and the 35 cm tall reactor (length = 20 cm, breadth = 20 cm) was constructed by polymethyl methacrylate plastics with a heating/cooling coil around. The location of each electrode was displayed in Fig. 1(B), if (b), (c), (d), (e) and (f) or (b), (c), (e) and (f) or (b), (d) and (f) or (c) and (e) were moved from the reactor individually different inter-electrode distance with value of 20, 10, 6.7 and 5 cm could be obtained, respectively. GAC which packed as bed electrode between anode and cathode was easily repolarized because of its high contact resistance which attributing to lower the influence of short circuit and enhance electric efficiency. A pump was used to pump the phenol feed (pH 7.1) in reactor from a reservoir and the volume of the reservoir was always greater than that of the reactor so that the behavior of the whole system could be approximated to a well mixed reactor [24]. The reaction temperature (25 °C) was controlled with circulating water recycled from a temperature-controlled water bath and monitored with glass thermometers immersed in the exit and inlet of the column [8].

2.3. Procedure

It was expected that the electrochemical reactor used in the work could remove phenol by both electrochemical oxidation and adsorption. In this work, GAC used as a bed electrode was expected to keep high phenol removal efficiency during the continuous running of the bed electrode as long as a suit-
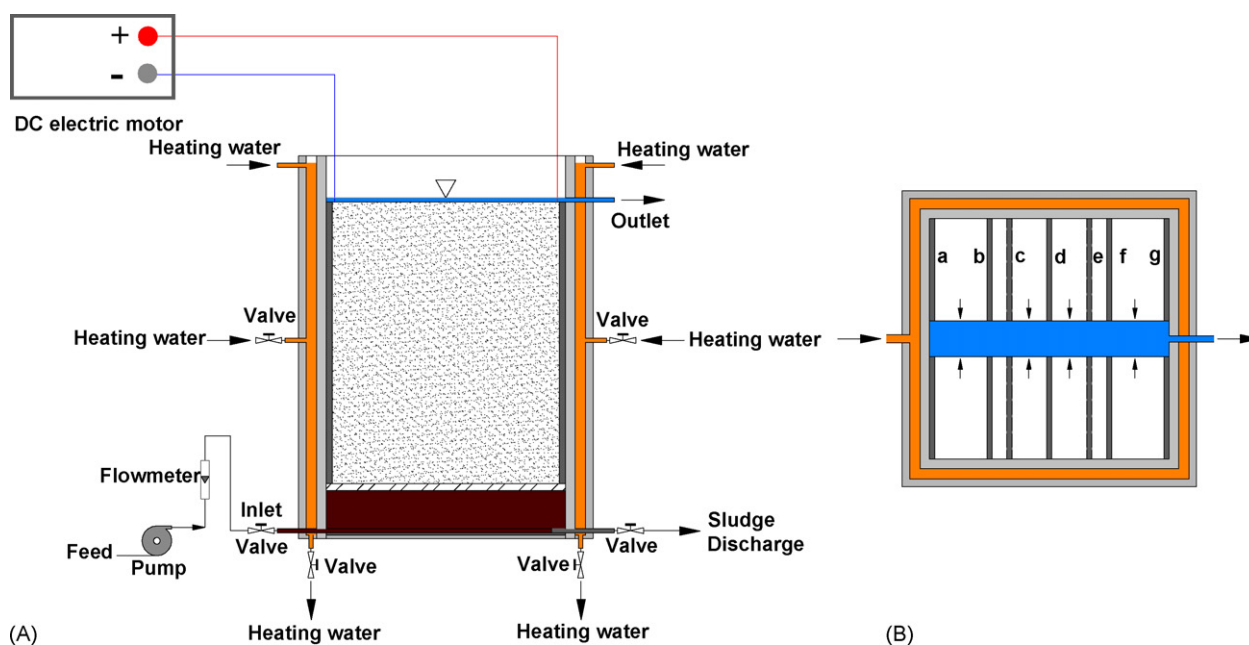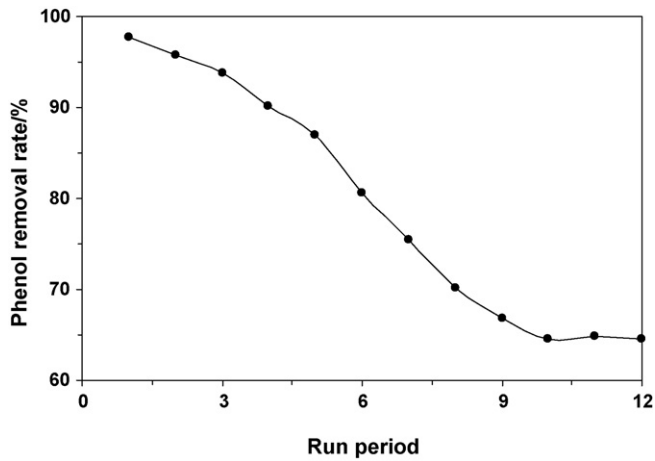

Fig. 1. Experimental set-up of TDE reactor.

Fig. 2. Pre-treatment of activated carbon filling in TDE reactor under the conditions of $C_0 = 500$ mg/L, $Q = 3.89 \times 10^{-6}$ m^3/s, $U = 10$ V, $I = 20$ A, $d = 5$ cm, pH 7.1 and $T = 25\,^{\circ}$C.

able electric energy is employed [7]. In order to eliminate the influence of adsorption by activated carbon, pre-treatment of GAC was very important during the oxidation process. Under the condition of phenol concentration $C_0 = 500$ mg/L, reaction time $t = 60$ min, voltage $U = 10$ V, current $I = 20$ A, inter-electrode distance $d = 5$ cm, a static state experiment was carried out.

Fig. 2 shows the dependence of phenol removal efficiency on running period. The curve demonstrates removal rate of phenol decreases with the increasing of running period until becoming a constant, which illustrates oxidation velocity for phenol is slower than that of adsorption because of the high adsorption ability of fresh activated carbon so that attributing to the accumulation of phenol on surface of activated carbon at beginning of reaction. With the increasing of running period, adsorption ability of activated carbon decreases which results in dynamic equilibrium between oxidation velocity and adsorption velocity that makes removal rate a constant. Then the system was used to conduct the following experiments.

Seen from Table 1, phenol was oxidized during TDE process under different conditions. Test A was aimed to obtain the relation between residence time and phenol concentration outlet. In this experiment, phenol with an initial concentration of 500 mg/L was selected as the original substrate with the condition of voltage $U = 10$ V, current $I = 20$ A and inter-electrode distance $d = 5$ cm. Test B was to describe the effect of initial phenol concentration to the removal efficiency and input current, under constant parameters of influent $Q = 3.89 \times 10^{-6}$ m^3/s, voltage $U = 10$ V and inter-electrode distance $d = 5$ cm. When influent Q, initial phenol concentration C_0 and current I were fixed with value of 3.89×10^{-6} m^3/s, 500 mg/L and 20 A, respectively, the relation between inter-electrode distance and phenol removal efficiency and input voltage was obtained by test C.

2.4. Analytical method

Concentration of phenol was measured by standard method based on spectrophoto-metric analysis at 510 nm of the developed color resulting from the reaction of phenol with 4-aminoantipyrence [13]. The COD content and pH of all solutions and samples were determined according to standard methods for the examination of water and wastewater [25].

The COD method was used for the determination of the current efficiency [26–27]. In this method, the COD was measured during electrolyses and the average current efficiency (η) was calculated using the following equation:

$$\eta = \frac{[COD_0 - COD_t]FV}{8It}$$

Table 1
Design of the experiments

Test	Description	Influent Q ($\times 10^{-6}$ m^3/s)	Initial phenol concentration C_0 (mg/L)	Inter-electrode distance d (m)	Input voltage U (V)	Input current I (A)
A	$Q = 23.33$	23.33	500	0.05	10	20
	$Q = 11.70$	11.70	500	0.05	10	20
	$Q = 7.78$	7.78	500	0.05	10	20
	$Q = 5.83$	5.83	500	0.05	10	20
	$Q = 4.67$	4.67	500	0.05	10	20
	$Q = 3.89$	3.89	500	0.05	10	20
	$Q = 3.33$	3.33	500	0.05	10	20
	$Q = 2.92$	2.92	500	0.05	10	20
	$Q = 2.59$	2.59	500	0.05	10	20
B	$C_0 = 105$	3.89	105	0.05	10	4.6
	$C_0 = 210$	3.89	210	0.05	10	9.4
	$C_0 = 330$	3.89	330	0.05	10	14.2
	$C_0 = 410$	3.89	410	0.05	10	16.9
	$C_0 = 500$	3.89	500	0.05	10	19.5
	$C_0 = 620$	3.89	620	0.05	10	24.1
C	$d = 0.05$	3.89	500	0.05	10	20
	$d = 0.067$	3.89	500	0.067	5.4	20
	$d = 0.10$	3.89	500	0.10	3.2	20
	$d = 0.20$	3.89	500	0.20	1.3	20

where COD_0, COD_t and $COD_{t+\Delta t}$ are the initial COD ($g\,O_2/L$) and the COD at times t and Δt (s), respectively, I the current intensity (A), F the Faraday constant (96,487 C/mol), t the time (s), V the volume of the electrolyte (L) and 8 is a dimensional factor for unit consistence ($32\,g\,O_2\,mol\,O_2/4\,mol\,e^-\,mol\,O_2$).

3. Kinetic modeling

The movement and oxidation of phenol in TDE reactor all need energy and the former is provided by water flow and electric field, but the later is only affected by electro-chemistry reaction. Phenol molecule moves between anode and cathode regularly because of the force given by electric field. As moving regularly in the rector, phenol can be absorbed by activated carbon and oxidized through electrode process. Oxidation of phenol by $OH^\bullet$ plays important role in the regeneration of adsorption ability of activated carbon which attributing to continuous running of TDE reactor. Energy providing by electric motor could not be less than energy demanding which can be described by kinetic energy (motion energy demanding for phenol molecules movement) and potential energy (oxidation energy demanding for phenol molecules removal) in the TDE system for the dynamic equilibrium of adsorption velocity and oxidation velocity in phenol removal process. Contrasted to energy provided by electric motors, kinetic energy provided by water flow could be ignored.

The model employs the following basic assumptions:

- Suppose phenol molecules all are mass points and in the same state.
- All phenol molecules can carry charge affected by electric field and the charges carried are equal.
- Suppose phenol molecules are in the same state before and after treatment.
- Suppose the reaction time for every phenol molecules removal is equal.

Suppose the mass of a phenol molecules is m_i, theoretical energy demanding during removal process is E'_D, the number of phenol molecules is n and n' before and after treatment, the average speed obtained through electrode process is v, potential energy is E'_a and the utilization of energy providing is η, the relation between energy providing and theoretical energy demanding is

$$\eta W = (n - n')E'_D \tag{1}$$

where W is the energy providing by electric motor.

Theoretical energy demanding can be divided into kinetic energy and potential energy.

$$E'_D = \frac{1}{2}m_i v^2 + E'_a \tag{2}$$

Phenolic waste water is feed in the reactor with flow rate of Q, the mass of phenol before and after treatment can be calculated by following equations:

$$M_0 = K_c C_0 Qt = nm_i \tag{3}$$

$$M_t = K_c C_t Qt = n'm_i \tag{4}$$

where M_0 and M_t are the mass of phenol in water before and after treatment, C_0 and C_t the concentration of phenol in water before and after treatment, K_c the conversion coefficient for mass of phenol and t is the reaction time.

Eqs. (1)–(4) can be combined to illustrate the relationship between energy providing and theoretical energy demanding.

$$\eta W = \frac{1}{2}K_c(C_0 - C_t)Qtv^2 + (n - n')E'_a \tag{5}$$

Because of the complete oxidation of phenol to carbon dioxide and overall electro-reaction of TDE system is as following [28–33],

$$C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^-$$
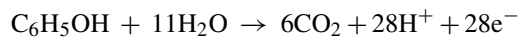
Potential energy can be expressed by Nernst equation [34–35].

$$(n - n')E'_a = E_a = -k_1 RT \ln K \tag{6}$$

where R is the air constant coefficient, T the temperature (K), k_1 the pre-exponential factor and K is the equilibrium constant for phenol oxidation.

Equilibrium constant K could be calculated from the curve of phenol oxidation with the dependence of phenol concentration on reaction time.

Substituting Eq. (6) to (5), Eq. (7) is obtained.

$$\eta W = \frac{1}{2}K_c(C_0 - C_t)Qtv^2 - k_1 RT \ln K \tag{7}$$

When the electric quantity carried by phenol molecules is q, the force afforded by electric field is expressed by

$$F = eq = \frac{Uq}{\varepsilon d}$$

where F is the electric field force, U the input voltage to system, e the electric field intensity, ε the dielectric constant of activated carbon and d is the inter-electrode distance.

It is obvious that normal speed toward the direction of electric field of phenol molecules is 0 when entering the TDE system, and under the function of electric field a certain speed can be obtained. Using the law of conservation of momentum, the speed of phenol molecule is written as

$$Ft = m_i v$$

According to the assumption, electric quantity is carried by phenol molecules removed during reaction process:

$$(n - n')q = It \tag{8}$$

where I is the input current to TDE reactor.

The average speed of phenol molecules can be described by Eq. (9).

$$v = \frac{W}{K_c \varepsilon d Q(C_0 - C_t)} \tag{9}$$

Eqs. (7) and (9) are combined as basic equation and the roots can be used to calculate energy providing by electric motor as Eq. (10).

$$W = K_c \eta \varepsilon^2 d^2 \frac{Q}{t}(C_0 - C_t)$$

$$\times \left(1 \pm \sqrt{1 + \frac{2tk_1 RT \ln K}{K_c \eta^2 \varepsilon^2 d^2 Q(C_0 - C_t)}}\right) \qquad (10)$$

It is difficult for the application of Eq. (10) to calculate energy providing because of many unknown parameters. Proper mathematics method is used to simplify the new energy equation.

Under temperature T, the constant is ε, the variable parameters are η, C_0, E, Q and d. Suppose the removal rate of phenol is E, the effective volume of the TDE reactor is V. Commanding $K_c \varepsilon^2 = K_1$ and $2k_1 RT = K_2$, K_1 and K_2 which are constant only affected by kinds of pollutants during the oxidation process are named characteristic parameters of the electro-chemistry reaction.

The linear type of new energy equation can be represented by

$$\frac{d^2 Q^2 C_0 E \ln K}{W^2 V} = \frac{1}{K_1 K_2} - \frac{2}{K_2}\frac{\eta d^2 Q^2 C_0 E}{WV} \qquad (11)$$

4. Results and discussion

4.1. The effect of residence time

From many reports [36–37], under a certain electric condition, electro-oxidation for phenol concentration could be obtained from the slope of linear curve, by the equation:

$$C_t = C_0 \exp(-Kt)$$

Relationship between flow rate Q and residence time t is shown in Table 2. Fig. 3 illustrates the effect of different residence time to phenol removal efficiency with initial phenol concentration $C_0 = 500$ mg/L, input voltage $U = 10$ V, input current $I = 20$ A and inter-electrode distance $d = 5$ cm. From the curve of phenol degradation, phenol concentration outlet dependence on residence time obeys the first-order reaction and the phenol removal rate increases from 12.48 to 82.5% with time ranges between 10 and 90 min. A good fitness of experimental data with first-order equation is shown ($R^2 = 0.9856$) by the curve with equilibrium constant K of 0.018 min^{-1} under the certain reaction condition. Took cost for phenol treatment as consideration, residence time of $t = 60$ min was selected in this experiment.

A good fitness can be seen with the dependence of experimental data on Eq. (11) in Fig. 4. A linear relation between $d^2 Q^2 C_0 E \ln K / W^2 V$ and $\eta d^2 Q^2 C_0 E / WV$ is well done with

Table 2
Relationship between influent Q and reaction time t using TDE set-up

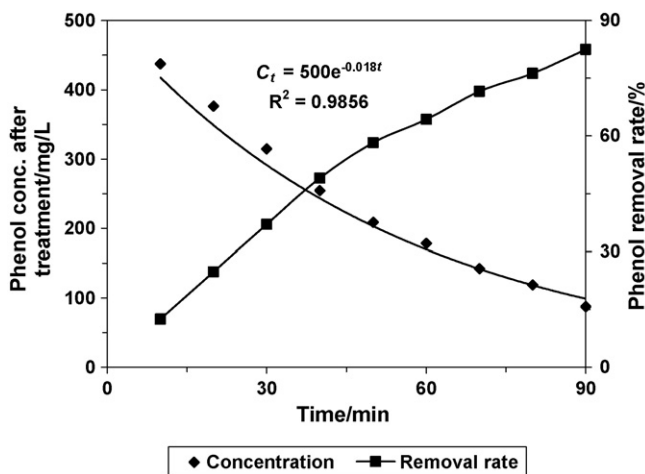| Q ($\times 10^{-6}$ m^3/s)	t (min)	Q ($\times 10^{-6}$ m^3/s)	t (min)
23.33	10	3.89	60
11.70	20	3.33	70
7.78	30	2.92	80
5.83	40	2.59	90
4.67	50	2.33	100

Fig. 3. Effect of different residence time for phenol degradation in TDE reactor with $C_0 = 500$ mg/L, $U = 10$ V, $I = 20$ A, $d = 5$ cm, pH 7.1 and $T = 25\,^\circ$C.

rational correlation ration ($R^2 = 0.9851$), furthermore, linear relationship was more obvious when residence time $t \geq 40$ min ($R^2 = 0.9937$). As far as new energy equation is concerned, Fig. 4 reveals that the degradation of phenol could be described by new kinetics model.

Since $2/K_2 = 9 \times 10^{-5}$, $1/(K_1 K_2) = 3 \times 10^{-19}$, then $K_1 = 1.5 \times 10^{14}$ and $K_2 = 2.22 \times 10^4$, characteristic parameters (K_1, K_2) should be constants to describe phenol oxidation under this experimental condition.

4.2. The effect of initial phenol concentration

In Fig. 3, an initial phenol concentration of 500 mg/L was employed. Experiments were conducted to investigate change of input current and phenol removal efficiency affected by initial phenol concentration. The results are displayed in Fig. 5. As seen in this figure, as the initial phenol concentration increases from 105 to 620 mg/L, phenol removal efficiency of the sample of waste water decreases from 87.7 to 64%, previous work also supports this phenomenon [38], but the input incurrent was
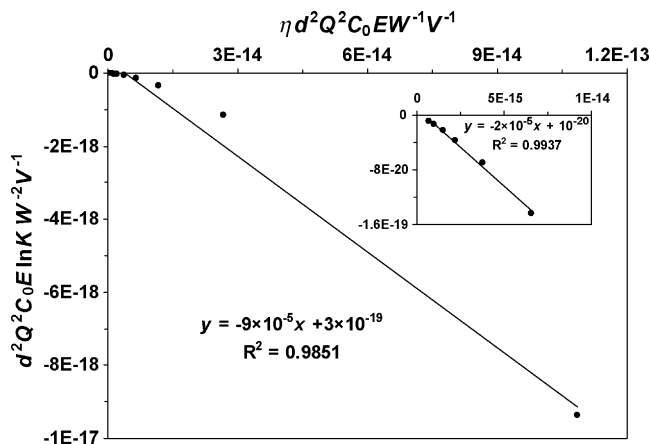

Fig. 4. Experimental data analysis using kinetics model of energy under condition of different residence time with $C_0 = 500$ mg/L, $U = 10$ V, $I = 20$ A, $d = 5$ cm, pH 7.1 and $T = 25\,^\circ$C.
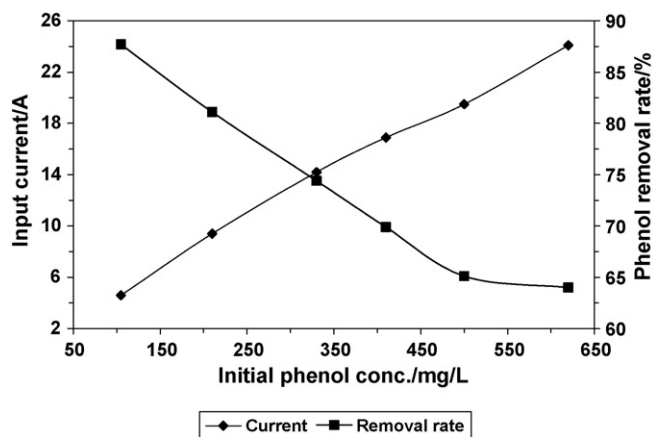
Fig. 5. Effect of initial phenol concentration for phenol removal rate and input current in TDE reactor with $Q = 3.89 \times 10^{-6}$ m^3/s, $d = 5$ cm, $U = 10$ V, pH 7.1 and $T = 25\,°$C.

increased from 4.6 to 24.1 A for keeping the dynamic equilibrium of phenol oxidation. Such an increase of input current is because of the increasing of electric quantity with phenol molecules at the same residence time which could be explained by Eq. (8).

Fit of experimental data and new energy equation is shown in Fig. 6. From this figure, $d^2 Q^2 C_0 E \ln K / W^2 V$ and $\eta d^2 Q^2 C_0 E / WV$ also could be described by linear relation with good fitness ($R^2 = 0.9883$) and characteristic parameters ($K_1 = 1.67 \times 10^{14}$, $K_2 = 2 \times 10^4$) are essentially equal with previous values which demonstrates the homoeostasis of these parameters during a certain pollutant oxidation.

4.3. The effect of inter-electrode distance

For inquisition of effect of inter-electrode distance on phenol removal efficiency and input voltage, this experiment was conducted with the description of their relation in Fig. 7. This figure gives an account of inter-electrode which has great effect on phenol removal efficiency and input voltage. Phenol removal efficiency increases from 65.8 to 80.1% and input voltage decreases from 10 to 1.3 V with the increase of inter-electrode distance
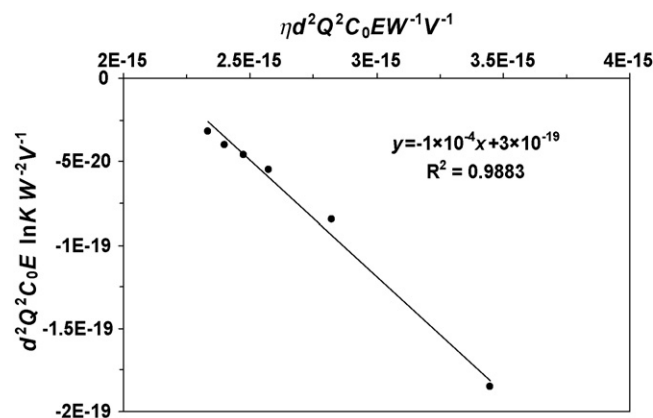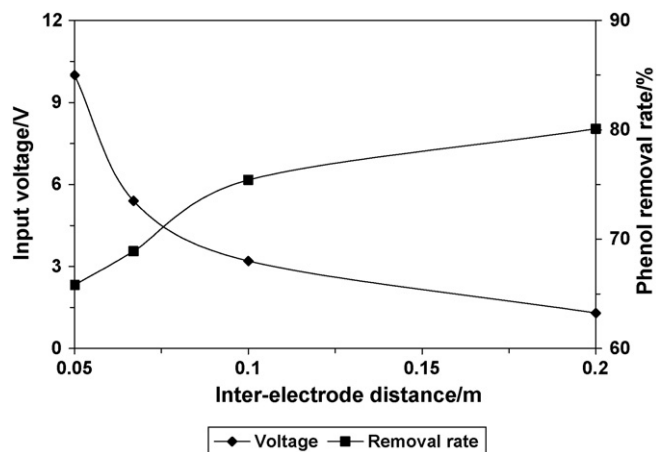

Fig. 7. Effect of different inter-electrode distance for phenol removal rate and input voltage in TDE reactor with $C_0 = 500$ mg/L, $Q = 3.89 \times 10^{-6}$ m^3/s, $I = 20$ A, pH 7.1 and $T = 25\,°$C.

from 5 to 20 cm. This change probably occurs because the electrostatic effects depend on the inter-electrode distance, so when the distance increases, the movement of produced ions would be slower and they would have more opportunity to aggregate [39] and produce more hydroxyl radicals which could give a rapid oxidation for phenol pollutants that leads to the increase of phenol removal rate at the same residence time.

Fig. 8 illustrates the linear fitness of data of this experiment and new energy model ($R^2 = 0.9968$). From this figure, characteristic parameters could be obtained with the value of $K_1 = 1.5 \times 10^{14}$ and $K_2 = 2.22 \times 10^4$.

Figs. 4 and 8 also demonstrate the higher phenol removal rate the higher accurate of new energy equation because of the increasing current efficiency during electro-chemistry process.

4.4. The energy equation for phenol oxidation in TDE reactor

Based on previous experiments, characteristic parameters which could be used in TDE reactor design were obtained. The
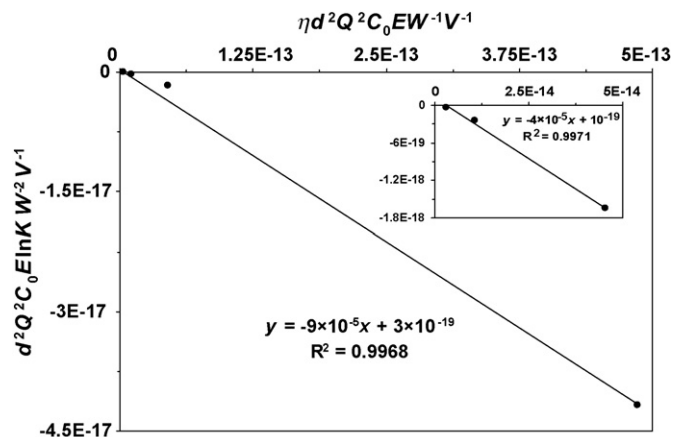

Fig. 6. Experimental data analysis using kinetics model of energy under condition of different initial phenol concentration with $Q = 3.89 \times 10^{-6}$ m^3/s, $d = 5$ cm, $U = 10$ V, pH 7.1 and $T = 25\,°$C.

Fig. 8. Experimental data analysis using kinetics model of energy under condition of different inter-electrode distance with $C_0 = 500$ mg/L, $Q = 3.89 \times 10^{-6}$ m^3/s, $I = 20$ A, pH 7.1 and $T = 25\,°$C.

errors of measurement lead to the narrow inconsistency of the value of characteristic parameters. Given a substitution of average value of K_1 and K_2 to new kinetics model, new energy equation can be used to demonstrate the relation between energy demanding and energy providing.

We can obtain two value of energy by the application of this equation. As "−" is used, the value is for the startup of TDE reactor for phenol oxidation. Only "+" can be used to be considered as the minimum energy providing. Equation as following is to describe the phenol oxidation by TDE reactor:

$$W = 1.56 \times 10^{14} \eta \frac{d^2}{V} C_0 E Q^2$$
$$\times \left(1 + \sqrt{1 + \frac{V \ln K}{3.63 \times 10^{13} \eta^2 d^2 Q^2 C_0 E}}\right)$$

For different organic pollutants oxidation, the characteristic parameters K_1, K_2 are different. Before the design of TDE reactor, similar lab-scale experiment should be carried out to obtain the value of characteristic parameters in order to have an accurate design for TDE reactor.

5. Conclusions

Theoretical development and experimental investigation in this study have demonstrated that using new kinetics model could describe electro-chemistry mechanism of TDE system and characteristic parameters (K_1, K_2) which could be obtained from simple lab-scale experiment play important roles in the design of TDE reactor. Using data process and analysis, characteristic parameters for phenol oxidation were educed. Since the degradation for phenol could be described by first-order kinetic model properly, a new kinetic model of phenol oxidation process was proposed to describe the relationship between energy demanding and energy providing. The results obtained from the kinetic model are in good agreement with experimental data.

Acknowledgements

References

[1] V.L. Santos, V.R. Linardi, Biodegradation of phenol by a filamentous fungi isolated from industrial effluents-identification and degradation potential, Proc. Biochem. 39 (2004) 1001–1006.

[2] Y.M. Awad, N.S. Abuzaid, The influence of residence time on the anodic oxidation of phenol, Sep. Purif. Technol. 18 (2000) 227–236.

[3] R. Alnaizy, A. Akgerman, Advanced oxidation of phenolic compounds, Adv. Environ. Res. 4 (2000) 232–244.

[4] P.I. Iotov, S.V. Kalcheva, Mechanism approach to the oxidation of phenol at a platinum/gold electrode in an acid medium, J. Electrochem. 442 (1998) 19–26.

[5] A. Silvana, A. Daniel, A.S. Omowunmi, A new electrocatalytic mechanism for the oxidation of phenols at platinum electrodes, Electrochem. Commun. 5 (2003) 681–688.

[6] R.E. Sioda, T.Z. Fahidy, B. Frankowska, An application of reactor theory principles to the confinement of electrochemically generated unstable radical ions, J. Electroanal. Chem. 560 (2003) 43–49.

[7] Y. Xiong, H.T. Karlsson, An experimental investigation of chemical oxygen demand removal from the wastewater containing oxalic acid using three-phase three-dimensional electrode reactor, Adv. Environ. Res. 7 (2002) 139–145.

[8] B.K. Korbahti, A. Tanyolac, Continuous electrochemical treatment of phenolic wastewater in a tubular reactor, Water Res. 37 (2003) 1505–1514.

[9] D.L. He, S. Mho, Electrocatalytic reactions of phenolic compounds at ferric ion co-doped $SnO_2:Sb^{5+}$ electrodes, J. Electroanal. Chem. 568 (2004) 19–27.

[10] Y. Castrillejo, M.R. Bermejo, A.I. Barrado, R. Pardo, E. Barrado, A.M. Martínez, Electrochemical behavior of dysprosium in the eutectic LiCl–KCl at W and Al electrodes, Electrochim. Acta 50 (2005) 2047–2057.

[11] R.A. Torres, W. Torres, P. Peringer, C. Pulgarin, Electrochemical degradation of p-substituted phenols of industrial interest on Pt electrodes. Attempt of a structure–reactivity relationship assessment, Chemosphere 50 (2003) 97–104.

[12] G. Sine, C. Comninellis, Nafion-assisted deposition of microemulsion-synthesized platinum nanoparticles on BDD. Activation by electrogenerated $^\bullet$OH radicals, Electrochim. Acta 50 (2005) 2249–2254.

[13] N.H. Ince, I.G. Apikyan, Combination of activated carbon adsorption with light-enhanced chemical oxidation via hydrogen peroxide, Water Res. 34 (2000) 4169–4176.

[14] C. Comninellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, J. Appl. Electrochem. 25 (1995) 23–28.

[15] C. Comninellis, C. Pulgarin, Anodic oxidation of phenol for waste water treatment, J. Appl. Electrochem. 21 (1991) 703–708.

[16] C. Comninellis, G.P. Vercesi, Characterization of DSA type oxygen evolving electrode-choice of coating, J. Appl. Electrochem. 21 (1991) 335–345.

[17] F. Gloagucn, P. Convert, S. Gamburzev, O.A. Velev, S. Srinivasan, An evaluation of the macro-homogeneous and agglomerate model for oxygen reduction in PEMFCs, Electrochem. Acta 43 (1998) 3767–3772.

[18] A.A. Kulikovsky, Analytical model of the anode side of DMFC: the effect of non-Tafel kinetics on cell performance, Electrochem. Commun. 5 (2003) 530–538.

[19] A. Visintin, E.B. Castro, S.G. Real, W.E. Triaca, C. Wang, M.P. Soriaga, Electrochemical activation and electrocatalytic enhancement of a hydride-forming metal alloy modified with palladium, platinum and nickel, Electrochim. Acta 51 (2006) 3658–3667.

[20] H.B. Shao, J.M. Wang, Z. Zhang, J.Q. Zhang, C.N. Cao, Electrochemical impedance spectroscopy analysis on the electrochemical dissolution of aluminum in an alkaline solution, J. Electroanal. Chem. 549 (2003) 145–150.

[21] C. Dan, B.V. Bossche, L. Bortels, G. Nelissen, J. Deconinck, Numerical simulation of transient current responses in diluted electrochemical ionic systems, J. Electroanal. Chem. 505 (2001) 12–23.

[22] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, Electrochim. Acta 39 (1994) 1857–1862.

[23] L. Lipp, D. Pletcher, The preparation and characterization of tin dioxide coated titanium electrodes, Electrochim. Acta 42 (1997) 1091–1099.

[24] A.M. Polcaro, S. Palmas, F. Renoldi, M. Mascia, Three-dimensional electrodes for the electrochemical combustion of organic pollutants, Electrochim. Acta 46 (2000) 389–394.

[25] G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based electrodes, Electrochim. Acta 48 (2003) 1655–1663.

[26] P. Canizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes, Water Res. 39 (2005) 2687–2703.

[27] P. Canizares, C. Sáez, J. Lobato, M.A. Rodrigo, Electrochemical treatment of 2,4-dinitrophenol aqueous wastes using boron-doped diamond anodes, Electrochim. Acta 49 (2004) 4641–4650.

[28] M.A. Maluleke, V.M. Linkov, Partial electrochemical oxidation of phenol on ceramic-based flat-sheet type electromembrane reactors, Sep. Purif. Technol. 32 (2003) 377–385.

[29] X.Y. Li, Y.H. Cui, Y.J. Feng, Z.M. Xie, J.D. Gu, Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes, Water Res. 39 (2005) 1972–1981.

[30] A. Perreta, W. Haennia, N. Skinnera, X.-M. Tang, D. Gandinib, C. Comninellis, Electrochemical behavior of synthetic diamond thin film electrodes, Diamond Relat. Mater. 8 (1999) 820–823.

[31] J.L. Boudenne, O. Cerclier, J. Galéa, E.V. Vlist, Electrochemical oxidation of aqueous phenol at a carbon black slurry electrode, Appl. Catal. A 143 (1996) 185–202.

[32] J. Iniesta, P.A. Michaud, M. Panizza, G. Gerisola, A. Aldaz, C. Comninellis, Electrochemical oxidation of phenol at boron-doped diamond electrode, Electrochim. Acta 46 (2001) 3574–3578.

[33] Y.J. Feng, X.Y. Li, Electro-catalytic oxidation of phenol on several metal-oxide electrodes in aqueous solution, Water Res. 37 (2003) 2399–2407.

[34] D.I. Bronin, I.Y. Yaroslavtsev, H. Nafe, F. Aldinger, Identification of the reaction mechanism of the Pt, $O_2/La(Sr)Ga(Mg)O_{3-\alpha}$ electrode system, Electrochim. Acta 49 (2004) 2438–2440.

[35] I.B. Gornushkin, B.W. Smith, J.D. Winefordner, A kinetic study of diffusion in the electrothermal atomizer with a graphite filter by laser excited atomic fluorescence, Spectrochim. Acta, Part B 51 (1996) 1679–1693.

[36] A.V. Diniz, N.G. Ferreira, E.J. Corat, V.J. Trava-Airoldi, Efficiency study of perforated diamond electrodes for organic compounds oxidation process, Diamond Relat. Mater. 12 (2003) 577–582.

[37] Y.J. Li, F. Wang, G.D. Zhou, Y.M. Ni, Aniline degradation by electrocatalytic oxidation, Chemosphere 53 (2003) 1229–1234.

[38] S.H. Lin, C.T. Shyu, M.C. Sun, saline wastewater treatment by electrochemical method, Water Res. 32 (1998) 1059–1066.

[39] N. Daneshvar, H. Ashassi Sorkhabi, M.B. Kasiri, Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections, J. Hazard. Mater. B112 (2004) 55–62.