



The influence of TiO₂ and aeration on the kinetics of electrochemical oxidation of phenol in packed bed reactor

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ABSTRACT

The electrochemical oxidation of phenolic wastewater in a lab-scale reactor, packed into granular activated carbon (GAC) with Ti/SnO₂ anodes and stainless steel cathodes, was interpreted in this study. GAC saturated rapidly if it was only used as sorbent, but application of suitable electric energy for the system simultaneously could recover the adsorption ability of GAC and maintain the continuous running effectively. The titanium dioxide (TiO₂) as catalyst and airflow were also applied to the electrochemical reactor to examine the enhancement for phenol oxidation process. Results revealed that the electrochemical degradation of phenol could be reasonably described by first-order kinetics. In addition, it was illustrated that acid region, increased voltage, more dosage of TiO₂ and higher aeration intensity were all beneficial parameters for phenol oxidation rates. By inspecting the relationship between the rate constants (*k*) and influencing factors, respectively, an overall kinetic model for phenol oxidation was proposed. The kinetics obtained from the experiments under corresponding electrochemical conditions could provide an accurate estimation of phenol concentration effluent and better design of the packed bed reactor.

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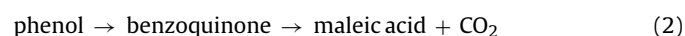
1. Introduction

The hydroxyl radicals (OH[•]) with an exceptional oxidizing power [1,2] have been considered as an effective oxidant for complete combustion of organic pollutants, especially for both phenol and its derivatives. Based on the chemical structures and characters of pollutants, many methods such as Fenton oxidation [3,4], photochemical oxidation [5–7] or direct electrochemical oxidation [8–10] were used to eliminate these types of contaminations from raw water of several chemical industries. The processes are presented as effective, selective, economical, and clean alternatives for dealing with wastewaters bearing high loads of organic compounds, especially for some bio-refractory organic pollutants such as phenol and its derivatives with privileges of fewer or no reagents, simple later disposal, less acreage, running conveniently and less sludge, etc. [11]. However, only low removal yields can be achieved by these ways. Furthermore, others problems, which are related to the high stability of most organic matters in water and to the hindered

mass transfer to the hydroxyl radicals, are responsible for rather low space-time yields and high costs for wastewater treatment. 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. On the other hand, materials have high overpotential for oxygen evolution as anodes is the key controlled way for enhancing the current efficiency during electrochemical oxidation process in packed bed reactor (PBR). Since the discovery of dimensionally stable anodes (DSAs) that could obtain the retardation of oxygen evolution, much works have been carried out on preparing new type of DSAs for electrochemical applications [12]. For the semiconductive character of coated layer on DSAs, reactive hydroxyl radicals are produced by water discharge at high overpotentials, as interpreted by Eq. (1) [13,14]:



As for the highly destructive ability of OH[•], a proposed pathway for phenol degradation was suggested as follows [12,15]:



It is easier for maleic acid to be oxidize to carbon dioxide, thus the overall reactions are interpreted as Eq. (3) [16].



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It is considerably pointed out that benzoquinone (shown in Eq. (2)), which is more hazardous than phenol, is easily formed and should be completely oxidized to CO_2 and water by adequate OH^\bullet .

From analysis above, the problem is to be recognized that some ways, including catalyst must be conducted to enhance the generation of OH^\bullet . The purpose of this study was to provide effective ways for enhancement of the generation of hydroxyl radicals to obtain completely oxidation of phenol using PBR. Ti/SnO_2 anodes with high overpotential were used for resisting water oxidation so as to increase the current efficiency. For increasing the oxidation rate of phenol, TiO_2 as catalyst and airflow for speeding mass transfer and supplying the essential oxygen were also used. Using different dosage of TiO_2 and aeration intensity (described by air–liquid ratio, ALR), kinetic modeling incorporate with variety of voltage, dosage of TiO_2 and applied ALR was obtained to determine the oxidation rate of phenol. The acquirement of relationship between removal efficiency and applied voltage, dosage of TiO_2 or applied ALR could give an integrated estimation of phenol concentration effluent. The expected advantages from this modification were as follows: simultaneous reaction of adsorption by granular activated carbon (GAC) and completely oxidation by hydroxyl radicals generated during electrode process; utilization of DSAs anodes for lowering oxygen evolution in order to increase current efficiency; lowered energy consumption using catalyst and airflow for enhancing the phenol oxidation efficiency; selection of reaction conditions on the basis of higher phenol elimination in both stages of the operation; an accurate estimation of phenol concentration effluent by the effective kinetics.

2. Experimental

2.1. Materials and chemicals

Distilled water was used for the preparation of synthetic wastewater and phenol was obtained from Merck (99.5% pure). The

reagents containing sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) used for the experiments and analysis were obtained in extra pure condition. TiO_2 (Degussa P25) purchased from Aldrich was used in suspension as catalyst. Ti/SnO_2 material and stainless steel were used for anodes and cathodes, respectively. Titanium electrodes with high congregation of OH^\bullet [17] have an area of $20\text{ cm} \times 20\text{ cm}$ doped SnO_2 with thickness of $3\text{ }\mu\text{m}$ [18] 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 voltage ranged between 0 and 30 V. The granular activated carbon with iodine adsorption value of 1000 mg/g, purchased from Huaxin Company, China, has an average particle size of approximately 2 mm, a specific surface of $1028\text{ m}^2/\text{g}$ according to the BET method and a specific weight of 0.375 kg/L. The 5.25 kg GAC was seethed in distilled water for the discharge of air filled in interstices of all the particles.

2.2. Experimental set-up

A continuous electrochemical reactor constructed by polymethyl methacrylate plastics was designed in our laboratory with working volume, length, breadth and height of 14 L, 20 cm, 20 cm and 35 cm, respectively. Anodes and cathodes were fixed in the reactor with the gap of 5 cm. GAC filled between anode and cathode with the height of 35 cm is easily repolarized as another electrode because of the electric field with high gradient. A micropore plate was installed in the reactor for homogeneous distribution of raw water, TiO_2 suspension and air; it also could support the weight of GAC and electrodes. Fig. 1 shows a schematic view of the electrolysis cell. Our reactor is characterized by very high specific surface areas and space-time yields, and can be operated as bipolar system. Electrolyses were carried out at constant temperature, $25 \pm 1\text{ }^\circ\text{C}$. Two water-jacketed reservoirs (8 L) were used for raw water and TiO_2 suspension, and the temperature was controlled by circulating water recycled from a temperature controlled water

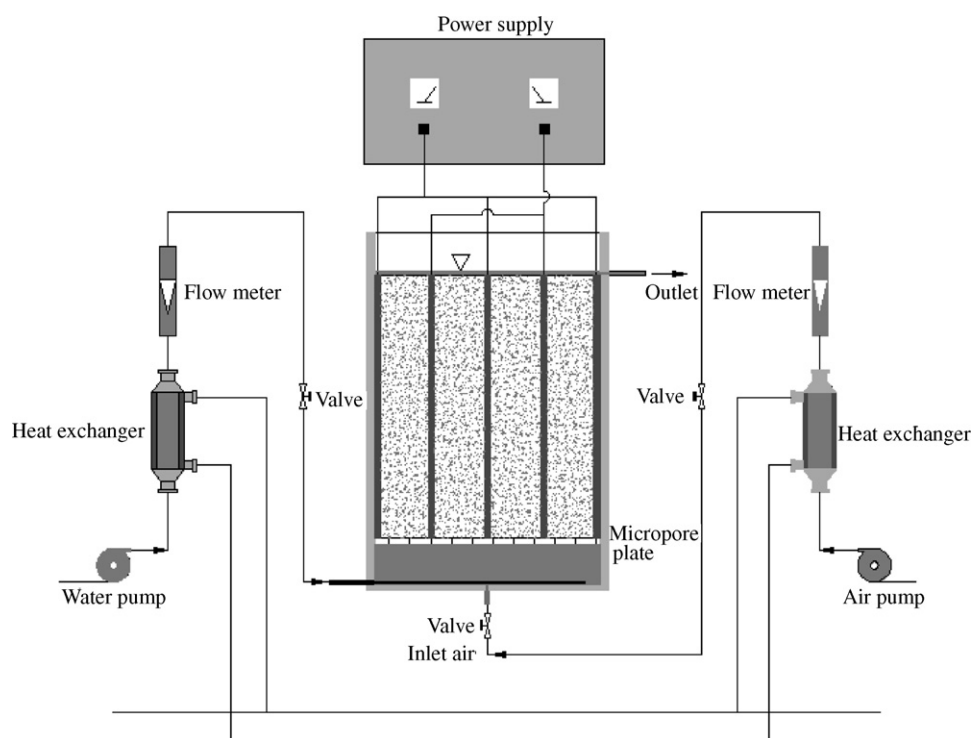


Fig. 1. Schematic design of an electrolysis laboratory plant for wastewater treatment.

Table 1
Design of the experiments

| Test | Description | U (V) | Current (A) | pH value | ALR, air-liquid ratio | TiO ₂ concentration (g/L) |
|------|-----------------------------|-------|-------------|----------|-----------------------|--------------------------------------|
| 1 | A (adsorption) | 0 | 0 | 6.5 | 0 | 0 |
| | B (U) | 20 | 40 | 6.5 | 0 | 0 |
| | C (U+ALR) | 20 | 40 | 6.5 | 1.2 | 0 |
| | D (U+TiO ₂) | 20 | 40 | 6.5 | 0 | 0.5 |
| | E (U+ALR+TiO ₂) | 20 | 40 | 6.5 | 1.2 | 0.5 |
| 2 | pH 3.4 | 20 | 40 | 3.4 | 0 | 0.5 |
| | pH 6.5 | 20 | 40 | 6.5 | 0 | 0.5 |
| | pH 8.2 | 20 | 40 | 8.2 | 0 | 0.5 |
| | pH 10.3 | 20 | 40 | 10.3 | 0 | 0.5 |
| 3 | U = 8 | 8 | 14.5 | 6.5 | 0 | 0 |
| | U = 12 | 12 | 22.3 | 6.5 | 0 | 0 |
| | U = 16 | 16 | 30.7 | 6.5 | 0 | 0 |
| | U = 20 | 20 | 40 | 6.5 | 0 | 0 |
| | U = 25 | 25 | 47.2 | 6.5 | 0 | 0 |
| | | | | | | |
| 4 | ALR = 0 | 20 | 40 | 6.5 | 0 | 0 |
| | ALR = 0.6 | 20 | 40 | 6.5 | 0.6 | 0 |
| | ALR = 1.2 | 20 | 40 | 6.5 | 1.2 | 0 |
| | ALR = 3.0 | 20 | 40 | 6.5 | 3.0 | 0 |
| | ALR = 4.2 | 20 | 40 | 6.5 | 4.2 | 0 |
| 5 | TiO ₂ = 0 | 20 | 40 | 6.5 | 0 | 0 |
| | TiO ₂ = 0.25 | 20 | 40 | 6.5 | 0 | 0.25 |
| | TiO ₂ = 0.40 | 20 | 40 | 6.5 | 0 | 0.40 |
| | TiO ₂ = 0.50 | 20 | 40 | 6.5 | 0 | 0.50 |
| | TiO ₂ = 0.60 | 20 | 40 | 6.5 | 0 | 0.60 |

bath monitored with glass thermometers. Pumps were used to pump wastewater, TiO₂ suspension and air to the PBR in trickle mode.

2.3. Experimental procedure

During the experimental period, a total of five sets of tests were designed (Table 1) with different purposes under constant initial phenol concentration of 1603.5 mg/L. The first set of tests was conducted under different experimental conditions including applied voltage, aeration intensity and addition of catalyst (TiO₂) under constant pH value of 6.5 of raw water while the secondary set of tests was carried out under the varied pH values which were adjusted by adding H₂SO₄ or NaOH in the reservoir before pumped into the PBR. The third set of tests was performed with various applied voltage of 8, 12, 16, 20 and 25 V to identify the effect on phenol electrochemical oxidation efficiency with pH 6.5. In order to determine the enhancement of phenol degradation by the addition of air and catalyst, the fourth and fifth sets of the tests were carried out to obtain the relationship between different air-liquid ratios, dosage of TiO₂ and rate constants. The airflow rate and flow rate of TiO₂ suspension could be calculated by different reaction times. All the experiments were operated without any pH adjustment of effluent. The resulting solutions were filtered to remove any traces of GAC and then were analyzed for phenol concentration.

2.4. Analytical methods

Concentration of phenol was measured by standard method based on spectrophotometric analysis at 510 nm of the developed color resulting from the reaction of phenol with 4-aminoantipyrene and the phenol removal rate was calculated by $[(C_0 - C_t)/C_0] \times 100\%$, where C_0 and C_t are phenol concentration of raw water and at time t . The pH value of all solutions and samples were determined according to standard methods for the examination of water and wastewater [19].

3. Results and discussion

3.1. Electrochemical oxidation of phenol under different experimental conditions

Fig. 2 illustrates the results of the reduction of phenol concentration under various experimental conditions. Curve (A) in Fig. 2 shows the dependence of phenol concentration outlet on different residence time in GAC bed without applied cell voltage, airflow or TiO₂. In other words, it is a type of adsorption curve for phenol elimination under continuous water flows. At the beginning of the adsorption process, most of phenol numerators could be adsorbed by fresh GAC particles and the removal efficiency reaches 55%. The phenol concentration rapidly increases with the continuous running until the increasing trend gets very slow, which indicates that the GAC bed is close to reaching its maximum adsorption capacity. Seen from the curve (A), it is obvious that the phenol removal efficiency is independence of the residence time of wastewater but

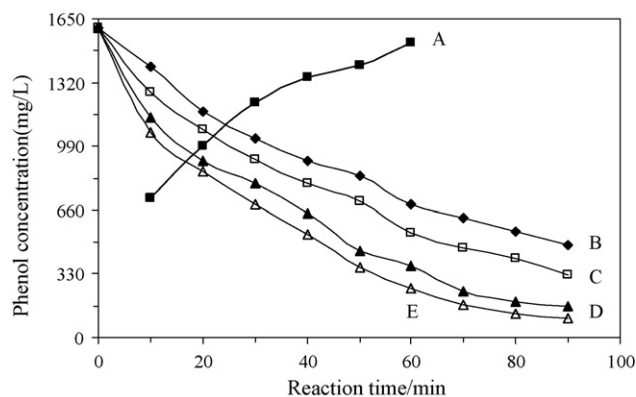


Fig. 2. Changes of phenol concentration with time under different experimental conditions [operating conditions: pH 6.5, temperature = 25 ± 1 °C, (A) $U=0$, ALR=0, $[TiO_2]=0$; (B) $U=20$ V, ALR=0, $[TiO_2]=0$; (C) $U=20$ V, ALR=1.2, $[TiO_2]=0$; (D) $U=20$ V, ALR=0, $[TiO_2]=0.5$ g/L; (E) $U=20$ V, ALR=1.2, $[TiO_2]=0.5$ g/L].

affected by the adsorption characteristic of the fresh GAC. The other curves in Fig. 2 show the electrochemical oxidation results of phenol with applied voltage U , U and catalyst TiO_2 of 0.5 g/L, U and ALR of 1.2, U and catalyst TiO_2 of 0.5 g/L and ALR of 1.2, respectively, under constant voltage of 20 V. The curves (B)–(E) all demonstrate the phenol concentration effluent decreases with the increase of reaction times under the constant cell voltage of 20 V, and the addition of TiO_2 or airflow could obtain perfect enhancement of phenol removal efficiency. These experiments indicate that if the phenol removes only by adsorption of the GAC bed, the removal rate decreases rapidly and finally approaches zero due to the saturation of the GAC. In contrast, the application of GAC as a bed electrode can be expected to keep high phenol removal efficiency for wastewater treatment during the continuous use of the bed electrode as long as adsorption velocity and electrochemical oxidation velocity are equal.

3.2. Kinetic modeling for electrochemical oxidation of phenol

It is obvious that the curves (B)–(E) in Fig. 2 indicate the electrochemical oxidation of phenol follows the first-order kinetic modeling as expressed by Eq. (4) and these results are in accordance with previous literatures [11,20,21].

$$\frac{C_t}{C_0} = e^{-kt} \quad (4)$$

where C_0 , C_t are phenol concentration of raw water and at time t (mg/L), k is the first-order reaction rate constant (min^{-1}), and t is the reaction time (min).

During the oxidation process, electrochemical conditions play the leading roles in phenol degradation even if without any catalyst or airflow. In a word, the oxidation rate of phenol could be increased by the function of TiO_2 and airflow, but the efficiency of phenol elimination is controlled only by voltage and current applied to the reactor in essence. Many previous papers reported that there is a linear relation between applied current and phenol removal rate under constant reaction time [15,16,22,23], furthermore, the voltage and current could not be given a linear description [24,25] but a power relationship, which indicates the electric resistance of the system is not a constant with the variety of applied voltage from these experiments.

Since the electrochemical oxidation of phenol could be described by first-order kinetics even under the application of TiO_2 and airflow, as well as the proof in the cited literatures, it is assumed that the reaction rate constant (k) is considered being affected by several key factors, including voltage (U), dosage of TiO_2 ($[\text{TiO}_2]$) and aeration intensity ($[\text{ALR}]$). A pure empirical form of Eq. (5) is then used to present their relations:

$$k = f(U, \text{TiO}_2, \text{ALR}) = m[U]^a e^{(b[\text{ALR}])} e^{(c[\text{TiO}_2])} \quad (5)$$

where m , a , b and c are constants.

By Eq. (5), without addition of TiO_2 and airflow, k is only affected by applied voltage. The value for constant m could be obtained by the data analysis of the relation between k and U .

3.3. Effect of pH on electrochemical oxidation of phenol

The effect of different pH value of 3.4, 6.5, 8.2 and 10.3 on the oxidation of phenol and the relationship between $\ln(C_t/C_0)$ and time (t) was shown in Fig. 3. It can be seen that the reduction of phenol concentration in electrochemical solution is more efficient under acidic environment than that of the alkaline ones and this phenomena was reported by Fockede and Van Lierde [24] and Iniesta et al. [26].

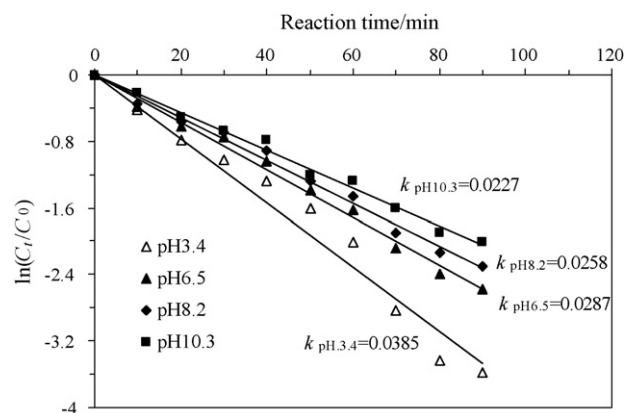


Fig. 3. Kinetic effects of pH on electrochemical oxidation of phenol under applied voltage $U = 20$ V, pH 6.5, temperature = 25 ± 1 °C and $[\text{TiO}_2] = 0.5$ g/L.

It could be interpreted that oxygen evolution reduces the overall current efficiency for both direct and indirect oxidation of organic pollutants, which decreases the rate constants for phenol degradation [27]. Therefore, the acidic region is easily to control the oxygen evolution so as to decrease the power loss. In other words, lower pH could enhance the oxidation degree for phenol removal.

Such increase of phenol removal efficiency is for the increase of undissociated molecules of phenol under acidic region, which causing the enhancement of adsorption ability of GAC [28]. The electrochemical oxidation of phenol occurs subsequently by bipolar GAC leading to the oxidation rate be more rapid at pH 3.4 than that of pH 10.3.

3.4. Effect of voltage on electrochemical oxidation of phenol

For inquisition of effect of varied voltage of 8, 12, 16, 20 and 25 V with corresponding current of 14.5, 22.3, 30.7, 40 and 47.2 A on reaction rate constant of phenol oxidation, these experiments were conducted with the description of their relation in Fig. 4 under constant pH value of 6.5. Accordingly, a considerable increase of the rate constant with the increasing voltage can be observed from this figure. For an applied voltage of 8 V, i.e. under the condition of open circuit, the rate constant is only 0.0068 min^{-1} , while it is 0.0164 min^{-1} under the cell voltage of 25 V. The latter is about two times higher than the former. These enhancement effects are for the increase in the driving force for the electrons transfer of the electrode reaction, in addition to the increase of current, which is attributed to the increase of ionic transport so as to increases the

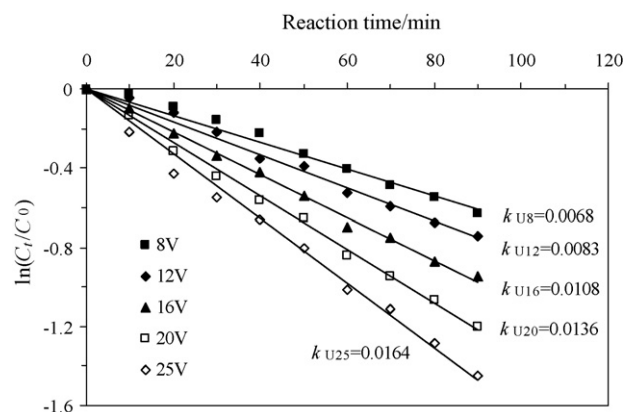


Fig. 4. Kinetic effects of applied voltage U on electrochemical oxidation of phenol under pH 6.5 and temperature = 25 ± 1 °C.

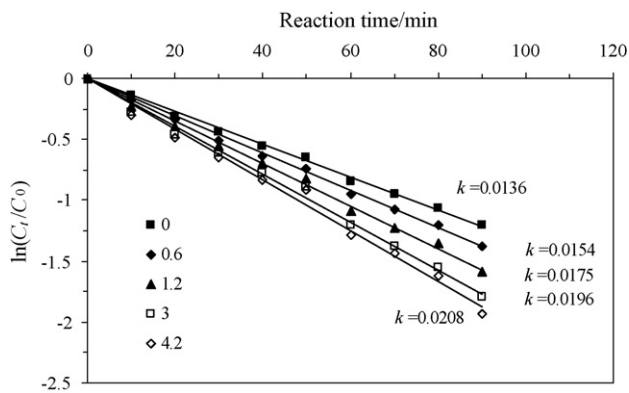


Fig. 5. Kinetic effects of ALR on electrochemical oxidation of phenol under applied voltage $U = 20$ V, pH 6.5 and temperature = 25 $^{\circ}$ C.

rate of generation of OH^{\bullet} responsible for the phenol oxidation process, with increasing voltage. This indicates potential is the major driving force for the respective phenomena of interest in electrochemical oxidation process [29]. It is proposed in this study that the exponential dependence of the first-order kinetic constant (k) on the voltage can be expressed as Eq. (6).

$$k = m[U]^a \quad (6)$$

According to the experimental results, $m = 0.0008$ and $a = 0.9376$ ($R^2 = 0.9988$), Eq. (6) can be represented in the form of

$$k = 0.0008[U]^{0.9376} \quad (7)$$

3.5. Effect of airflow on electrochemical oxidation of phenol

For the purposes of agitating the GAC in order to speed mass transfer and supply the essential oxygen for electrochemical reactions, the air was sparged by a micropore plate in the electrochemical reactor [30]. Fig. 5 gives a description of the phenol oxidation rate constants with different air-liquid ratios at constant applied voltage of 20 V and pH of 6.5. This figure clearly shows that the higher the ALR, the greater reaction rates would be obtained from the experiments.

In this study, it was proposed that the rate constant affected by the ALR can be expressed as Eq. (8):

$$k = k_1 e^{b[\text{ALR}]} \quad (8)$$

where k_1 is constant. Computed data of current experiment shows that $k_1 = 0.0145$, $b = 0.0946$ ($R^2 = 0.9064$). Therefore, the above equation might be rewritten as Eq. (9):

$$k = 0.0145 e^{0.0946[\text{ALR}]} \quad (9)$$

Seen from Eq. (9), the degradation rate constant is slightly affected by ALR, which means the aeration process is not an economical choice for the enhancement of phenol removal efficiency regardless of accelerating of mass transfer and sufficing the oxygen demand for the reaction process.

3.6. Effect of TiO_2 concentration on electrochemical oxidation of phenol

TiO_2 with energy bandgap of 3.2 eV acts not only as a catalyst support, but also interacts with the supported phase as a promoter [31] and can be easily activated during photochemical process [7,32]. Ti anodes coated SnO_2 might help to develop convenient channels for electrons transition and help to enhance the electrocatalytic characteristics and it is perhaps for the additional energy bands could be induced in the structure of coating metal oxides [12].

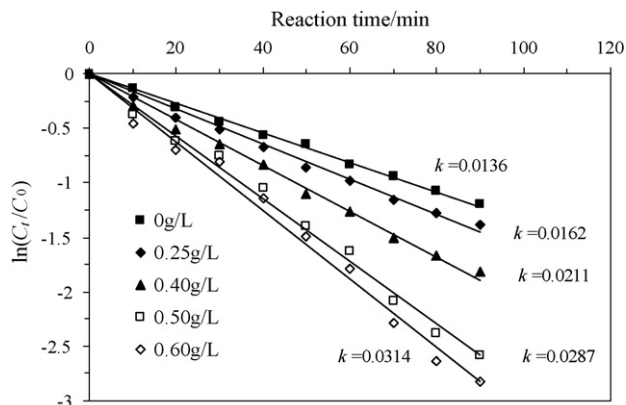
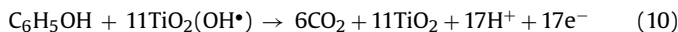
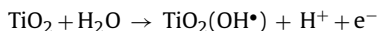


Fig. 6. Kinetic effects of TiO_2 concentration on electrochemical oxidation of phenol under applied voltage $U = 20$ V, pH 6.5 and temperature = 25 ± 1 $^{\circ}$ C.

Furthermore, addition of semiconductor of TiO_2 could decrease the unwanted power loss to oxygen generation because of its high oxygen evolution potential and be likely to increase the generation of hydroxyl radicals just as the application of DSA. The mechanism is possible interpreted as follows [33]:



Electrochemical oxidation of phenol expressed by Eq. (10), contrasted to Eq. (3), is more likely to occur on higher oxygen overpotential surfaces that contain SnO_2 material. For the rare report of TiO_2 catalyst applied in PBR, we proposed the possible mechanism, further investigation is still required to understand better all the roles played by these metal oxides.

The test was performed with varied of TiO_2 concentration of 0.25, 0.40, 0.50, 0.60 g/L respectively at pH 6.5 while voltage of 20 V to test the catalytic ability by the oxidation rate constants. The results were displayed in Fig. 6. It is seen from this figure that the addition of TiO_2 was an effective way to improve the electrochemical oxidation of phenol. When the concentration of TiO_2 was ranged between 0 and 0.50 g/L, the increase of TiO_2 concentration made the rate constant increased rapidly; but when the concentration of TiO_2 reached up to 0.50 g/L, the rate constant increased slightly. In this study, a relationship between $[\text{TiO}_2]$ and k was proposed as the form in Eq. (11).

$$k = k_2 e^{c[\text{TiO}_2]} \quad (11)$$

where k_2 is constant. According to current experimental results, $k_2 = 0.0126 \text{ min}^{-1}$ and $c = 1.4803$ ($R^2 = 0.9354$). The above equation can be represented as Eq. (12):

$$k = 0.0126 e^{1.4803[\text{TiO}_2]} \quad (12)$$

3.7. Development of rate constant equation

A series of experiments were conducted in this study to inspect the effects of key factors, including voltage, pH, catalyst and aeration intensity on the oxidation of phenol. From previous section, the constants of m , a , b and c with the values of 0.0008, 0.9376, 0.0946 and 1.4803, respectively, have been determined. By substituting these values to Eq. (5), a comprehensive form of k can be obtained:

$$k = 0.0008[U]^{0.9376} e^{(0.0946[\text{ALR}])} e^{(1.4803[\text{TiO}_2])} \quad (13)$$

When electrochemical oxidation of phenol was under the conditions of $U = 20$ V, $[\text{TiO}_2] = 0.5$ g/L, ALR = 1.2 with constant tem-

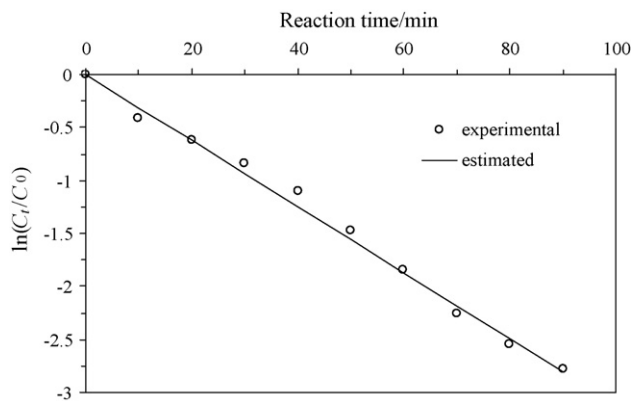


Fig. 7. Comparison of the estimated data with the experimental data under applied voltage $U=20$ V, ALR = 1.2, $[\text{TiO}_2]=0.5$ g/L, pH 6.5 and temperature = 25 ± 1 °C.

perature and pH value of 25 °C and 6.5, Eq. (4) could be arranged as Eq. (14).

$$\frac{C_t}{C_0} = e^{-0.0008[U]^{0.9376} e^{0.0946[\text{ALR}]} e^{1.4803[\text{TiO}_2]} t} \quad (14)$$

Using Eq. (14), the calculated results and the experimental data are plotted in Fig. 7 ($R^2 = 0.9931$). This figure demonstrates that the results obtained from kinetic modeling are in good agreement with experimental data although the estimated value of phenol concentration is slightly lower than that of the experimental data when the reaction time is less than 20 min and between 70 and 90 min but slightly higher than the experimental data when the time is from 30 to 60 min.

4. Conclusions

Experimental investigation has demonstrated that the phenol can be eliminated continuously by electrochemical oxidation process using Ti/SnO₂ anodes. Seen from the experiments, GAC was saturated rapidly without the assistance of electric energy. When voltage of 20 V was applied under different reaction conditions with constant temperature of 25 ± 1 °C, pH 6.5, respectively, the adsorption ability of GAC all could be recovered. The acid regions could increase the oxidation of phenol. The operational factor of applied voltage played the most important roles in determining the oxidation rate of phenol, the addition of TiO₂ and airflow could obviously increase the reaction process. Hence, corresponding experiments were conducted to obtain the effect on rate constants by different applied voltage, dosage of TiO₂ and ALR. Using first-order kinetics to describe the electrochemical oxidation process of phenol, a kinetic model of phenol oxidation process was proposed to calculate the phenol concentration effluent: $C_t = C_0 e^{-0.0008[U]^{0.9376} e^{0.0946[\text{ALR}]} e^{1.4803[\text{TiO}_2]} t}$. The results calculated from the kinetic model are in good agreement with experimental data and the rate for phenol oxidation could be easily estimated under the given electrochemical conditions.

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References

- [1] K. Ito, W. Jian, W. Nishijima, A.U. Baes, E. Shoto, M. Okada, Comparison of ozonation and AOPs combined with biodegradation for removal of THM precursors in treated sewage effluents, *Water Sci. Technol.* 38 (1998) 179–186.
- [2] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today* 53 (1999) 51–59.
- [3] M.E. Lindsey, M.A. Tarr, Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide, *Chemosphere* 41 (2000) 409–417.
- [4] N. Kang, D.S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, *Chemosphere* 47 (2002) 915–924.
- [5] D. Curco, S. Malato, J. Blanco, J. Gimenez, P. Marco, Photocatalytic degradation of phenol: comparison between pilot-plant-scale and laboratory results, *Solar Energy* 56 (1996) 387–400.
- [6] J. Gimenez, D. Curco, P. Marco, Reactor modeling in the photocatalytic oxidation of wastewater, *Water Sci. Technol.* 35 (1997) 207–213.
- [7] Z. Ding, G.Q. Lu, P.F. Greenfield, A kinetic study on photocatalytic oxidation of phenol in water by silica-dispersed titania nanoparticles, *J. Colloid Interface Sci.* 232 (2000) 1–9.
- [8] P.I. Iotov, S.V. Kalcheva, Mechanistic approach to the oxidation of phenol; at a platinum/gold electrode in an acid medium, *J. Electroanal. Chem.* 442 (1998) 19–26.
- [9] S. Andreescu, D. Andreescu, O.A. Sadik, A new electrocatalytic mechanism for the oxidation of phenols at platinum electrodes, *Electrochem. Commun.* 5 (2003) 681–688.
- [10] D. He, S. Mho, Electrochemical reactions of phenolic compounds at ferric ion co-doped SnO₂:Sb⁵⁺ electrodes, *J. Electroanal. Chem.* 568 (2004) 19–27.
- [11] 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.
- [12] 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.
- [13] G. Sine, C. Comninellis, Nafion[®]-assisted deposition of microemulsion-synthesized platinum nanoparticles on BDD: activation by electrogenerated OH radicals, *Electrochim. Acta* 50 (2005) 2249–2254.
- [14] J.L. Boudenne, O. Cerclier, J. Galea, E.V. Vlist, Electrochemical oxidation of aqueous phenol at a carbon black slurry electrode, *Appl. Catal. A* 143 (1996) 185–202.
- [15] Y.M. Awad, N.S. Abuzaid, The influence of residence time on the anodic oxidation of phenol, *Sep. Purif. Technol.* 18 (2000) 227–236.
- [16] J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, C. Comninellis, Electrochemical oxidation of phenol at boron-doped diamond electrode, *Electrochim. Acta* 46 (2001) 3573–3578.
- [17] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, *Electrochim. Acta* 39 (1994) 1857–1862.
- [18] L. Lipp, D. Pletcher, The preparation and characterization of tin dioxide coated titanium electrodes, *Electrochim. Acta* 42 (1997) 1091–1099.
- [19] APHA/AWWA, Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, Washington, DC, 1992.
- [20] 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.
- [21] R. Alnaizy, A. Akgerman, Advanced oxidation of phenolic compounds, *Adv. Environ. Res.* 4 (2000) 233–244.
- [22] 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.
- [23] 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.
- [24] E. Fockede, A. Van Lierde, Coupling of anodic and cathodic reactions for phenol electro-oxidation using three-dimensional electrodes, *Water Res.* 36 (2002) 4169–4175.
- [25] E.A. Abd El Meguid, S.S. Abd El Rehim, E.M. Moustafa, Electroplating of iron from alkaline gluconate baths, *Thin Solid Films* 443 (2003) 53–59.
- [26] J. Iniesta, J. Gonzalez-Garca, E. Expsito, V. Montiel, A. Aldaz, Influence of chloride ion on electrochemical degradation of phenol in alkaline medium using bismuth doped and pure PbO₂ anodes, *Water Res.* 35 (2001) 3291–3300.
- [27] 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.
- [28] R.J. Martin, K.O. Iwugo, The effects of pH and suspended solids in the removal of organics from waters and wastewaters by the activated carbon adsorption process, *Water Res.* 19 (1982) 73–82.
- [29] J.C. Card, G. Valentin, A. Storck, The activated carbon electrode: a new, experimentally verified mathematical model for the potential distribution, *J. Electrochem. Soc.* 137 (1990) 2736–2745.
- [30] A. Alvarez-Gallbergos, D. Pletcher, The removal of low level organics via hydrogen peroxide formed in a viticulated vitreous carbon cathode cell. Part 2: The removal of phenols and related compounds from aqueous effluents, *Electrochim. Acta* 44 (1999) 2483–2492.
- [31] C. Martin, I. Martin, V. Rives, Effect of sulfate removal on the surface texture and acid-base properties of TiO₂ (anatase), *J. Math. Sci.* 30 (1995) 3847–3852.
- [32] J. Marugan, D. Hufschmidt, M. Lopez-Muoz, V. Selzer, D. Bahnemann, Photonic efficiency for methanol photooxidation and hydroxyl radical generation on silica-supported TiO₂ photocatalysts, *Appl. Catal. B* 62 (2006) 201–207.
- [33] 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.