Partial Degradation of Phenol by Advanced Electrochemical Oxidation Process

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The partial electrocatalytic degradation of phenol to organic acids has been investigated using an undivided electrolytic reactor with a β -PbO₂ anode containing fluorine resin. It was found that the decrease of benzoquinone (BQ) formed during phenol dedgadation and the acceleration of the process from phenol to organic acids are possible under an optimized operating condition. A possible pathway for phenol degradation was proposed, and a mathematical model for phenol and BQ evolution was developed. Operating parameters such as initial pH, current density, and temperature of the reaction were found to greatly impact the degradation rate of the phenol and even the pathway. Higher removal rate of phenol and BQ can be achieved at an appropriate temperature and higher current density in acidic medium preferably at pH 4. Under these conditions, phenol would be more likely degraded in the pathway from phenol to organic acids rather than through the BQ. When phenol is completely removed, the toxicity of the wastewater would be lessened suitable for biological process treatment. Accounting for the decrease of instantaneous current efficiency (ICE) during degradation, partial degradation would be highly economical for wastewater treatment, which would be an alternative process in practical application.

Introduction

Many industries, such as oil refineries and coke, chemical, and plastic plants, are found to be the sources of phenolic pollutants (1). Due to the resistance to common microorganisms, phenolic wastes cannot be treated by biological action. Moreover, they are toxic even in the presence of low concentration (2); therefore, the treatment will be of considerable importance in environmental protection.

Various technologies and processes, such as extraction (3), activated carbon adsorption (4), chemical oxidation (5), and biodegradation (6) have been conventionally attempted for phenolic wastewater treatment. They can be mainly classified as (a) complete oxidation of the contaminants to CO_2 , water, and other inorganic products, (b) modification or alteration of the chemical structures of the organic molecules to make the separation well or easier, and (c) partial destruction of the molecules to make it less toxic or more biodegradable.

Recently, electrochemical method for organic wastewater treatment has attracted a great deal of attention (7-11). The treatment of phenolic wastewater has been the subjects of many investigators, which mainly focused on the full

mineralization of phenols to CO_2 (1, 12–15). The mineralization or oxidation of phenol is principally depended on the hydroxyl radical electrogenerated on the surface of the electrodes. Therefore, the processes are called advanced electrochemical oxidation processes (AEOPs). However, there were few papers using AEOPs aiming at the partial degradation of phenols to make it possible by biological treatment.

Practically, the complete oxidation of phenol to carbon dioxide by electrochemical treatment will not be economical due to high-energy consumption. Partial oxidation of phenol, a ring opening reaction of phenol, results in organic acids of a biological nutrient requiring less energy consumption. Thus, the partial oxidation of organic biorefactory pollutants will provide us a valuable pretreatment technique for subsequent cheap biological treatment.

Benzoquinone (BQ) and aliphatic carboxylic acids such as maleic acid and oxalic acid are the principal intermediates of phenol degradation. BQ represents one of the first byproducts formed. Aliphatic carboxylic acids such as maleic acid represent products of the ring fracture, and carbon dioxide represents the final products of oxidation (14). When phenol is degraded to aliphatic products, the wastewater will become more biodegradable and much less toxic (16). Therefore, as to the partial degradation of phenol, attention should be paid to the stages from phenol to organic acids.

p-Benzoquinone (BQ) has been reported as the main intermediate before the ring opening to the formation of aliphatic carboxylic acids and its degrading rate is slower than that of phenol (*15*). Moreover, BQ is even much more toxic than phenol (*17*). Therefore, it is necessary to decrease the amount of BQ formed and to accelerate the ring opening process.

The present investigation is to focus on the partial degradation of phenol to organic acids on a β -PbO₂ anode containing fluorine resin and to simulate a mathematical model based on the pathway of partical phenol degradion. Parameters obtained could be clearly examined and predicted the behavior of phenol degraditon. Therefore it could be helpful to find the optimized operating conditions of partial degradation and to better understand the degradation process.

Experimental Section

Anode Preparation. The anode used here was a modified β -PbO₂ electrode (Φ 45 × 200 mm), which was codeposited with fluorine resin on a cylindrical ceramic tube. The preparation procedures were principally the following: chemical deposition, α -PbO₂ preliminary-deposition, and β -PbO₂ deposition. Prior to the deposition, the ceramic cylinder was polished with grit paper, poached in hot NaOH solution (20%) for hours, and then washed in boiled water.

In the chemical deposition procedure, the pretreated cylinder was immersed into the solution containing 0.05 mol L^{-1} Pb(Ac)₂ and 0.1 mol L^{-1} NH₄Ac to form PbO₂, performing at thermostatically at 35–40 °C and pH 8–9.5 adjusted with 28% ammonium, and then moved to (NH₄)₂S₂O₈ (0.1 mol L^{-1}) solution. To accelerate the process, a catalyst of AgNO₃ (0.3 mol L^{-1}) was added into the (NH₄)₂S₂O₈ solution simultaneously. The deposition was taken for about 1 h and repeated three times.

Electrochemical deposition of $\alpha\text{-PbO}_2$ was carried out galvanostatically in 0.11 mol L $^{-1}$ PbO + 3.5 mol L $^{-1}$ NaOH solution at 80 °C, setting voltage under 1–2 V and current 20–100 A m $^{-2}$. Compressed air was served to mix the solution well.

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FIGURE 1. The schematic diagram of the experimental setup: A. electrocatalysis reactor, B. circulated pump, C. water batch, D. reservoir, E. magetic stirrer, F. to biological process, G. sampling port, H. thermometer, and I. power supply.

The predeposited anode was then doped with fluorine and codeposited with fluorine resin in the solution containing Pb(NO₃)₂ (0.45–0.60 mol L⁻¹), HNO₃ (0.08–0.40 mol L⁻¹), KF (0.025–0.035 mol L⁻¹), and fluorine resin (2–8 mL L⁻¹, about 60% tetrafluoroethlyene) under 2.6–3.0 V and current 500–600 A m⁻² to convert the α -PbO₂ into β -PbO₂ form. The electrolyte was adjusted at pH 0.5–1.5 and maintained at 80 °C. During the electrolyte to eliminate NO₂⁻ formed, which may cause adhered-PbO₂ to be redissolved. The deposition was carried for more than 1 h.

Apparatus. Figure 1 shows the schematic diagram of the experimental setup. The anode of β -PbO₂ and the cathode of Ni–Cr–Ti alloy grid (20 mesh) were concentrically assembled into the undivided electrolytic cell with a final volume of about 0.33 dm³. The supporting electrolyte of 1 g L⁻¹ Na₂SO₄ and certain concentration of phenol pollutant was pumped through the reactor and then returned to the reservoir for recycling. The reservoir was placed in a water bath to regulate the reaction temperature desired. Constant current was maintained at the desired level with only minor adjustments of the applied voltage. During each run, samples were taken from the sampling port in the reservic for analysis at appropriate intervals.

Analysis. Analyses of phenol and its oxidation products were carried out on a high-performance liquid chromatograph (HPLC, Gilson, France). Aliquots of $25 \,\mu$ L were injected to the HPLC, running with mobile phase of acetonitrile/ water (v/v) at 58/42, and an addition of 2 mL of concentrated H₃PO₄ per liter of solution. The separation was performed using an ODS-18 reversed phase column (Alltech, USA) at the flowrate of 1.5 mL min⁻¹ and column temperature of 25 °C. An UV detector was used with the wavelength set at 254 nm. Organic acids were determined by ion chromatography (IC, Alltech, USA) with a mobile phase of sodium carbonate (0.85 mmol L⁻¹)/sodium bicarbonate (0.9 mmol L⁻¹) at a flowrate of 1.5 mL min⁻¹. The detector was an Alltech 550 conductivity detector at 35 °C.

Determination of the Current Efficiency. The COD (chemical oxygen demand) method was used for determining the current efficiency during the phenol degradation (*18*). The COD was measured by the standard method (closed reflux/photometry) (*19*). The instantaneous current efficiency



FIGURE 2. The variation of main products and toxicity in the degradation of phenol. Operational conditions: initial phenol concentration 100 mg L⁻¹; circulated rate 1800 mL min⁻¹; temperature 25 °C; K₂SO₄ 1.0 g L⁻¹; current density 7.5 mA cm⁻²; pH 5.6.

(ICE) was calculated using the following relations

$$ICE = \frac{|(COD)_t - (COD)_{t+\Delta t}|}{8 \cdot I \cdot \Delta t} \cdot F \cdot V$$

where COD_t, COD_{t+ Δt} —the COD at time *t*, *t*+ Δt (g O₂ dm⁻³), respectively, *F*—the Faraday constant (96487C mol⁻¹), *V*—the volume of the electrolyte (dm³), and *I*—the current (A).

Toxicity Test. Results of the toxicity are presented either as EC_{50} or as toxicity factor (*f*):

$$f = 1/EC_{50} (L mg^{-1})$$

The EC_{50} is defined as the concentration of the tested compounds resulting in a 50% reduction of respiration rate of activated sludge.

Results and Discussions

Phenol Oxidation. The main products formed during the electrochemical oxidation are benzoquinone (BQ), fumaric acid, and oxalic acid. Figure 2 typically shows the main products in the phenol degradation. It can be seen from the figure that phenol and BQ are vanished almost at the same time in 2 h. The concentration of organic acids increases at the first 40 min and then begins to decrease till complete removal within 4 h. Hydroquinone, catechol, and maleic acid were also detected in very small quantities in the degradation of higher initial concentration of phenol. Hydroquinone is the first product formed by oxidation of the phenol molecule. The oxidation of BQ, after ring opening, leads to the formation of aliphatic carboxylic acids such as fumaric acid and oxalic acid. The final products are carbon dioxide and water.

In general, the degradation of phenol follows the sequences below: (1) oxidation of phenol to other hydroxylated or oxygenated compounds, especially quinonic compounds (cyclic intermediates), (2) the ring opening reaction to form organic acids, and (3) mineralization of organic acids to carbon dioxide.

However, the experimental results in Figure 2 show that the degradation is not simple in the sequences (1)-(2)-(3)as recognized by many authors (12, 15). First, the organic acids are presented in the solution from the very beginning of electrocatalysis and are always observed in the experiment. This observation is different from that reported in the literature (14). Second, the evolution tendencies of the organic acids and the quinonic compounds are also different from the observation by Kirk (14) and Savall (15). The maximum concentration of organic acid was found to be greater than that of quinonic compounds. Although, cyclic intermediates could be presented in a lower amount if the ring opening reaction is higher than that of phenol oxidation to quinonic compounds. However, this interpretation would be paradoxical with the classical pathway where the oxidation of BQ to organic compounds had been considered as the ratedetermining step in phenol degradation (15), i.e., the rate constant for BQ oxidation would be smaller than that of its formation. On the basis of these considerations, there might exist another way where phenol degradation to organic acids was not through BQ. Some investigators noticed the similar phenomenon as "electrochemical cold combustion" on the anode (20). In agreement with this, there might exist the electrochemical oxidation of phenol to organic acids through and not through quinonic compounds simultaneously. The following diagram may represent the principal pathway of phenol degradation. Nevertheless, reaction in any path would not be a single step; it will be admissible to concern main reaction steps for those intermediates relatively stable and detectable.



In the above reaction pathway, A represents the original organic compound (phenol), B is the quinonic compounds, mainly the benezoquinone (BQ), D is the organic acids, and F is the final substrates, CO₂. K_i (i = 1, 2, 3, 4) is the apparent rate constant (min⁻¹).

It has been very interesting to propose a model for partial degradation of phenol to evaluate the influence of affected factors. Some assumptions should be involved to simplify the model: (a) the reactions took place on the surface of the anode and the degradation of phenol should be mainly attributed to the hydroxyl radical produced on the anode. The overall steps for phenol degradation would principally involve such stages: mass transport of organic compounds from the bulk of the solution toward the surface of the anode, adsorption of organic compound onto the catalytic sites of the anode, and the reaction between hydroxyl radical and adsorbed organic molecular. In our experiment, mass transports should not be a rate-determining stage since the circulating rate of the electrolyte was set in a reasonable range at 1800 mL min⁻¹ for the total 0.33 L of solution. Adsorption of low concentration of organic compounds onto the anode would also be rather fast. Therefore, the overall stage should be a reaction-controlled process. (b) Due to the strong oxidation ability of the hydroxyl radical, there would be no hydroxyl radical accumulation in the solution. Consequently, all reactions were simplified to be pseuo-firstorder kinetics. The apparent rate constant K_i is related to the true rate constant k_i as follows (21):

$$K_i = k_i \theta_{\rm OH} A / V$$

where *A* is the effective area of the anode (m²), *V* is the volume of the electrolyte (m³), and θ_{OH} is the fractional surface coverage of OH radicals on the anode in the steady state.

Taking into account all the assumptions, the following set of differential equations could be obtained:

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -K_1[A] - K_2[A] = -K[A]$$
$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = K_2[A] - K_3[B]$$

where $K = K_1 + K_2$ is the total apparent rate constant (min⁻¹)



FIGURE 3. Phenol degradation at different initial phenol concentration. Operational conditions: circulated rate 1800 mL min⁻¹; temperature 25 °C; K₂SO₄ 1.0 g L⁻¹; current density 7.5 mA cm⁻²; pH 5.6.

and [A] and [B] represent the concentration of phenol and BQ, respectively.

The integration constants can be evaluated from the initial conditions:

at time
$$t = 0$$
, $[A] = [A]_0$; $[B] = 0$

The generalized kinetic model is given by

$$[\mathbf{A}] = [\mathbf{A}_0] \exp(-Kt)$$

$$[B] = \frac{K_2[A_0]}{K - K_3} \left[\exp(-K_3 t) - \exp(-Kt) \right]$$

Moreover, to evaluate the ratio between phenol oxidation to organic acids and through BQ oxidation to organic acids, the selectivity α is defined as

$$\alpha = \frac{K_1}{K_2}$$

To explore the feasibility of the model, partial degradation of phenol at different initial concentrations was examined. Figure 3 shows the effect of initial concentrations of phenol (100 mg L⁻¹, 200 mg L⁻¹, 400 mg L⁻¹) on the evolutions of phenol and benzoquinone. In the figure, the symbols represent the experimental data, while the lines are the calculating curve fitted by the model that proposed above. Obviously, the curves for phenol degradation were fitted very well for three initial phenol concentrations. Also it was fitted well for the BQ evolution in the concentration of 100 mg L⁻¹, while for the 400 mg L⁻¹ the fitted line by using the model is laid a little lower than that of the experimental data when

TABLE 1. Calculated Re	esults in Different Initia	I Concentration of Phen	ol		
[A]₀ (mmol L ⁻¹)	K (10 ⁻² min ⁻¹)	K_1 (10 ⁻² min ⁻¹)	K_2 (10 ⁻² min ⁻¹)	K_3 (10 ⁻² min ⁻¹)	α
0.9977	3.90 ± 0.18	2.61 ± 0.08	1.33 ± 0.11	21.2 ± 1.8	1.97
1.9074	4.32 ± 0.20	3.09 ± 0.06	1.23 ± 0.14	5.95 ± 0.98	2.51
3.6242	4.57 ± 0.18	3.71 ± 0.08	0.85 ± 0.10	1.95 ± 0.40	4.36

TABLE 2. Calculated Results in Different Initial	I pH	0f	Electrol	yte
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рН	[A] ₀ (mmol L ⁻¹)	<i>K</i> (10 ⁻² min ⁻¹)	K_1 (10 ⁻² min ⁻¹)	K_2 (10 ⁻² min ⁻¹)	<i>K</i> ₃ (10 ⁻² min ⁻¹)	α
3.0	0.9905	6.00 ± 0.56	4.64 ± 0.45	1.36 ± 0.11	4.96 ± 0.64	3.43
4.0	1.0668	7.78 ± 0.90	6.15 ± 0.79	1.63 ± 0.11	6.38 ± 0.54	3.78
5.0	0.9896	3.32 ± 0.20	2.28 ± 0.12	1.04 ± 0.08	10.6 ± 1.4	2.19
7.5	0.9903	$\textbf{3.63} \pm \textbf{0.17}$	2.81 ± 0.04	$\textbf{0.82}\pm\textbf{0.13}$	11.7 ± 2.3	3.41

phenol degradation is proceeded longer than 150 min. The reason for this observation is that it may be related to the simplification in the model that omits some minor products such as hydroquinone and catechol, which were detected in the presence of small amount in the degradation of higher initial concentration of phenol. Nevertheless, the model is essentially suitable for all concentrations tested and much better in lower concentration. The kinetics parameters calculated are listed in Table 1.

It can be seen from Table 1 that the apparent reaction constant *K* for phenol elimination is around 0.04 min⁻¹, slightly elevated from 0.0392 min⁻¹ to 0.0457 min⁻¹ when initial phenol concentration increased from 100 mg L⁻¹ to 400 mg L⁻¹. This indicates that initial phenol concentration affects the rate of phenol removal insignificantly. The model therefore could be well used to predict the phenol degradation with initial concentration ranged from 100 mg L⁻¹ to 400 mg L⁻¹. As shown in the table, with the increase of initial phenol concentration *K*₁ increases, while *K*₂ decreases, i.e., α enlarges.

As shown in Figure 3, the higher the initial phenol concentration is, the greater the amount of BQ is formed. However, K_3 sharply decreases with the increase of the initial phenol concentration. Therefore, in higher initial phenol concentration, the removal of BQ would be much more difficult and slower. Thus, BQ elimination would be favored at low concentration.

By using the model proposed we could better understand the electrocatalytic degradation of phenol in solution and obtain optimal operating conditions to accelerate degradation process and to minimize the formation of BQ. To ensure and optimize partial phenol degradation, important operating parameters including initial pH of the electrolyte, reaction temperature, and current density have been further examined.

Effect of pH. Figure 4 shows the effects of initial pH on phenol and benzoquinone evolution. The phenol removal rate possesses its maximum at pH 4.0 and then begins to decrease at pH 5.0 and at pH 7.5, and it even resumes to slightly increase. Since the anode is perfectly stable in acidic media, no attempt has been made to explore the phenol degradation in higher alkaline medium.

The kinetics parameters calculated are listed in Table 2. It can be seen that the values of K_1 and α are bigger at pH 4 than that at pH 5 and 7, which indicates that phenol elimination is more likely to be achieved in low pH. However, K_2 is smaller in higher pH media, and K_3 increases with the increase of pH. Therefore, in higher pH medium, the formation of BQ from phenol would be inhibited, while the decomposition of BQ would be promoted. Taking account of phenol removal as well as the low concentration of BQ in the process, phenol degradation at pH 4 would be preferred.

Effect of Temperature. Figure 5 shows the effects of temperature on the phenol and benzoquinone evolution. Parameters calculated are listed in Table 3.



FIGURE 4. Effect of pH on phenol degradation. Operational conditions: initial phenol concentration 100 mg L⁻¹; circulated rate 1800 mL min⁻¹; temperature 25 °C;K₂SO₄ 1.0 g L⁻¹; current density 7.5 mA cm⁻².

Obviously, both K_1 and K increased with the increase of temperature. Therefore the electrochemical reaction of phenol is highly temperature dependent, and an increase in temperature will strongly facilitate the degradation of phenol. The α value decreased with the temperature increased. Therefore K_1 is much more likely temperature dependent than K₂, which denoting that the oxidation reaction of phenol to organic acids is more temperature dependent than that of pathway through BQ. The removal rate of BQ should be very slow due to the small value of K₃ at 5 °C and would be much more suitable in higher temperature accounting for K_3 increases with temperature. These phenomena may be related to the high activation energy of the BQ (35.56KJ mol⁻¹, calculated by the Arrhenius law according to K₂ listed in Table 3.). Therefore it might be convenient to operate at high temperature for the complete removal of BQ. However, according to the insignificant increasing magnitude of K_3

TABLE 3. Calculated Results in Different Temperature of Reaction								
<i>T</i> (K)	[A] ₀ (mmol L ⁻¹)	<i>K</i> (10 ⁻² min ⁻¹)	K_1 (10 ⁻² min ⁻¹)	K_2 (10 ⁻² min ⁻¹)	K_3 (10 ⁻² min ⁻¹)	α		
278	0.9828	1.61 ± 0.07	1.19 ± 0.04	0.43 ± 0.03	4.22 ± 0.32	2.76		
298	0.9977	3.88 ± 0.14	2.55 ± 0.02	1.33 ± 0.12	21.4 ± 2.3	1.92		
313	1.0242	6.61 ± 0.42	4.25 ± 0.13	2.37 ± 0.29	22.7 ± 3.7	1.80		

	TABLE 4.	Calculated	Results	in	Different	Current	Density	/ of	Electrol	yte
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CD^a (mA cm ⁻²)	[A]₀ (mmol L ⁻¹)	<i>K</i> (10 ⁻² min ⁻¹)	K_1 (10 ⁻² min ⁻¹)	K_2 (10 ⁻² min ⁻¹)	<i>K</i> ₃ (10 ⁻² min ⁻¹)	α
3.2 10.7 27.5	0.9977 1.0162 0.9795	$\begin{array}{c} 3.92 \pm 0.15 \\ 5.71 \pm 0.27 \\ 8.28 \pm 0.74 \end{array}$	$\begin{array}{c} 2.68 \pm 0.09 \\ 3.90 \pm 0.19 \\ 7.55 \pm 0.62 \end{array}$	$\begin{array}{c} 1.25 \pm 0.06 \\ 1.81 \pm 0.09 \\ 0.73 \pm 0.12 \end{array}$	$\begin{array}{c} 17.8 \pm 1.4 \\ 25.7 \pm 3.8 \\ 33.2 \pm 4.6 \end{array}$	2.14 2.15 10.3

^a CD: current density.



FIGURE 5. Effect of temperature on phenol degradation. Operational conditions: initial phenol concentration 100 mg L^{-1} ; circulated rate 1800 mL min⁻¹; K₂SO₄ 1.0 g L^{-1} ; current density 7.5 mA cm⁻²; pH 5.6.

from temperature 25 °C to 40 °C, there is no need treating wastewater at much higher temperature in practical application.

Effect of Current Density. Figure 6 shows the effect of current density on the phenol and benzoquinone evolution. Parameters calculated are listed in Table 4.

With the increase of current density, *K* and *K*₁ are greatly increased. Therefore phenol removal is more likely to be degraded to organic acids and will be faster at a higher current density. *K*₃ is also elevated in higher current density, showing that the quinionic ring is apt to be broken down. Meanwhile, the selectivity coefficient α is dramatically increased from 2.14 to 10.3 with the increases of current density from 3.2 mA cm⁻² to 27.5 mA cm⁻². This means that the phenol degradation to organic acids through BQ would be insignificant at 27.5 mA cm⁻², and the degradation pathway could be further simplified from phenol to the organic acids. Thus the degradation process has been turned into the so-called



FIGURE 6. Effect of current density on phenol degradation. Operational conditions: initial phenol concentration 100 mg L⁻¹; circulated rate 1800 mL min⁻¹; K₂SO₄ 1.0 g L⁻¹; temperature 25 °C; pH 5.6.

"electrochemical cold combustion". Figure 7 shows the evolution of ICE during phenol degradation at different current density. Obviously, higher ICE will be achieved at higher current density tested.

Effectiveness of Partial Degradation of Phenol. As shown in Figure 7, ICE at 27.5 mA cm⁻² quickly decreases in the first 30 min and then gradually descends. Through HPLC and IC analyses, the main intermediates were aliphatic carboxylic acids after 30 min. Therefore the principal reaction has been turned to the mineralization of aliphatic carboxylic acids to CO_2 . Owing to its low current efficiency, in practical use, it is not necessary to degrade phenol to the final products of CO_2 . It may be more worthwhile to treat phenol to the biodegradable stage—aliphatic carboxylic acids followed by an economical biological process.

Data of toxicity of the identified compounds are presented in Table 5. The toxicity of the solution (f_{mix}) in the degradation



FIGURE 7. Evolution of ICE at different current density. (current density (mA cm⁻²): \diamond 3.2; \circ 10.7; \diamond 27.5). Operational conditions: initial phenol concentration 100 mg L⁻¹; circulated rate 1800 mL min⁻¹; K₂SO₄ 1.0 g L⁻¹; temperature 25 °C; pH 5.6.

TABLE 5. Toxicity (EC₅₀) and Toxicity Factor (f) of Phenol and Its Main Intermediates^a

compound	EC ₅₀ (mg L ⁻¹)	<i>f</i> (L mg ⁻¹⁾
phenol	2.67	0.37
benzoquinone	0.01	100
hydroquinone	0.50	2.00
maleic acid	30.3	0.03
oxalic acid	54.9	0.02
^a Data sources: refs 16	and 22.	

were determined by the following expression

$$f_{\rm mix} = \frac{\sum f_{\rm i}C_{\rm i}}{\sum C_{\rm i}}$$

where C_i is the concentration of intermediates.

Obviously, among all the compounds, benzoquione is the most toxic one. As is well-known that, for a biological process, EC₅₀ of benzoquinone should not be lower than 3 mg L⁻¹, i.e., f = 0.33 L mg⁻¹. Therefore it would be conservative to conclude that the wastewater will be suitable for biological treatment when the EC_{50} of the wastewater is below 3 mg L⁻¹. What we have been interested in is to explore when the toxicity of the wastewater will reach the level suitable for biological treatment. Figure 2 shows the variation of the toxicity (f_{mix}) during phenol degradation. The value of EC₅₀ reaches the peak in no more than 10 min and then sharply decreases until 100 min. The value of $f_{\rm mix}$ changes very slowly and insignificantly after 120 min treatment. As shown in Figure 2, when phenol is almost completely removed at 120 min, the $f_{\rm mix}$ is about 0.06 L mg⁻¹, which has reached the level for biological process. Consequently, it may be applicable to degrade phenol when it is completely removed. This indicates that partial degradation of phenol followed by a biological process would be feasible. Partial degradation

of phenol would be an alternative for wastewater pretreatment.

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