

# The cooperative electrochemical oxidation of chlorophenols in anode–cathode compartments

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## Abstract

By using a self-made carbon/polytetrafluoroethylene (C/PTFE) O<sub>2</sub>-fed as the cathode and Ti/IrO<sub>2</sub>/RuO<sub>2</sub> as the anode, the degradation of three organic compounds (phenol, 4-chlorophenol, and 2,4-dichlorophenol) was investigated in the diaphragm (with terylene as diaphragm material) electrolysis device by electrochemical oxidation process. The result indicated that the concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was 8.3 mg/L, and hydroxyl radical (HO•) was determined in the cathodic compartment by electron spin resonance spectrum (ESR). The removal efficiency for organic compounds reached about 90% after 120 min, conforming to the sequence of phenol, 4-chlorophenol, and 2,4-dichlorophenol. And the dechlorination degree of 4-chlorophenol exceeded 90% after 80 min. For H<sub>2</sub>O<sub>2</sub>, HO• existed in the catholyte and reduction dechlorination at the cathode, the mineralization of organics in the cathodic compartment was better than that in the anodic compartment. The degradation of organics was supposed to be cooperative oxidation by direct or indirect electrochemical oxidation at the anode and H<sub>2</sub>O<sub>2</sub>, HO• produced by oxygen reduction at the cathode. High-performance liquid chromatography (HPLC) allowed identifying phenol as the dechlorination product of 4-chlorophenol in the cathodic compartment, and hydroquinone, 4-chlorocatechol, benzoquinone, maleic, fumaric, oxalic, and formic acids as the main oxidation intermediates in the cathodic and anodic compartments. A reaction scheme involving all these intermediates was proposed.

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**Keywords:** Chlorophenol; C/PTFE O<sub>2</sub>-fed cathode; Degradation pathway; Electrochemical oxidation

## 1. Introduction

The demand for new technologies to remove or to detoxify organics, especially those are toxic to biological treatment processes from aqueous effluents, is widely recognized. The electrochemical method for treatment of such kind of wastewater has attracted a great attention recently, mainly because of its ease of control, amenability to automation, high efficiency and environmental compatibility [1]. At present, dimensionally stable anodes (DSA), which are typically prepared by thermal deposition of a thin layer of metal oxide (e.g., SnO<sub>2</sub>, PbO<sub>2</sub>, or IrO<sub>2</sub>) on a base metal, have been used for the oxidation of various organic pollutants, such as phenol, chlorophenols, benzoquinone, and dye wastewater [2,3]. Usually, electrochemical treatment can accomplish the mineralization of organic pollutants by the stronger oxidant of hydroxyl radicals, which are in

situ generated by the electrochemical reaction on the electrode surface [4].

For anodic oxidation of organic pollutant, it is difficult to achieve total mineralization because of low HO• concentration on the anode. Hence the study of more efficient electrochemical methods based on the indirect electro-oxidation of contaminants, for example, electrogeneration of strong oxidants, is now under way. Under some controlled conditions, the product of O<sub>2</sub> electro-reduction may be H<sub>2</sub>O<sub>2</sub>. The electrode materials used for O<sub>2</sub> electro-reduction can be divided into two groups. The first one involves electrodes, on which the O<sub>2</sub> electro-reduction proceeds predominantly through the intermediate formation of H<sub>2</sub>O<sub>2</sub>; while the second one involves electrodes, where both the four-electron and two-electron reactions take place. Carbon materials such as C/PTFE, carbon cloth, graphite felt, and reticulated vitreous carbon are classified into the first group and thus can be used as electrodes for the electrochemical production of H<sub>2</sub>O<sub>2</sub> [5–9]. Processes of indirect electro-oxidation of organic compounds by H<sub>2</sub>O<sub>2</sub>, generated during cathodic reduction of oxygen on the carbon/polytetrafluoroethylene (C/PTFE) O<sub>2</sub>-fed

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cathode, are promising for treating of organic toxicants, due to their environmentally safety and simplicity.

Generally, the electro-Fenton process can be performed in a no-diaphragm electrolysis device, where  $\text{H}_2\text{O}_2$  is produced on the cathode in an acidic medium and  $\text{Fe}^{2+}$  is added or offered by Fe anode [10–14]. We developed a novel electrochemical oxidation device and used it to treat the aqueous organic pollutant without adding metal catalyst. It was constructed by a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode (DSA), a self-made C/PTFE O<sub>2</sub>-fed cathode and an organic synthetic diaphragm between the anode and the cathode. In this electrolysis device, the degradation of organic pollutants was realized by the simultaneous oxidation of active anode and oxidant species electro-generated on the cathode [15].

In this paper, we present a detailed study on the degradation of phenol, 4-chlorophenol and 2,4-dichlorophenol in the novel electrochemical oxidation device. The degradation mechanism of aromatic compounds in the cathodic compartment has also been investigated in comparison with that in the anodic compartment.

## 2. Experimental

### 2.1. Preparation of cathode

A mixture of 1.2 g of carbon power and 3 g of 10% polytetrafluoroethylene (PTFE) was suspended in 0.28 mL of ethanol as dispersant. This suspension was mixed in 60–70 °C water bath, and the resulted wet paste was uniformly painted onto a face of a carbon cloth that was cold-pressed between two laminated steel plates. And further, the cathode was composed of two C/PTFE layers stacked onto a stainless steel screen of 200 mesh as current collector. The resulted electrode was then cut to obtain operational C/PTFE O<sub>2</sub>-fed cathodes of 4 cm × 4 cm and about 0.4 mm thick.

### 2.2. Procedures

Electrolysis was conducted in a terylene diaphragm cell of 100 mL. The anode was Ti/IrO<sub>2</sub>/RuO<sub>2</sub> net of 16 cm<sup>2</sup>. The cathode was a C/PTFE O<sub>2</sub>-fed electrode of 16 cm<sup>2</sup> fed with air. A schematic diagram of the experimental setup was shown in Fig. 1. A laboratory dc power supply with current–voltage monitor was employed to provide the electric power. The synthetic wastewater was used. The initial concentration was 100 mg/L, the reaction time was 120 min; the current density was 39 mA/cm<sup>2</sup>; the concentration of supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>) was 0.02 mol/L; the distance between electrodes was 2 cm; the initial pH was 7.0. Before experiment started, feeding air was 5 min in order to keep dissolved oxygen saturation. The feeding rate was 25 mL/s until the electrolysis process was over.

### 2.3. Analytical methods

The cyclic voltammetry (CV) spectra were recorded using a potentiostat/galvanostat (EG&G Model 273A) with a standard three-compartment cell consisting of a Pt wire as a

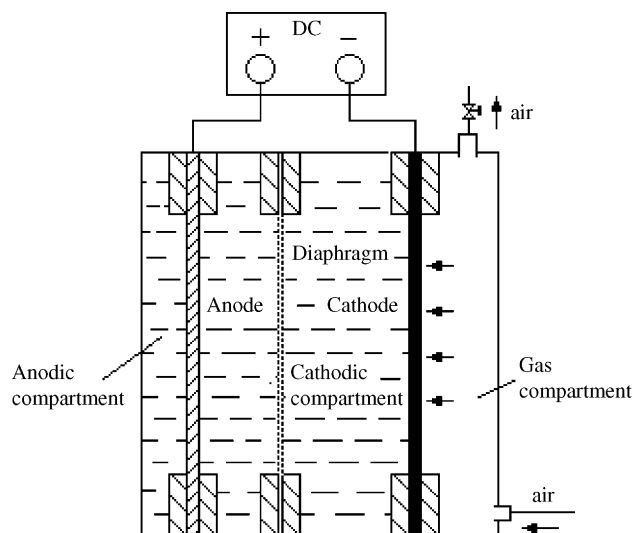


Fig. 1. Schematic diagram of apparatus in the divided cell.

counter electrode, an Ag/AgCl electrode as a reference, and the C/PTFE electrode (0.5 cm<sup>2</sup>) as a working electrode. A 0.02 mol/L Na<sub>2</sub>SO<sub>4</sub> solution was used as an electrolyte, which was saturated with oxygen (air, nitrogen) by feeding oxygen gas (air, nitrogen gas) to the cell for 30 min before the electrochemical measurements, and gas was continued throughout the electrolysis. During the experiment process, the temperature was kept constant at 25 °C. The scan rate was 20 mV/s.

The radicals were determined by electron spin resonance spectrum (ESR) measurements, which were performed in the X-band on a JES-FE3AX ESR spectrometer (JEOL, Tokyo, Japan) at room temperature. ESR spectrometer was set as follows: microwave frequency, 9.44 GHz; microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5 G; center field, 3367 G; scan width, 100 G; receiver gain,  $2 \times 10^3$ ; time constant, 0.3 s; sweep time, 4 min. The ESR spin trapping agent was 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 11.1 mmol/L).

The determination of aromatic compounds and its stable degradation products in electrolyzed solutions were carried out on high-performance liquid chromatography (HPLC, Shimadzu, Japan) by comparing the retention time of the standard compounds. Samples of 20  $\mu\text{L}$  previously filtered with PTFE filters of 0.45  $\mu\text{m}$  were injected to the HPLC. The separation was performed using a Znerisil ODS-SP C18 column (250 mm × 4.6 mm, 5  $\mu\text{m}$ ) at the flow rate of 1.0 mL/min and at column temperature of 25 °C. The aromatic compounds were determined by HPLC, running with mobile phase of methanol/water (v/v) at 80/20, and an UV detector was used with the wavelength set at 280 nm. The carboxylic acids were determined by HPLC, running with mobile phase of methanol/KH<sub>3</sub>PO<sub>4</sub> 25/75 (v/v) at pH 2.1 adjusted with H<sub>3</sub>PO<sub>4</sub>, and an UV detector (210 nm) was employed.

The H<sub>2</sub>O<sub>2</sub> concentration accumulated during electrolysis was determined by titration with permanganate using a standard procedure [11]. The chemical oxygen demand (COD) was measured by the standard method. The concentration of chloride ion in

electrolyzed solutions was determined by titration with mercury nitrate using a standard procedure.

### 3. Results and discussion

#### 3.1. The indirect electrochemical oxidation mechanism in the cathodic compartment

Fig. 2 shows the variation of pH value with electrolysis time in the cathodic and anodic compartments. In the diaphragm electrolysis device, where the terylene diaphragm was used, it could keep the pH > 12 in cathodic compartment and pH < 1 in anodic compartment [16] after 20 min electrolysis whether the original solution was acidic, neutral or alkaline solution.

Fig. 3 depicts CV curves in a 0.02 mol/L Na<sub>2</sub>SO<sub>4</sub> solution (pH 12.8 adjusted with NaOH solution) of the C/PTFE O<sub>2</sub>-fed electrode surface at different gas. There was high reduction peak (O<sub>2</sub>, air) at about -0.47 V in the presence of oxygen. However, this peak disappeared in the absence of oxygen (N<sub>2</sub>). According to redox potential, the two-electron reduction of O<sub>2</sub> to peroxide anion (HO<sub>2</sub><sup>-</sup>) led the formation of reduction current peak at the C/PTFE O<sub>2</sub>-fed electrode in a basic solution.

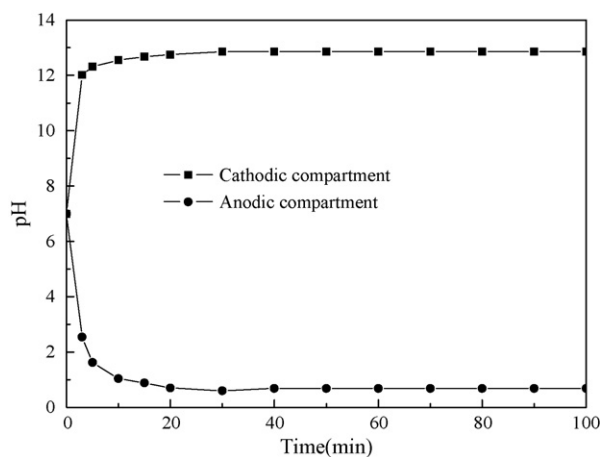


Fig. 2. Variation of pH-value with electrolysis time in the cathodic and anodic compartment.

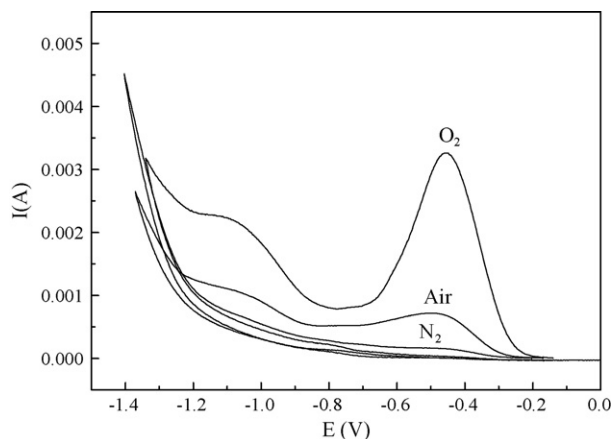


Fig. 3. Cyclic voltammograms corresponding to the reduction of O<sub>2</sub> on the C/PTFE O<sub>2</sub>-fed electrode at different gas.

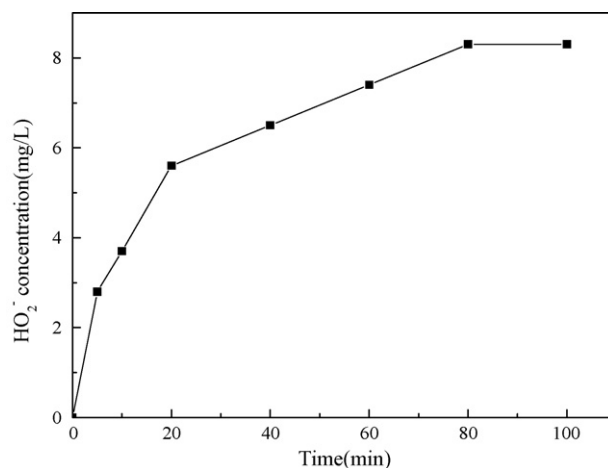
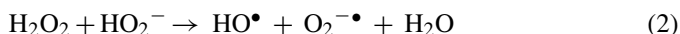
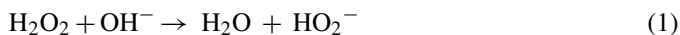


Fig. 4. Variation of accumulated HO<sub>2</sub><sup>-</sup> concentration with electrolysis time.

A titration method also was used to detect HO<sub>2</sub><sup>-</sup> concentration accumulated in the cathodic compartment. Fig. 4 shows the change of HO<sub>2</sub><sup>-</sup> concentration with electrolysis time. The amount of HO<sub>2</sub><sup>-</sup> is increased within 80 min electrolysis, and then the accumulation HO<sub>2</sub><sup>-</sup> tends to steady concentrations of 8.3 mg/L.

In basic electrolyte, H<sub>2</sub>O<sub>2</sub> may be converted to HO<sub>2</sub><sup>-</sup>, HO<sup>•</sup> and O<sub>2</sub><sup>-•</sup> as follows [17]:



The oxidizing power of HO<sub>2</sub><sup>-</sup>, HO<sup>•</sup> and O<sub>2</sub><sup>-•</sup> are stronger than H<sub>2</sub>O<sub>2</sub>, which can oxidize chlorophenols to smaller molecule intermediates or to CO<sub>2</sub> and H<sub>2</sub>O in the divided cell. ESR was used to quantitatively determine the free radical. Fig. 5 shows the typical ESR spectrum obtained by 15 min electrolysis in DMPO solution. The spectrum was composed of quartet lines with the peak height ratio of 1:2:2:1. The ESR parameters (hyperfine constants  $a_N = a_H = 14.0 \text{ G}$  and  $g\text{-value} = 2.0065$ ) coincided with those of DMPO-OH<sup>•</sup> adduct as demonstrated previously [18], confirming that the quartet signal is DMPO-OH<sup>•</sup> adduct. But the ESR spectra of the reactive product of free radical O<sub>2</sub><sup>-•</sup> and DMPO (DMPO-OOH<sup>•</sup> adduct) did not be determined. This can be attributed to that the concentration of DMPO-OOH<sup>•</sup> adduct was very low, or DMPO-OOH<sup>•</sup> adduct is unstable and it is prone to change to DMPO-OH<sup>•</sup> adduct.

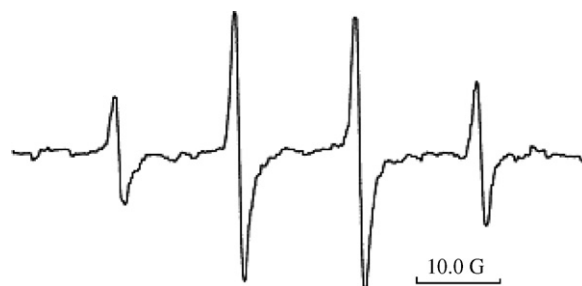


Fig. 5. ESR spectra of HO<sup>•</sup> radicals trapped by DMPO in the cathodic compartment.

### 3.2. The degradation of aromatic compounds

In the simulated organic wastewater, the removal efficiency of aromatic compounds and the COD removal efficiency increased with an increase in electrolysis time in the cathodic and anodic compartment (Fig. 6). The mineralization degree of aromatic compounds and COD removal in the cathodic compartment was better than that in the anodic compartment.

In general, lower pH is favorable to the electrochemical oxidation of organic pollutants. In the anodic compartment of the diaphragm cell, the mechanism of the electrochemical oxidation of organics at the metallic oxide Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode was very complex and not yet fully understood. It seems to be that two oxidation pathways are involved in direct anodic electrochemical oxidation process by MO<sub>x</sub>(OH•) or MO<sub>x+1</sub> produced on the

anode surface. In the presence of oxidizable organic compounds (R), MO<sub>x</sub>(OH•) radicals should predominantly cause their complete degradation to carbon dioxide and water (electrochemical cold combustion pathway). And MO<sub>x+1</sub> is supposed to react with R to generate medium oxidation products via heterogeneous catalytic oxidation at the active sites of the electrodes (chemical oxidation pathway). The degradation of aromatic compounds in the anodic compartment was supposed to be oxidized by MO<sub>x</sub>(OH•) or MO<sub>x+1</sub> produced on the anode surface [19]. But for anodic oxidation, it was difficult to achieve total mineralization because of low MO<sub>x</sub>(OH•) or MO<sub>x+1</sub> concentration on the anode. However, the oxidizing power of H<sub>2</sub>O<sub>2</sub>, HO• and O<sub>2</sub><sup>-•</sup> existed in the catholyte during O<sub>2</sub> electro-reduction on the C/PTFE cathode are very strong, which can oxidize organics to smaller molecule intermediates or to CO<sub>2</sub> and H<sub>2</sub>O [20]. Therefore, the mineralization of organics in the cathodic compartment was better than that in the anodic compartment.

The COD removal of aromatic compounds increased with the increasing electrolysis time (Fig. 6). The total COD removal was lower than the corresponding degradation fraction of the target phenols in three kinds of aromatic compounds. This can be attributed to that aromatic compounds are oxidized to smaller molecule intermediates. The results indicated that the removal efficiency for organic compounds reached about 90% after 120 min, conforming to the sequence of phenol, 4-chlorophenol and 2,4-dichlorophenol. 4-Chlorophenol and 2,4-dichlorophenol are derivatives of phenol which contains chlorine atom(s) in the aromatic ring. The organics became more difficult to be oxidized with the increase of the number of chlorine atom in the aromatic ring.

### 3.3. The degree of dechlorination

The concentration of chloride ion released from the target aromatic compounds during the electrochemical oxidation was measured to evaluate the dechlorination degree. It is the chlorine substituent that mainly account for the toxicity of aromatic compounds. Therefore, the degree of dechlorination indirectly represents the detoxification degree. During the degradation process of 4-chlorophenol and 2,4-dichlorophenol (2,4-D), the changes of the concentration of chloride ion with electrolysis time in the cathodic and anodic compartment was illustrated in Fig. 7.

As shown in Fig. 7, the initial solutions of 4-chlorophenol and 2,4-dichlorophenol had the dissociative chloride ion. The chloride ion concentration of 4-chlorophenol and 2,4-dichlorophenol increased in the both anodic and cathodic compartment with an increasing of electrolysis time during 0–80 min electrolysis and 0–100 min, respectively, but the concentration of chloride ion in the anodic compartment was higher than that in the cathodic compartment in the same synthetic wastewater. This attributed to the fact that in the initial period of the experiment, the chloride ions of the cathodic compartment could diffuse to the anodic compartment through terylene diaphragm, due to the electrostatic repulsion from the negatively charged cathode. Therefore, their concentration in the anodic compartment was high. For 4-chlorophenol, the concentration of chloride ion reached highest after 80 min, and the degree of dechlorination reached about

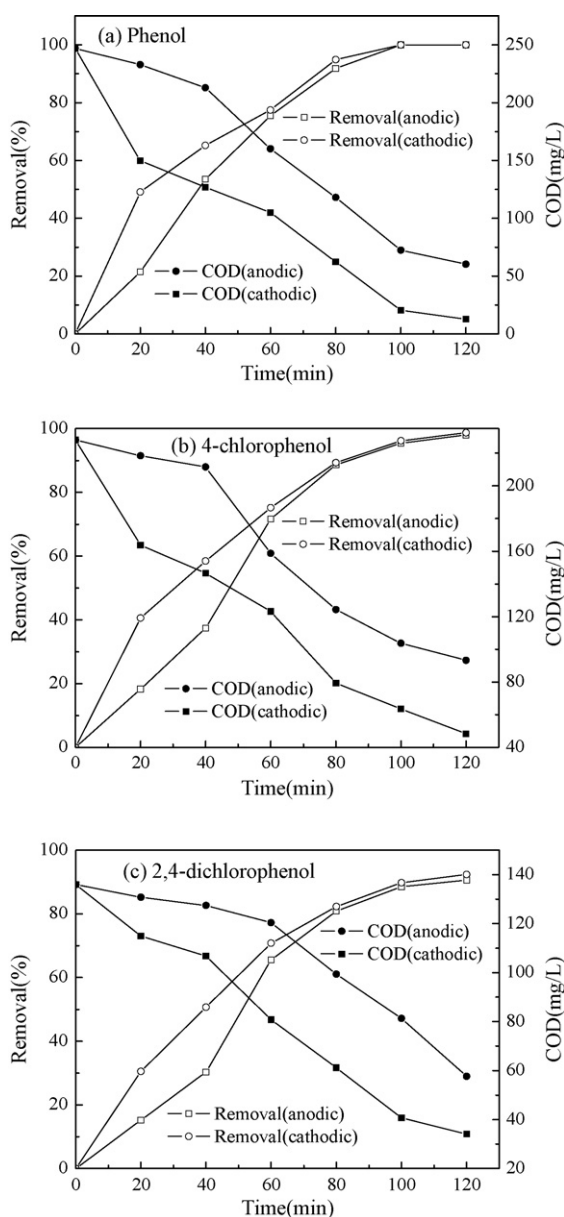


Fig. 6. Removal of organics and COD in cathodic and anodic compartments during electrolysis.



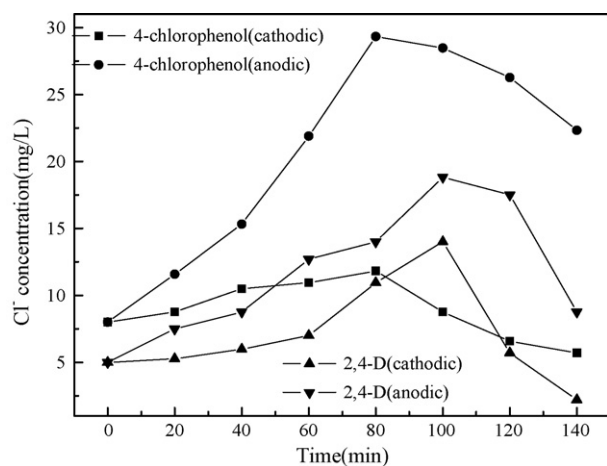
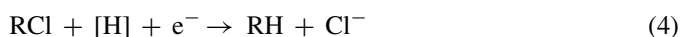


Fig. 7. Variation of  $\text{Cl}^-$  concentration in the cathodic and anodic compartments with electrolysis time.

95.3%. After 100 min, the concentration of chloride ion for 2,4-dichlorophenol reached the highest, and the degree of dechlorination reached about 75.4%. With the increase of electrolysis time, the concentration of chloride ion decreased in two compartments. Results indicated that chloride ion was already oxidized to  $\text{Cl}_2$  at the anode, as reported for the electrolysis of chlorophene with BDD anode [21], and  $\text{Cl}_2$  was immediately driven away from the reaction system [22]. The dechlorination effect of 4-chlorophenol was better than that of 2,4-dichlorophenol. This can be attributed to that 2,4-dichlorophenol possesses one more chlorine atom than 4-chlorophenol in the aromatic ring, and the dechlorination difficulty of organics increased with the increase of the number of chlorine atom in the aromatic ring.

In the cathodic compartment, the mechanism of the electrocatalytic destruction of carbon–chlorine bond ( $\text{R}-\text{Cl}$  molecule) was described by the following equations. First, chemisorbed hydrogen atom ( $[\text{H}]$ ) was formed on the cathodes surface by reduction of water [23].



Hydrogenolysis of the  $\text{C}-\text{Cl}$  bond then proceeded. In the cathodic compartment, the chloride ion was released by the two methods, which one was reduction dechlorination, and other was hydroxylation oxidation.

### 3.4. Identification of intermediates and their evolution

These intermediates were unequivocally identified by comparing their retention times and UV–vis spectra with those of pure compounds. It is noteworthy that the dechlorination of 2,4-dichlorophenol to monochlorophenol and phenol has been reported by other researchers [24,25], whereas degradation of 4-chlorophenol to hydroquinone and 4-chlorocatechol using anodic oxidation has been described by some researchers [26]. It is well-known [27] that electrochemical degradation of the generated aromatic compounds leads to a mixture of carboxylic acids. Figs. 8 and 9 show the evolution of the soluble species

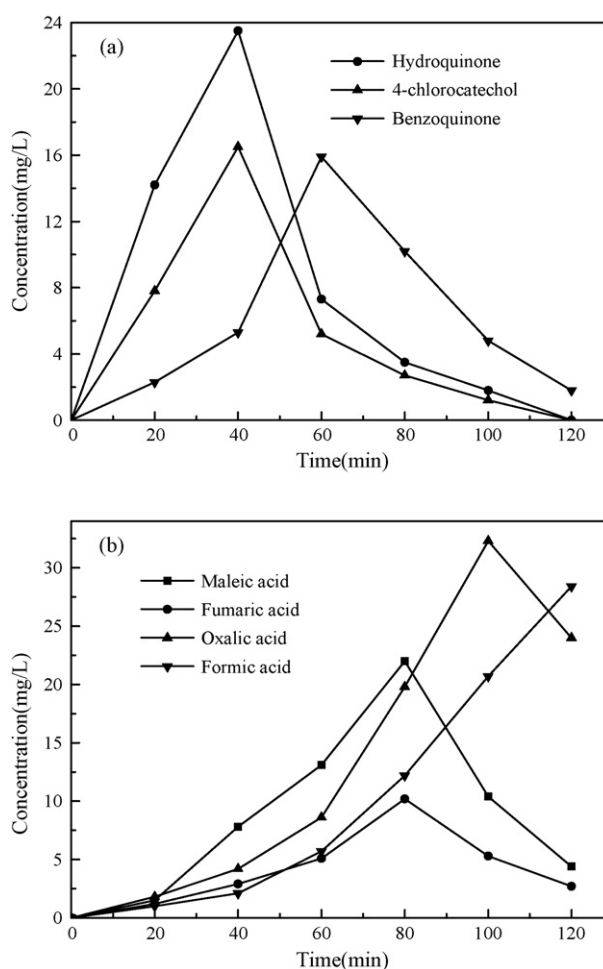


Fig. 8. Change of intermediates concentration of 4-chlorophenol in the anodic compartment.

detected in the anodic and cathodic compartment during the degradation of 4-chlorophenol. A fast formation and destruction of main intermediates can be observed.

Fig. 8(a) shows the concentration of the primary products hydroquinone and 4-chlorocatechol increases at the first 40 min and then begins to decrease till complete removal within 120 min in the anodic compartment. Their hydroxylated derivative benzoquinone reached its peak concentration at about 60 min and then reduced to below its detection limit at 120 min. Through HPLC analyses, the main intermediates were aliphatic carboxylic acids (maleic, fumaric, oxalic, and formic acids) after 60 min. As can be seen in Fig. 8(b), maleic and fumaric acids attained a maximum concentration at 80 min, further being quickly degraded to oxalic and formic acids. After 120 min most of aliphatic carboxylic acids were transformed into carbon dioxide and water. These results indicate that in the anodic compartment all aromatic intermediates were transformed into carboxylic acids, because they reacted rapidly with  $\text{MO}_x(\text{OH}^\bullet)$  or  $\text{MO}_{x+1}$  produced on the anode surface.

A different behavior was found for degradation 4-chlorophenol in the cathodic and anodic compartments. Fig. 9(a) shows that phenol is the dechlorination products in the cathodic

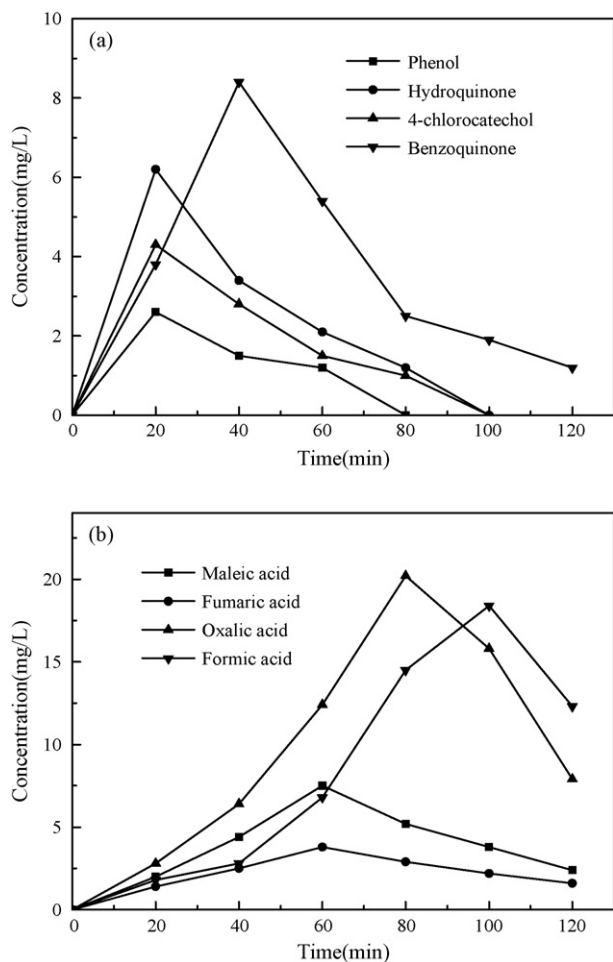


Fig. 9. Change of intermediates concentration of 4-chlorophenol in the cathodic compartment.

compartment. This attributed to the fact that 4-chlorophenol was found to dechlorinate to phenol at the C/PTFE  $O_2$ -fed cathode. Therefore, it was feasible to degrade chlorinated contaminants by electrochemical reduction to non-chlorinated intermediates. It was reason that the mineralization of organics in the cathodic compartment was better than that in the anodic compartment. The concentration of phenol increased at the first 20 min and then began to decrease till complete removal within 80 min. It has been shown previously that phenol is oxidized to form hydroquinone and benzoquinone [12], which would suggest that degradation of phenol follows the benzoquinone pathway.

In the cathodic compartment, similar concentration–time plots were found for the same intermediates, however, the amounts of them were lower than that of the anodic compartment (see Figs. 8 and 9). The aromatic compounds products (hydroquinone, 4-chlorocatechol, and benzoquinone) and carboxylic acids intermediates (maleic, fumaric, oxalic, and formic acids) were found at a small amount and during shorter time in the cathodic compartment than that in the anodic compartment. For example, Fig. 9(a) shows a small accumulation of hydroquinone up to 6.2 mg/L at 20 min of electrolysis in the cathodic compartment and its complete mineralization in 100 min, whereas for the anodic compartment in Fig. 8(a), this

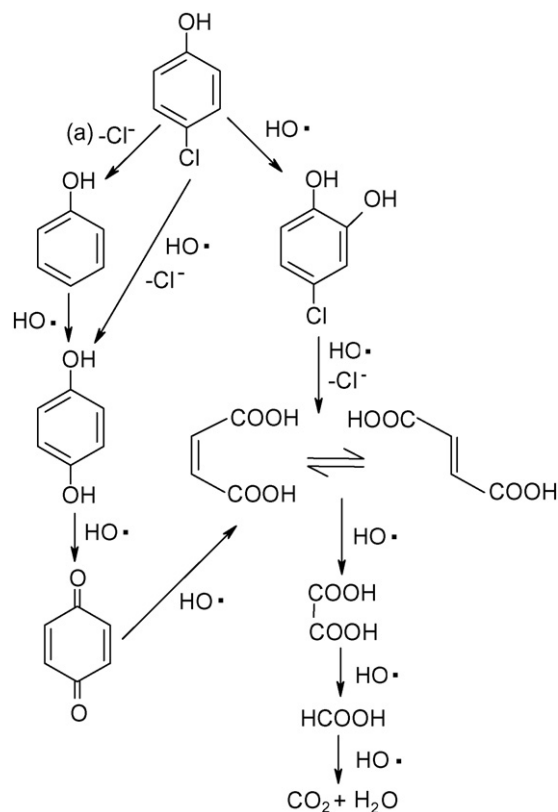


Fig. 10. Proposed reaction sequence for degradation of 4-chlorophenol in the cathodic and anodic compartments.

hydroquinone persists for 120 min, reaching 23.5 mg/L as maximum in 40 min. This experiment clearly demonstrated that 4-chlorophenol was effectively dechlorinated and rapidly oxidized in the cathodic compartment. The C/PTFE  $O_2$ -fed cathode can not only reductively dechlorinate 4-chlorophenols, but also catalyzed the two-electron reduction of  $O_2$  to hydrogen peroxide ( $H_2O_2$ ), which was consistent with CV conclusions (see Fig. 3).

Fig. 10 presents a pathway for the degradation of 4-chlorophenol in the cathodic and anodic compartment by the C/PTFE  $O_2$ -fed electrode system. The degradation pathway in the cathodic compartment was proposed as follows: 4-chlorophenol was found to dechlorinate to phenol (pathway a). Hydroxylation on the C(4)-position of phenol led to hydroquinone. Whereas, a parallel  $HO^\bullet$  attacked on C(4)-position of 4-chlorophenol yields hydroquinone with loss of  $Cl^-$ . Hydroquinone was subsequently dehydrogenated to benzoquinone. The oxidation of benzoquinone, after ring opening, led to the formation of aliphatic carboxylic acids such as maleic acid and fumaric acid, which were degradation to oxalic acid, and further formed formic acid. Parallel hydroxylation on the C(2)-position of 4-chlorophenol led to 4-chlorocatechol, which was converted into maleic acid and fumaric acid [26]. The final products were carbon dioxide and water [14].

The degradation reaction of 4-chlorophenol in diaphragm electrolysis device was supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and  $HO_2^-$ ,  $HO^\bullet$  produced by oxygen reduction at the cathode. Owing to its low current efficiency, in practical use, it was not

necessary to degrade 4-chlorophenol to the final products of CO<sub>2</sub>. It may be more worthwhile to treat 4-chlorophenol to the biodegradable stage-aliphatic carboxylic acids followed by an economical biological process.

#### 4. Conclusions

The electrochemical degradation of chlorophenols was studied in the diaphragm electrolysis device (a terylene diaphragm) with Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode and C/PTFE O<sub>2</sub>-fed cathode which generated H<sub>2</sub>O<sub>2</sub> by a two-electron reduction of oxygen gas fed to the cathode. After 80 min, the accumulation H<sub>2</sub>O<sub>2</sub> reached steady concentrations of 8.3 mg/L in the cathodic compartment. HO• was determined in the cathodic compartment of the diaphragm O<sub>2</sub> by ESR. The removal efficiency for organic compounds reached about 90% after 120 min, conforming to the sequence of phenol, 4-chlorophenol and 2,4-dichlorophenol, which suggested that with the increase of the number of chlorine atom in the aromatic ring, the organics became more difficult to be oxidized. And the dechlorination degree of 4-chlorophenol exceeded 90% after 80 min. The oxidizing power of H<sub>2</sub>O<sub>2</sub>, HO• and O<sub>2</sub><sup>-•</sup> existed in the catholyte during O<sub>2</sub> electro-reduction on the C/PTFE cathode are very strong, which can oxidize organics to smaller molecule intermediates or to CO<sub>2</sub> and H<sub>2</sub>O. And 4-chlorophenol was reduction dechlorination at the cathode. Therefore the mineralization of organics in the cathodic compartment was better than that in the anodic compartment. The degradation of organics was supposed to be cooperative oxidation by direct or indirect electrochemical oxidation at the anode and H<sub>2</sub>O<sub>2</sub>, HO• produced by oxygen reduction at the cathode. HPLC allowed identifying phenol as the dechlorination product of 4-chlorophenol in the cathodic compartment, and hydroquinone, 4-chlorocatechol, benzoquinone, maleic, fumaric, oxalic, and formic acids as the main oxidation intermediates in the cathodic and compartments. The combined process of reduction and oxidation was in favor of improving 4-chlorophenol degradation efficiency.

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#### References

- [1] C. Cominellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, *J. Appl. Electrochem.* 25 (1995) 23–28.
- [2] U. Leffrang, K. Ebert, K. Flory, Organic waste destruction by indirect electrooxidation, *Sep. Sci. Technol.* 30 (1995) 1883–1889.
- [3] N.B. Tahar, A. Savall, Electrochemical degradation of phenol in aqueous solution on bismuth doped lead dioxide: a comparison of the activities of various electrode formulations, *J. Appl. Electrochem.* 29 (1999) 277–283.
- [4] J.E. Vitt, D.C. Johnson, The Importance of anodic discharge of H<sub>2</sub>O in acidic oxygen-transfer reactions, *J. Electrochem. Soc.* 139 (1992) 774–779.
- [5] J.S. Do, C.P. Chen, In situ oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated on the modified graphites, *J. Appl. Electrochem.* 24 (1994) 936–942.
- [6] C. Leon, D. Pletcher, Removal of formaldehyde from aqueous solutions via oxygen reduction using a reticulated vitreous carbon cathode cell, *J. Appl. Electrochem.* 25 (1995) 307–314.
- [7] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2,4-D, *J. Appl. Electrochem.* 30 (2000) 475–482.
- [8] J. Iniesta, E. Exposito, Electrochemical treatment of industrial wastewater containing phenols, *J. Electrochem. Soc.* 149 (2002) D57–D62.
- [9] K.B. Lee, M.B. Gu, S.H. Moon, Degradation of 2,4,6-trinitrotoluene by immobilized horseradish peroxidase and electrogenerated peroxide, *Water Res.* 37 (2003) 983–992.
- [10] T. Harrington, D. Pletcher, The removal of low levels of organics from aqueous solutions using Fe(II) and hydrogen peroxide formed in situ at gas diffusion electrodes, *J. Electrochem. Soc.* 146 (1999) 2983–2989.
- [11] A.A. Gallegos, D. Pletcher, The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell. 2. The removal of phenols related compounds from aqueous effluents, *Electrochim. Acta* 44 (1999) 2483–2492.
- [12] Z.C. Wu, M.H. Zhou, D.H. Wang, Synergetic effects of anodic–cathode electrocatalysis for phenol degradation in the presence of iron(II), *Chemosphere* 48 (2002) 1089–1096.
- [13] Z.M. Qiang, J.H. Chang, C.P. Huang, Electrochemical regeneration of Fe<sup>2+</sup> in Fenton oxidation processes, *Water Res.* 37 (2003) 1308–1319.
- [14] E. Brillas, B. Boye, I. Sires, Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode, *Electrochim. Acta* 49 (2004) 4487–4496.
- [15] H. Wang, J.L. Wang, Electrochemical degradation of 4-chlorophenol using a novel Pd/C gas diffusion electrode, *Appl. Catal. B: Environ.*, in press.
- [16] 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.
- [17] J.M. Fang, R.C. Sun, D. Salisbury, Comparative study of hemicelluloses from wheat straw by alkali and hydrogen peroxide extractions, *Polym. Degrad. Stab.* 66 (1999) 423–432.
- [18] S.A. Cheng, W.K. Fung, K.Y. Chan, Optimizing electron spin resonance detection of hydroxyl radical in water, *Chemosphere* 52 (2003) 1797–1805.
- [19] P. Canizares, J.A. Domingues, M.A. Rodrigo, Effect of the current intensity in the electrochemical oxidation of aqueous phenol wastes at an activated carbon and steel anode, *Ind. Eng. Chem. Res.* 38 (1999) 3779–3785.
- [20] E. Brillas, R.M. Bastida, E. Uosa, Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon–PTFE O<sub>2</sub>-fed cathode, *J. Electrochem. Soc.* 142 (1995) 1733–1741.
- [21] Sirés J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan, M.A. Oturan, Catalytic behavior of the Fe<sup>3+</sup>/Fe<sup>2+</sup> system in the electro-Fenton degradation of the antimicrobial chlorophene, *Appl. Catal. B: Environ.* 72 (2007) 382–394.
- [22] J.L. Boudenne, O. Cerclier, Performance of carbon black-slurry electrodes for 4-chlorophenol oxidation, *Water Res.* 33 (1999) 494–504.
- [23] P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Menard, J. Lessard, Electrocatalytic dehydrochlorination of pentachlorophenol to phenol or cyclohexanol, *Environ. Sci. Technol.* 34 (2000) 1265–1268.
- [24] A.I. Tsyganok, I. Yamanaka, K. Otsuka, Dechlorination of chloroaromatics by electrocatalytic reduction over palladium-loaded carbon felt at room temperature, *Chemosphere* 39 (1999) 1819–1831.
- [25] Y. Yasman, V. Bulatov, I. Rabin, M. Binetti, I. Schechter, Enhanced electro-catalytic degradation of chloroorganic compounds in the presence of ultrasound, *Ultrason. Sonochem.* 13 (2006) 271–277.
- [26] B. Boye, M.M. Dieng, E. Brillas, Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, *Environ. Sci. Technol.* 36 (2002) 3030–3035.
- [27] E. Brillas, B. Boye, M.M. Dieng, Peroxi-coagulation and photoperoxi-coagulation treatments of the herbicide 4-chlorophenoxyacetic acid in aqueous medium using an oxygen-diffusion cathode, *J. Electrochem. Soc.* 150 (2003) E148–E154.