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Electrochemical degradation of phenol using electrodes of Ti/RuO_2–Pt and Ti/IrO_2–Pt

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ABSTRACT

Electrochemical degradation of phenol was evaluated at two typical anodes, Ti/RuO_2–Pt and Ti/IrO_2–Pt, for being a treatment method in toxic aromatic compounds. The influences of current density, dosage of NaCl, initial phenol concentration on electrochemical phenol degradation were investigated. It was found that Ti/RuO_2–Pt anode had a higher oxygen evolution potential than Ti/IrO_2–Pt anode, which will increase the current efficiency for electrochemical degradation, and the instantaneous current efficiency (ICE) was relatively higher at the initial time during phenol electrolysis. HOCl formed during electrolysis would play an important role on the oxidation of phenol. For the Ti/RuO_2–Pt anode, phenol concentration decreased from around 8 mg/L to zero after 30 min of electrolysis with 0.3 g/L NaCl as supporting electrolyte at the current density of 10 mA/cm^2. Although phenol could be completely electrochemical degraded at both Ti/RuO_2–Pt and Ti/IrO_2–Pt anodes, phenol degradation was slower at the Ti/IrO_2–Pt anode than at the Ti/RuO_2–Pt anode due to the fact that passivation was to be found at the Ti/IrO_2–Pt anode.

1. Introduction

A wide variety of synthetic organic compounds have been brought into the environment by human activities, and many organic compounds are contaminating the ground and surface water. Aromatic compounds are common pollutants in the waste effluent discharged by many factories, such as chemical plants, petroleum refineries and pesticide, and pharmaceutical factories. Of all the organic pollutants causing problems around the world, aromatic hydrocarbons and chlorinated hydrocarbons are among the most harmful [1,2]. Phenolic products are toxic to humans and aquatic organisms and they are listed among the most common and serious environmental contaminants. Over 2 mg/L phenol concentration is toxic to fish and concentrations between 10 and 100 mg/L would result in death of aquatic life within 96 h [3]. According to the 80/778/EEC Directive, the maximum admissible concentration (MAC) of phenols in drinking water should not exceed 0.5 pg/L. Many industrial processes produce toxic wastewater, which are not easily biodegradable and require costly physical or physico-chemical pretreatment [4].

Electrochemistry is becoming a new alternative for wastewater treatment and is replacing the traditional processes. Electrochemical oxidation of various types of wastewater including the phenolic wastewater has been investigated by a lot of researchers [3,5–8]. Electrochemical reaction can effectively oxidize toxic organics [7–10]. With unique features such as simplicity and robustness in structure and operation, it is possible that the electrochemical process can be developed as a cost-effective technology for the treatment of aromatic pollutants, particularly for low volume applications [8]. Electrochemical wastewater treatment effect mainly depends on the nature of the anodes that are used in the process [10,11]. The difference in the effectiveness and performance of different anode materials for wastewater treatment demonstrates the complexity of the EC reaction mechanisms involved. The current efficiency of traditional electrodes is very low in organic degradation, such as using graphite and nickel [6]. Dimensionally stable anodes (DSAs), made by the deposition of a thin layer of metal oxides on a base metal, usually titanium, have been proved to be effective in organic degradation [5,10,12]. Research [1,8,10] shows that phenol is easy to be oxidized into maleic acid with RuO_2 and Pt as anode, respectively. It has been reported that the oxidation of phenol can stop with such products as maleic acid and oxalic acid for Pt anodes [3,13]. It is very difficult for maletic acid degradation on most researched anodes [3,4,10,14–19]. For maleic acid degradation, there must have been other pathways, other than “reduction”

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on cathode proposed by most researchers [8,10]. However, with sufficient hydroxyl radicals, maleic acid could be oxidized directly to oxalic acid, which can be oxidized readily to CO_2 [8,10]. Feng et al. [20,25] have investigated the performance of $Ti/TiO_2–RuO_2$ for removal of ammonia, Tanaka et al. [21,26] have demonstrated the effectiveness of Ti/RuO_2 and Pt for degradation of orgnics contained in landfill leachate, respectively. However, the anodes did not have long service time. With PbO_2 electrodes, phenol can be completely removed [10,18]. Whereas, the actual application of PbO_2 electrodes will be limited due to the fact that the possible toxicity of Pb would leach from the working anode. And hence, it remains a subject to develop anodes with long service life and excellent performance for degradation of aromatic organics.

In order to increase conductivity and current density, various electrolytes such as Na_2SO_4, H_2SO_4 and their mixtures were added to the medium during the electrochemical conversion of phenol [3,9,19,22]. However, very few investigators [2] have used NaCl as supporting electrolyte. In the presence of chloride ion during electrolysis, Cl_2 gas is discharged on the anode above 2.1872 V potential [20,23]. Following the discharge of Cl_2 gas, HOCl formation occurs with hydrolysis reaction [21,24]. HOCl is a strong oxidant, which oxidizes the phenol in solution, while the oxidant ability is decreased by formation of OCl^- [2,22,25]. Meanwhile, hypochlorous acid (HOCl) is replenished in the medium with the electrochemical reaction of NaCl. This represents the indirect oxidation of phenol, however, direct oxidation also occurs on the anode [23,26], most likely with a different mechanism. Phenol is easy to be oxidized into maleic acid with RuO_2 and Pt as anode, respectively. The intermediate maleic acid has been proved and it is suggested that maleic acid is reduced to succinic acid at the cathode followed by oxidation to malonic and acetic acid, and then finally to carbon dioxide by anode oxidation [1,10].

The aim of that work is to find anodes with high performance of electrochemical phenol degradation and have long service time. In the present study, phenol, which is the basic unit of aromatic compounds, was used as the model organic for electrochemical degradation. Anodes of Ti coated with RuO_2 and doped with Pt ($Ti/RuO_2–Pt$) and Ti coated with IrO_2 and doped with Pt ($Ti/IrO_2–Pt$) were examined for their performance in electrochemical phenol degradation. In order to investigate the phenol degradation effect and related reaction mechanisms, phenol concentration, TOC, free radicals and cyclic voltammograms with different concentration of NaCl as supporting electrolyte were measured, and the role of hypochlorous acid formed during electrolysis was also analyzed.

2. Materials and methods

2.1. Electrochemical apparatus

A continuous electrochemical cell was designed in our laboratory with a net working volume of 300 mL (Fig. 1). A Cole Parmer model peristaltic pump was used to circulate the phenol solution from a 1000-mL beaker to the electrochemical cell at a speed of 100 mL/min. The 300-mL electrolysis cell was made of acryl plates with four outer spots for the electrodes assembled. For each cell, two types of electrodes, $Ti/RuO_2–Pt$, $Ti/IrO_2–Pt$ of 75 cm^2 (15 cm × 5 cm) prepared by TohoTech company (Japan) were used as the anode and Ti plate with the same area as the cathode with a distance of 10 mm between the two electrodes. The emerging areas of the anode and cathode in the treated solution were same, which was 50 cm^2. A dc potentiostat (HuanAn YaGuang Electronic Company) with a voltage range of 0–50 V and a current range of 0–5 A was employed as power supply for electrochemical organic degradation. A magnetic stirrer was used to homogenize the phenol solution.

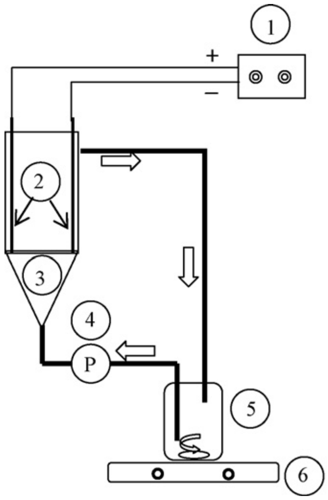

Fig. 1. Schematic diagram of the electrochemical apparatus. (1) DC power supply (5 A × 50 V); (2) electrodes; (3) electrochemical cell (300 mL); (4) peristaltic pump; (5) cyclic beaker (1 L); (6) stirrer.

2.2. Experimental design

In the present study, phenol solutions with different initial concentrations of 8, 20, 40 and 80 mg/L were prepared for electrolysis experiments. To investigate the effect of sodium chloride (NaCl) dosage on the phenol degradation, the NaCl of 0.1, 0.3, 0.5 mg/L (w/v) were added into the phenol solutions as the supporting electrolyte, respectively. Electrolysis experiments were performed under galvanostatic control at different current densities of 10 and 20 mA/cm^2, respectively. A 1000 mL of synthetic phenol solution prepared as above was poured into the beaker, the reaction started with the application of specified current density and the solution was mixed at a constant 300 rpm by the magnetic stirrer. At 10 min intervals, 10 mL of samples were drawn from the beaker for phenol and TOC analysis. The electrolysis was ceased when either 99% of initial phenol was converted or 2 h elapsed.

2.3. Detection of free radicals species

To measure the production of free radicals formed during the electrochemical treatment, NaCl solution containing 50 μmol/L RNO (*p*-nitrosodimethylaniline) was used because RNO reacts rapidly with hydroxyl radicals selectively. The bleaching of RNO solution by hydroxyl radicals was measured by absorbance changes at 440 nm [5]. RNO solution of 1000 mL was poured in the beaker, and circulated at the flow rate of 100 mL/min NaCl at different dosage of 0.1, 0.3, 0.5 and 1.0 g was mixed in distilled water as electrolyte, respectively. While electrolysis was performed under galvanostatic control at 0.5 and 1.0 A, respectively, resulting in current densities of 10 and 20 mA/cm^2. Samples were taken at intervals of 1 or 5 min and absorbance of RNO solution was measured by 722S spectrophotometer (Shangai Delicacely Scientific Facility Co., Ltd.).

2.4. Cyclic voltammetry (CV)

In order to investigate the behavior of $Ti/RuO_2–Pt$ and $Ti/IrO_2–Pt$ anodes during the electrolysis of the phenol solution, the cyclic voltammetry experiments were operated by a computer controlled CS300 electrochemical workstation using a three-electrode cell

(Company of Huazhong Electronic), Pt is chosen as the counter electrodes, and Hg/HgCl electrode as the reference electrode, and the working anodes are Ti/RuO_2–Pt and Ti/IrO_2–Pt having a size of 1.0 cm × 1.0 cm. The electrolyte of 0.05 M NaCl solution containing 8 mg/L phenol was used. The potential was scanned at the scan rate of 100 mV/s, starting from 0 V, and the scan range was run from −2.5 to 2.5 V.

2.5. Analytical methods

Concentration of phenol was measured by 4-amido-antipyrine titration, and COD was determined by K_2CrO_7 oxidation according to Chinese Method of Water and Wastewater measurement [27]. pH was measured by pH S-3Cprecision pH/mV meter.

The TOC was measured by a TOC analyzer (1030, Aurora) based on the combustion-infrared method. Surface morphology of cathode was characterized ex situ by atomic force microscopy (Digital Instruments, Dimension^{TM}3000, USA).

3. Results and discussion

3.1. Phenol electrolysis

Performance of Ti/RuO_2–Pt and Ti/IrO_2–Pt for phenol degradation with different NaCl dosages (Fig. 2).

It can be seen from Fig. 2 that Ti/RuO_2–Pt and Ti/IrO_2–Pt have similar effect in the electrochemical phenol degradation with different dosages of NaCl at the same current density, i.e., the concentration of phenol decreased with respect to treatment time, and the phenol removal ratios increased with the increasing of NaCl dosages. However, there were a little slower about the phenol degradation rate with Ti/IrO_2–Pt anode than with Ti/RuO_2–Pt anode. Furthermore, with Na_2SO_4 as supporting electrolyte, electrochemical degradation of phenol was very slow at both anodes, which was similar with study of Li et al. [8], who found that with the Ti/RuO_2 and Pt anodes only 40% or less of the TOC was removed after a long treatment period. It was suggested that NaCl, which could be oxidized to form a strong oxidant of HOCl, could promote the degradation of phenol. As shown in Fig. 2, with 0.1 g/L NaCl as supporting electrolyte, the phenol concentration almost did not decrease in about the initial 5 min, while the phenomenon was not observed with 0.3 g/L and 0.5 g/L NaCl as supporting electrolyte. This is due to the fact of that HOCl could not be enough produced with lower NaCl (0.1 g/L) at the beginning. Although complete phenol removal was achieved by all of the anodes, the performance of Ti/RuO_2–Pt was better than that of Ti/IrO_2–Pt at same experiment condition. For the Ti/RuO_2–Pt anode, phenol concentration decreased from around 8 mg/L to zero after 30 min of electrolysis with 0.3 and 0.5 g/L NaCl as supporting electrolyte at the current density of 10 mA/cm^2 (Fig. 2(A)), while it reached zero after approximately 20 min at 20 mA/cm^2 (Fig. 2(C)). On the other hand, the Ti/IrO_2–Pt showed slower removal ratio compared to the Ti/RuO_2–Pt. At different current density of 10 and 20 mA/cm^2, phenol concentration decreased from around 8 mg/L to zero after 50 min (Fig. 2(B)) and 30 min during electrolysis (Fig. 2(D)), respectively. It was found that the potential increased during the electrolysis (Table 1), although the potential did not increase significantly. That must due to the fact that the NaCl was consumed to produce HOCl with respect of time, which resulted into the decrease of conductivity. Although both about the same voltage input and the same dosage of NaCl solution for the two types of anodes in the electrolysis cells, different times for complete phenol removal were taken (Table 1), i.e., less electric energy with the Ti/RuO_2–Pt than that with the Ti/IrO_2–Pt was consumed to achieve complete phenol removal. Considering the economy factor, it is clear from Table 1 that at current density of 10 mA/cm^2 with 0.3 g/L NaCl as supporting electrolyte was best for degradation of 8 mg/L phenol contaminated water by Ti/RuO_2–Pt anode.

Fig. 3 shows the variation of TOC during the phenol electrolysis with NaCl as supporting electrolyte. TOCs decreased to zero in the given treatment period for both Ti/RuO_2–Pt and Ti/IrO_2–Pt, the similar tendency of change in TOC and phenol concentration was observed, meaning that phenol was completely oxidized into CO_2 in the end of the electrolysis.

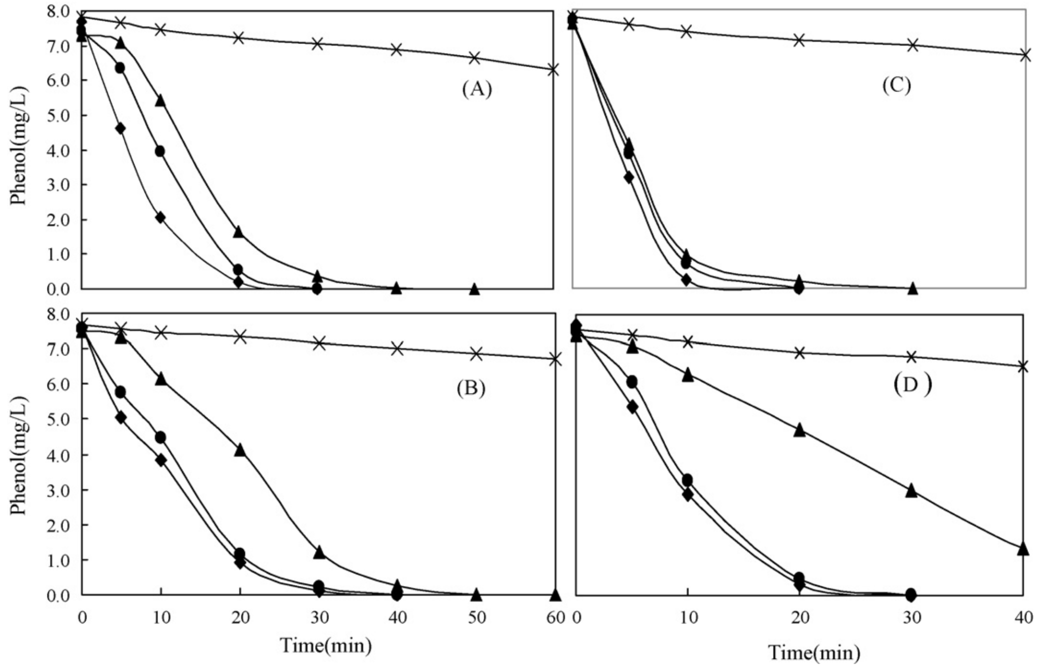

Fig. 2. Electrochemical degradation of 8 mg/L phenol in 1000 mL electrolyte as a function of time for different dosage of NaCl as supporting electrolyte. (A) I = 10 mA/cm^2, Ti/RuO_2–Pt; (B) I = 10 mA/cm^2, Ti/IrO_2–Pt; (C) I = 20 mA/cm^2, Ti/RuO_2–Pt; (D) I = 20 mA/cm^2, Ti/IrO_2–Pt. (♦) 0.5 g/L NaCl; (●) 0.3 g/L NaCl; (▲) 0.1 g/L NaCl; (×) 0.5 g/L Na_2SO_4.

Table 1
Potential as function of time during electrochemical degradation of 8 mg/L phenol at different current density with different dosages of NaCl as supporting electrolyte

Electrode	Current density (mA/cm^2)	NaCl (g/L)	Initial potential (V)	End potential (V)	Degradation time (min)
Ti/RuO_2–Pt	10	0.1	12.90	13.80	50
Ti/IrO_2–Pt	10	0.1	12.80	13.60	60
Ti/RuO_2–Pt	10	0.3	8.40	9.10	30
Ti/IrO_2–Pt	10	0.3	8.40	9.20	40
Ti/RuO_2–Pt	10	0.5	7.10	8.00	30
Ti/IrO_2–Pt	10	0.5	7.10	8.10	40
Ti/RuO_2–Pt	20	0.1	26.60	28.40	30
Ti/IrO_2–Pt	20	0.1	26.80	28.60	90
Ti/RuO_2–Pt	20	0.3	18.80	19.70	20
Ti/IrO_2–Pt	20	0.3	18.80	19.90	30
Ti/RuO_2–Pt	20	0.5	16.20	17.40	20
Ti/IrO_2–Pt	20	0.5	16.30	17.60	30

3.2. *Passivation of electrodes*

Since the formation of films on the surface of Ti/IrO_2–Pt anode was observed during the electrolysis, the change of performance of anodes with the service time was investigated. Fig. 4 shows that the electrochemical oxidation ability of Ti/IrO_2–Pt anode dropped quickly after serviced for 10 h at the current density of 10 mA/cm^2 with 0.3 g/L NaCl as supporting electrolyte. The phenol concentration decreased from around 8 mg/L to zero in 40 and 90 min by the first service and the 10 h service time, respectively. However, no formation of polymeric film and no change of performance on the Ti/RuO_2–Pt anode were observed after servicing for 10 h (data not shown), which demonstrated that the Ti/RuO_2–Pt was more suitable for phenol removal than Ti/IrO_2–Pt. It was found that some yellow substances were deposit on the Ti/IrO_2–Pt anode. Some substances were appeared to be adhered to the surface of the anode after electrolysis (Fig. 5). It can be seen from Fig. 5 that after using the surface of Ti/IrO_2–Pt anode was more rough than that of unused. The yellow substances could be partly washed off by dilute H_2SO_4 solution. After washing the electrode, the electrodes remain yellow–brown. The washed-off-solution was analyzed by HPLC. Benzoquinone and hydroquinone were found in a higher quantity in the solution (data not shown). It is well known that the ability of phenol to foul electrodes and the tarry deposit forming on electrodes during phenol oxidation is attributed to phenolic polymerization products. The oxidation of phenolic compounds at solid electrodes produces phenoxy radicals, which are responsible for coupling to form a passivating polymeric film on the electrodes [28].

According to the cyclic voltammograms (Fig. 6), the Ti/IrO_2–Pt anode had a lower oxygen evolution potential than the Ti/RuO_2–Pt anode, with values of 1.20 and 1.58 V (vs. the standard Hg/HgCl), respectively. The low over-potential of the Ti/IrO_2–Pt anode would shorten the lifetime of the hydroxyl radicals, and would hinder the oxygen to transfer from the radicals to organic oxidation which leads to the accumulation of polymeric products in electrochemical oxidation. The organic film formed on the Ti/IrO_2–Pt would deactivate the anode oxidizability. Since high oxygen evolution potential can decrease the unwanted power loss to oxygen generation [9,11], it will increase the current efficiency for electrochemical degradation. The radical reaction forming molecular oxygen was probably restrained because of the high over-potential of the Ti/RuO_2–Pt anode, which was favorable to organic oxidation by hydroxyl radicals formed at the electrode surface. It was ascertained from Fig. 6 that the Ti/RuO_2–Pt anode was more effective than the Ti/IrO_2–Pt anode during the phenol electrolysis. Various strategies have been developed to address these surface fouling problems including the use of electrochemical pre-treatment [15], laser activation [29], chemical or electrochemical treatment and reducing the concentration and lifetime of phenoxy radicals [3,30]. The formation rate of tar depends on the concentration of phenoxy radicals, which can be limited by decreasing the concentration of phenol and minimizing the current density. The phenoxy radical lifetime can be decreased by decreasing pH in solution because the phenol oxidation potential decreases with pH while the phenoxy radical oxidation potential remains unchanged [31]. As some yellow substances were deposit on the Ti/IrO_2–Pt anode and no substance was deposit on Ti/RuO_2–Pt anode, which may be that reason that shapes of voltammetric lines were different between two anodes.

3.3. *Effect of initial concentrations of phenol on the degradation efficiency*

In order to investigate the treatment efficiency on high concentration of phenol, the experiments of electrochemical degradation of 20, 40 and 80 mg/L phenol solutions were carried out with a

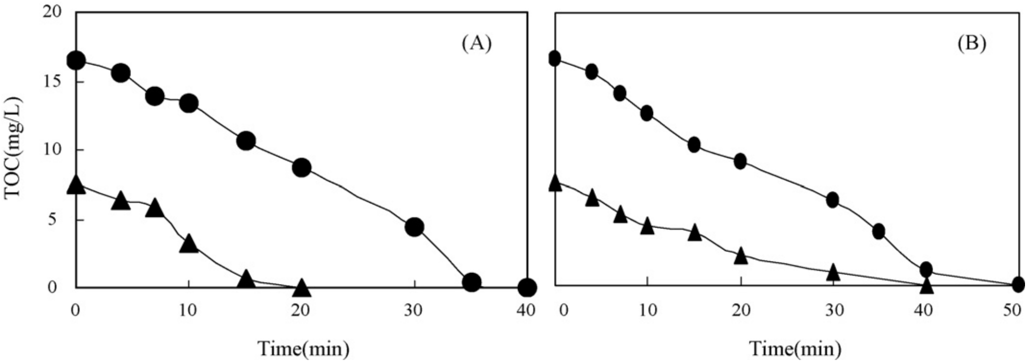

Fig. 3. TOC as a function of time with 0.3 g/L NaCl as supporting electrolyte. (A) Ti/RuO_2–Pt; (B) Ti/IrO_2–Pt; $I = 20\ mA/cm^2$, (▲) 8 mg/L; (●) 20 mg/L.

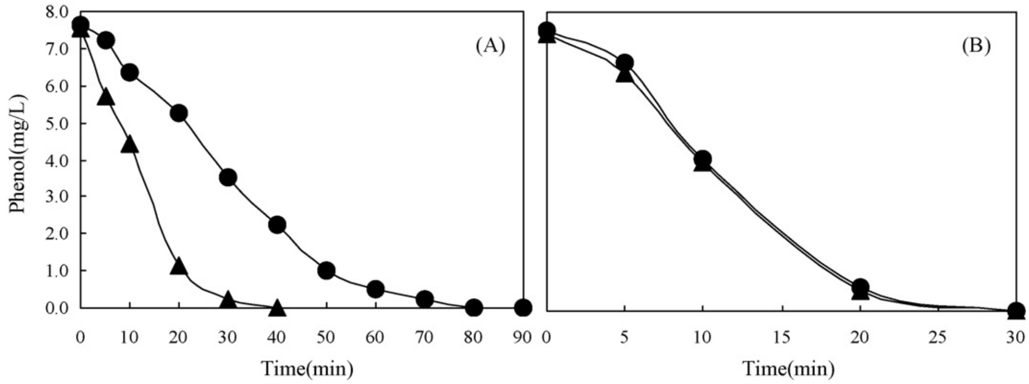

Fig. 4. Electrochemical degradation of 8 mg/L phenol in 1000 mL electrolyte as a function of time with 0.3 g/L NaCl as supporting electrolyte with different service time. (A) Ti/IrO_2–Pt; (B) Ti/RuO_2–Pt; I = 10 mA/cm^2, (▲) first service; (●) service 10 h later.

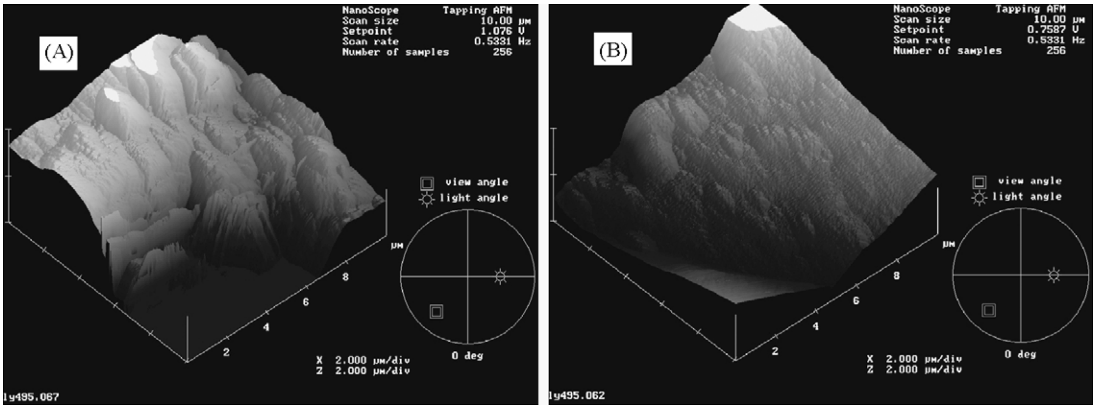

Fig. 5. AFM photograph of (A) an unused and (B) used for electrolysis Ti/IrO_2–Pt anode.

selecting current density and NaCl concentration. It is clear from Fig. 7 that complete phenol removal was achieved on high concentration of phenol as the electrolysis time was extended. At current density of 10 mA/cm^2 with 1.0 g/L NaCl as supporting electrolyte, the phenol concentration decreased from around 20, 40 and 80 mg/L to zero after 30, 60 and 130 min, respectively. The electrolysis time for complete removal of phenol was proportional to the concentration of phenol. In conclusion, the Ti/RuO_2–Pt anode also performs well for electrochemical degradation of high concentration of phenol solution with appropriate current density and NaCl as supporting electrolyte.

3.4. Change of pH during the phenol electrolysis

Fig. 8 shows the change of pHs during the electrolysis process at different conditions, where the pHs were not controlled. As shown in Fig. 6, the similar trend of the pH change was observed at 0.3 NaCl–8 mg/L phenols, 0.3 NaCl–20 mg/L phenol, i.e., the pH increased at the beginning, and then decreased, finally remained nearly constant. However, the pH reached the maximum value of 9.3 at 0.3 NaCl–8 mg/L phenol in the first 5 min, and then the

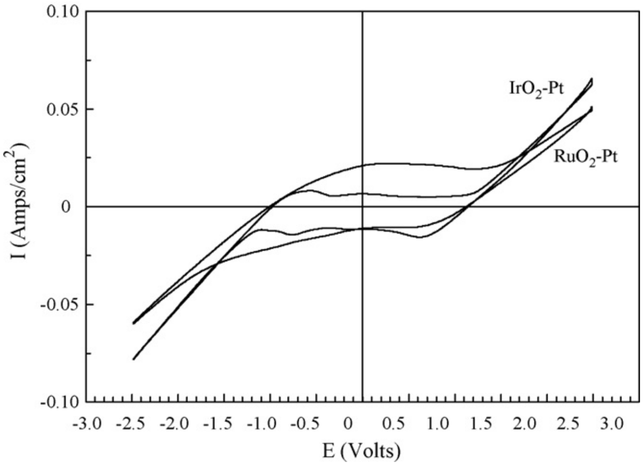

Fig. 6. Cyclic voltammograms of the anode materials Ti/RuO_2–Pt, and Ti/IrO_2–Pt obtained at a scan rate of 100 mV/s in 8 mg/L phenol, 0.05 M NaCl, 25 °C, pH 7.6 (E vs. Hg/HgCl).

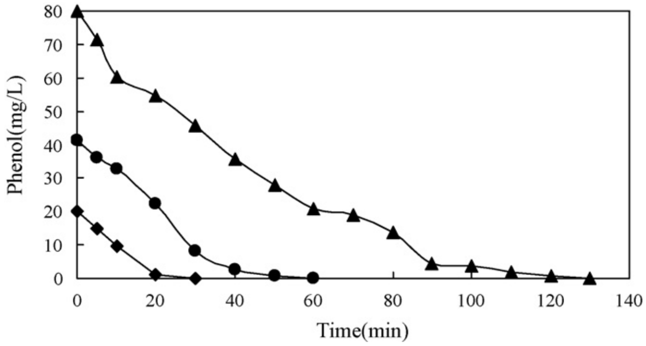

Fig. 7. Electrochemical degradation of 20, 40 and 80 mg/L phenol in 1000 mL electrolyte as a function of time with 1.0 g/L NaCl as supporting electrolyte. Ti/RuO_2–Pt, I = 10 mA/cm^2. (◆) 20 mg/L; (●) 40 mg/L; (▲) 80 mg/L.

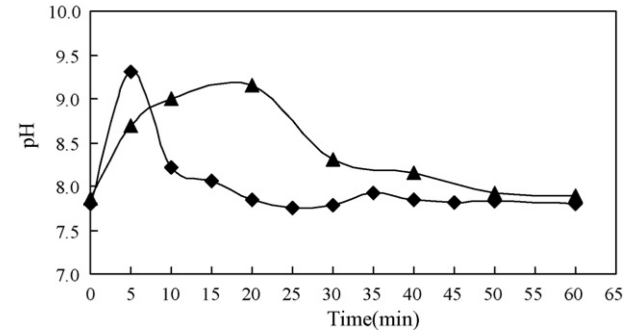

Fig. 8. The change of pH with time during electrochemical degradation of 8 and 20 mg/L phenol in 1000 mL electrolyte as a function of time with 0.3 g/L NaCl as supporting electrolyte. $I = 10\,\text{mA/cm}^2$, Ti/RuO_2–Pt; (♦) 8 mg/L phenol; (▲) 20 mg/L phenol.

pH began to drop sharply with the electrolysis time. On the other hand, the pH in the higher concentration phenol solution (20 mg/L) increased to 9.0 in the first 5 min, and then increased gradually to 9.2 in 20 min, and after that dropped in accordance with the electrolysis time. Initial pH rise could be attributed to the production of hydroxyl ions on the cathode, and the drop of pH was caused by gradual consumption of hydroxyl anions as well as production of hydrogen cations in dissociation reactions of HOCl and OCl^- along with the reaction of HOCl in the treated phenol solution [17]. Since HOCl was immediately consumed by oxidation of phenol in the higher concentration phenol solution, the pH was kept in the range of 9.0–9.3 for a longer period. Moreover, formation of different organic acids also resulted in the pH drop. The pH reached approximately 7.6 when the phenol was completely removed from the two concentrations of phenol solution [5,8,10,13,30].

3.5. *ICE with electrolysis time*

The COD method was used for the determination of the current efficiency. In this method, the COD was measured during electrolysis and the instantaneous current efficiency (ICE) was calculated using the following equations [13].

$$\text{ICE} = \frac{[\text{COD}_t - \text{COD}_{t+\Delta t}]FV}{8I\Delta t}$$

where COD_t and $\text{COD}_{t+\Delta t}$ are the COD (in gO_2/L) at times t and $t+\Delta t$ (in s), respectively, I the current intensity (A), F the Faraday constant (96,487 C/mol), t the time (in s),V the volume of the electrolyte (L) and 8 is a dimensional factor for unit consistence. It can be observed from Fig. 9 that ICE was relatively higher at the initial step of 0–10 min than the 10–20 min and the final step of 20–40 min, and the ICE for higher concentration of phenol solution was larger compared to lower concentration of phenol solution. Comninellis and Pulgarin [13] and Polcaro et al. [31] indicated that the initial organic concentration influenced the current efficiency, and that the current efficiency at greater initial organic concentrations was relatively high. This behavior was explained by the side reaction of oxygen evolution, i.e., the radicals formed could react rapidly with the organic matters before the oxygen evolution in a high initial organic concentration. The initial reaction at 0–10 min is the oxidation of phenol, which might be the oxidation of phenol to benzoquinone and further oxidation to a series of intermediate products with the aromatic ring opening. The ICE decreases rapidly in 10–20 min and the main reaction in this period is the oxidation of the intermediates formed in 0–10 min obviously, they were more difficult for electro-oxidation than phenol or benzoquinone. It is worthwhile to note that ICE increased again in the last step at both phenol concentrations, which is probably because of the formation of HOCl that promote the oxidation of intermediate products.

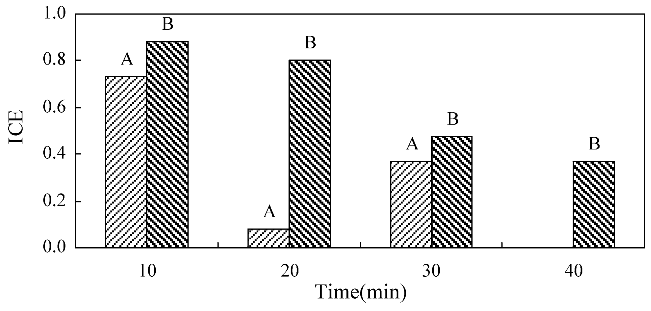

Fig. 9. Change in ICE with respect to treatment time for electrochemical degradation of 8 and 20 mg/L phenol solution. $I = 10\,\text{mA/cm}^2$, Ti/RuO_2–Pt, 0.3 g/L NaCl. (A) 8 mg/L; (B) 20 mg/L.

3.6. *Free radicals production*

3.6.1. *Mechanism of phenol oxidation*

The mechanism of electrochemical degradation of organic matter at anodes has been suggested by Comninellis [5]. Water is electrolyzed by anodic catalysis to produce adsorbed hydroxyl radicals.

$$H_2O + MO_x \rightarrow MO_x\,[^\bullet OH] + H^+ + e^- \quad (1)$$

The adsorbed hydroxyl radicals may form chemisorbed active oxygen.

$$MO_x\,[^\bullet OH] \rightarrow MO_{x+1} + H^+ + e^- \quad (2)$$

Meanwhile, the hydroxyl radicals will react with each other to form molecular oxygen to complete the electrolysis of the water molecules.

$$MO_x\,[^\bullet OH] \rightarrow M + O_2 + H^+ + e^- \quad (3)$$

Furthermore, another strong oxidant of hypochlorite may be produced in many wastewaters containing chlorides [32,33].

$$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^- \quad (4)$$

Organic matter (R) included in wastewater are oxidized by hydroxyl radicals [33].

$$R + MO_x\,[^\bullet OH] \rightarrow MO_x + CO_2 + z\,H^+ + z\,e^- \quad (6)$$

$$MO_{x+1} + R \rightarrow MO_x + RO \quad (7)$$

$$R + HOCl \rightarrow \text{product} + Cl^- \quad (8)$$

The mechanism of electrochemical oxidation of phenol have been carried out in the previous works [13,34]. It is well known that phenol oxidation starts with a one-electron transfer, leading to a phenoxy radical reaction [35], and some possible reactions of phenoxy radicals relates to radical–radical coupling, radical disproportionation, radical elimination or radical oxidation to cation and then followed by benzoquinone formation. Benzoquinone is absorbed onto the electrode surface and gives up an electron, and an adsorbed $^\bullet$OH radical would attack the benzoquinone [34,35]. Further oxidation of these intermediates yields harmless end-products CO_2 and H_2O. Li et al. [8] showed that the difference in the oxygen evolution potential for the different anodes could lead to different pathways of electrochemical phenol degradation. With sufficient hydroxyl radicals formed on the anode, maleic acid could be oxidized directly to oxalic acid, which can be oxidized readily to CO_2. HOCl formed in the presence of NaCl would dominate the oxidization of phenol to CO_2 during the electrochemical degradation of phenol in the present experiments.

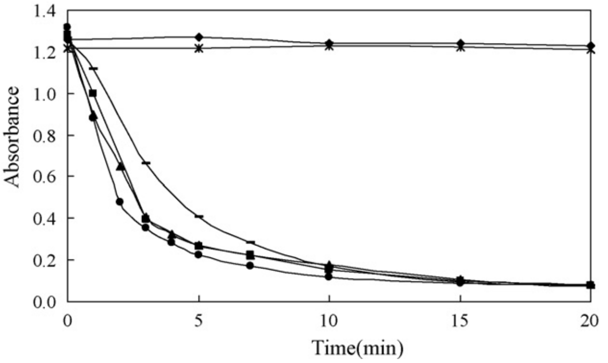

Fig. 10. Electrochemical bleaching of 50 μmol/L in 0.3 g/L NaCl solution as a function of treatment time at Ti/RuO_2–Pt and Ti/IrO_2–Pt anodes. (■) I = 10 mA/cm^2, Ti/RuO_2–Pt; (●) I = 20 mA/cm^2, Ti/RuO_2–Pt; (▬) I = 10 mA/cm^2, Ti/IrO_2–Pt; (▲) I = 20 mA/cm^2, Ti/IrO_2–Pt; (✱) I = 10 mA/cm^2, Ti/RuO_2–Pt, 0 mg/L NaCl; (♦) I = 10 mA/cm^2, Ti/IrO_2–Pt, 0 mg/L NaCl.

3.6.2. *Free radicals production during electrolysis*

Fig. 10 shows the absorbance of RNO sharply decreased in the initial 10 min at 10 and 20 mA/cm^2 with 0.3 g/L NaCl addition, and the bleaching ratio was up to 87%. It was clear that bleaching rate was quicker at the current density of 20 mA/cm^2 than 10 mA/cm^2, and it was quicker on Ti/RuO_2–Pt anodes than on Ti/IrO_2–Pt anodes under the same condition. However, it shows that the absorbance had almost no change without NaCl, indicating that formation of hypochlorous acid was an important bleaching factor during the electrolysis. As the ring of benzoquinone produced by the oxidation of phenol could be opened by hydroxyl radicals but not hypochlorous acid to form maleic acid and another small organic compound, which is believed to be important for phenol degradation, and the poor ability of Pt for producing hydroxyl radicals [20], the existing of RuO_2 or IrO_2 coating were indispensable. However, the existing of Pt would keep the electrode for a long service time. Comninellis [5] suggested that hydroxyl radicals react selectively with RNO, but hypochlorous acid play a very important role in the RNO bleaching from the present study, which would promote the phenol degradation. Li et al. [8] showed that phenol in Na_2SO_4 solution decreased from 490 mg/L to zero in 35 h with Ti/RuO_2 at current density of 20 mA/cm^2, but phenol solution with 1.0 g/L NaCl as supporting electrolyte was degraded from 80 mg/L to zero in 130 min at current density of 10 mA/cm^2 in present study (Fig. 6). Therefore, the NaCl presence is necessary for efficient degradation of phenol.

4. Conclusions

The electrochemical approach is a novel process for effective removal of phenol. In the present study, effect of current density, dosage of NaCl, initial phenol concentration on the performance of phenol electrolysis were investigated using Ti/RuO_2–Pt and Ti/IrO_2–Pt anodes.

Phenol could be readily mineralized at the Ti/RuO_2–Pt and Ti/IrO_2–Pt anodes; however, its degradation was considerably slower at the Ti/IrO_2–Pt anode. Complete TOC removal was achieved at both anodes with NaCl as supporting electrolyte. It was found that Ti/RuO_2–Pt anode had a higher oxygen evolution potential than Ti/IrO_2–Pt anode, which will increase the current efficiency for electrochemical degradation. Moreover, HOCl formed quickly with sodium chloride as supporting electrolyte and that would play an important role on the oxidation of phenol. With NaCl as supporting electrolyte, specific anode surface treatment of the RuO_2–Pt coating provided the anode with an apparent catalytic function for rapid organic oxidation that was mainly brought about by HOCl generated during electrolysis process. For the Ti/RuO_2–Pt anode, phenol concentration decreased from around 8 mg/L to zero after 30 min of electrolysis with 0.3 g/L NaCl as supporting electrolyte at the current density of 10 mA/cm^2. The ICE was relatively higher at the initial step and the final stepand. The ICE for higher concentration of phenol solution was larger compared to lower concentration of phenol solution.

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