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Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes

Xiao-yan Li[a,*], Yu-hong Cui[b], Yu-jie Feng[b], Zhao-ming Xie[a], Ji-Dong Gu[c]

[a]*Environmental Engineering Research Centre, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

[b]*Department of Environmental Science and Engineering, Harbin Institute of Technology, Nangang District, Harbin 150090, China*

[c]*Department of Ecology and Biodiversity, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

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Abstract

Laboratory experiments were carried out on the kinetics and pathways of the electrochemical (EC) degradation of phenol at three different types of anodes, Ti/SnO_2-Sb, Ti/RuO_2, and Pt. Although phenol was oxidised by all of the anodes at a current density of 20 mA/cm^2 or a cell voltage of 4.6 V, there was a considerable difference between the three anode types in the effectiveness and performance of EC organic degradation. Phenol was readily mineralized at the Ti/SnO_2-Sb anode, but its degradation was much slower at the Ti/RuO_2 and Pt anodes. The analytical results of high-performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC/MS) indicated that the intermediate products of EC phenol degradation, including benzoquinone and organic acids, were subsequently oxidised rapidly by the Ti/SnO_2-Sb anode, but accumulated in the cells of Ti/RuO_2 and Pt. There was also a formation of dark-coloured polymeric compounds and precipitates in the solutions electrolyzed by the Ti/RuO_2 and Pt anodes, which was not observed for the Ti/SnO_2-Sb cells. It is argued that anodic property not only affects the reaction kinetics of various steps of EC organic oxidation, but also alters the pathway of phenol electrolysis. Favourable surface treatment, such as the SnO_2-Sb coating, provides the anode with an apparent catalytic function for rapid organic oxidation that is probably brought about by hydroxyl radicals generated from anodic water electrolysis.
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Keywords: Anode; Electrochemistry; Electro-oxidation; Free radicals; Phenol; Wastewater treatment

1. Introduction

Aromatic compounds are common pollutants in the waste effluent from many industrial sectors, such as petroleum refineries, synthetic chemical plants, plastics, pulp and paper, textiles, detergent, pesticide and herbicide, and pharmaceutical factories. Wastewater containing aromatic chemicals is refractory, and is often toxic to biological treatment processes. Attempts have been made to degrade and destroy aromatic organics using various advanced oxidation processes (AOPs), including photochemical reactions, Fenton oxidation, ozonation, and supercritical water oxidation (Brillas et al., 1998; Esplugas et al., 2002). Electrochemistry is another alternative that has attracted considerable research attention (Comninellis, 1994; Rodgers et al., 1999; Brillas et al., 2000). Toxic organics can be effectively oxidised by electrochemical (EC) reaction

*Corresponding author. Tel.: +852 2859 2659; fax: +852 2559 5337.
E-mail address: xlia@hkucc.hku.hk (X.-Y. Li).

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(Brillas et al., 2000; Kötz et al., 1991; Chiang et al., 1995; Johnson et al., 1999; Feng and Li, 2003). With unique features such as simplicity and robustness in structure and operation, the EC process has the potential to be developed as a cost-effective technology for the treatment of aromatic pollutants, particularly for low-volume applications.

The effectiveness of EC wastewater treatment depends on the nature of the anodes that are used in the process (Feng and Li, 2003; Stucki et al., 1991; Chen, 2004). Traditional electrodes, such as graphite and nickel, show a poor current efficiency in organic degradation (Rodgers et al., 1999). Dimensionally stable anodes (DSAs) that are prepared by the deposition of a thin layer of metal oxides on a base metal, usually titanium, are found to have a varying degree of success. The widely used RuO_2 and IrO_2-based coating surface does not appear to have a high reactivity for organic oxidation (Comninellis, 1994; Feng and Li, 2003; Simod and Comninellis, 1997). Other DSA coating materials, such as PbO_2- and SnO_2-based coatings, have been introduced to improve the treatment performance. PbO_2 electrodes can be highly effective for complete organic destruction, e.g., EC incineration (Comninellis, 1994; Feng and Johnson, 1991; Houk et al., 1998; Schumann and Grundler, 1998). Hence, PbO_2 and similar anodes are considered to be of sufficient electro-catalytic capacity for organic oxidation (Comninellis, 1994; Feng and Li, 2003; Feng et al., 1995; Tahar and Savall, 1999; Tanaka et al., 2002). However, concern over the possible toxicity of Pb leaching from the working anode would hinder the actual application of PbO_2 electrodes. The SnO_2-based coating has shown a similar reactivity as that of PbO_2 for EC organic degradation (Rodgers et al., 1999; Kötz et al., 1991; Correa-Lozano et al., 1997; Polcaro et al., 1999). With further development and characterization, SnO_2 anodes are expected to offer a better solution for the enhancement and application of the EC process to organic degradation.

The difference in the effectiveness and performance of different anode materials for wastewater treatment demonstrates the complexity of the EC reaction mechanisms involved. It has been reported that the oxidation of phenol can stop with such products as maleic acid and oxalic acid for Pt anodes (Comninellis and Pulgarin, 1991; Gattrell and Kirk, 1993). However, complete phenol oxidation can be achieved for PbO_2 electrodes (Feng and Li, 2003; Schumann and Grundler, 1998; Iniesta et al., 2001). Hence, the degradation pathway of aromatic organics on different anodes remains a subject for investigation. It is unclear whether the anode surface property would affect the reaction kinetics or alter the pathway of organic oxidation. In the present laboratory study, phenol, which is the basic unit of aromatic compounds, was used as the model organic for EC degradation. Ti anodes coated with SnO_2 and doped with Sb (Ti/SnO_2-Sb) were examined for their performance in EC phenol degradation and compared to the Ti anodes coated with RuO_2 (Ti/RuO_2) and the Pt anodes. The intermediate products of the EC treatment process with different anodes were measured to determine the phenol degradation pathways and related reaction mechanisms.

2. Materials and methods

2.1. Electrode preparation

Three types of electrodes, Ti/SnO_2-Sb, Ti/RuO_2, and Pt, were used as anodes for the phenol oxidation study. The Ti/SnO_2-Sb anode was selected because of its expected electro-catalytic function for organic oxidation (Kötz et al., 1991; Stucki et al., 1991; Polcaro et al., 1999), Ti/RuO_2 is one of the most widely used DSA electrodes, and Pt is a common material in electrochemistry studies. The Ti plates (99.5%) were rectangular in shape with a dimension of $2 \times 3\,cm^2$ and a thickness of 1.5 mm. They were polished thoroughly with a 320-grit sandpaper, and then degreased in 40% NaOH at 80 °C for 2 h and etched in 15% oxalic acid at 98 °C for 2 h, followed by a thorough washing with de-ionized (DI) water. The treated Ti plates became grey, losing their metallic sheen.

The Ti/RuO_2 electrodes were prepared by the thermal deposition of RuO_2 on the Ti plates following the procedure described elsewhere (Johnson et al., 1999; Feng and Li, 2003; Li et al., 2002). Briefly, a fully polished Ti plate was dipped into a coating solution that consisted of 0.5 M $RuCl_3$ (Aldrich) in *n*-butanol (99 + %, Aldrich) with 10% by volume of concentrated HCl (37%). The wet coating surface was dried in an oven at 60 °C for 30 min. After repeating the dipping and drying ten times, the Ti plate was heated in airflow at an annealing temperature of 450 °C in a muffle oven for 1 h. The above procedure was repeated three times to produce the Ti/RuO_2 anodes.

The Ti/SnO_2-Sb electrodes were prepared by electro-deposition for the inner coating layer and thermal deposition for the outer layer, which is a procedure modified from methods described by others (Kötz et al., 1991; Correa-Lozano et al., 1997; Zhang, 2000). For electro-deposition, a Ti plate was placed as the cathode in 100 ml of alcohol solution containing 17.5 g $SnCl_4 \cdot 5H_2O$ (Aldrich), 0.73 g Sb_2O_3 (Aldrich), and 2 ml concentrated HCl (37%). A constant DC current of 0.12 A was charged for 25 min for electroplating the cathode, and Pt was used as the counter electrode. The inner coating layer on the Ti plate was dried in an oven at 400 °C for 2 h. For the thermal deposition of the outer layer, the Ti plate was dipped into a coating solution that consisted of 30 g $SnCl_4 \cdot 5H_2O$, 0.8 g Sb_2O_3 and

2.5 ml concentrated HCl (37%) in 50 ml *n*-butanol. After five dipping-drying cycles at an ambient temperature, the Ti plate was annealed in a muffle oven at 550 °C for 2 h. The above procedure was repeated five times to produce the Ti/SnO_2-Sb electrodes. The inner electroplating on the Ti plates was found to be essential for the improvement of the durability and stability of the SnO_2-Sb coating surface on the Ti anodes.

The electrodes ($1 \times 1\,cm^2$) were examined for their cyclic voltammetry (CV) by a computer-controlled potentiostat/galvanostat (Model 263, EG&G) using a three-electrode cell, with stainless steel as the counter electrode and the standard Ag/AgCl electrode (Cypress System) as the reference electrode.

2.2. Phenol electrolysis

EC phenol degradation was conducted in batch electrolysis cells that were 100-ml glass beakers, each with a cover cap with two open slits for assembling the electrodes. In combination with the working anodes described above, stainless steel plates of the same size ($2 \times 3\,cm^2$) were used as the cathodes. The two electrodes in each cell were placed 8 mm apart and facing each other. A DC potentiostat was employed as the power supply with a voltage output up to 20 V.

For an electrolysis test, 80 ml of a phenol solution of a predetermined concentration (100 or 490 mg/L) was placed in the cell with 0.25 M Na_2SO_4 as the electrolyte. A consistent DC current of 0.12 A was charged to the pair of electrodes, which resulted in a current intensity of $20\,mA/cm^2$. As an alternative, the same voltage of 4.6 V was supplied to the three different cells of the Ti/SnO_2-Sb, Ti/RuO_2, and Pt anodes. The EC cells were placed on a magnetic stirrer for continuous mixing, and the temperature stayed at around 25 °C without special control measures. Samples were withdrawn from the electrolyzed solutions at various intervals for chemical analysis of the phenol, the total organic carbon (TOC), and intermediate products.

2.3. Analytical methods

All chemicals were of reagent grade, and all water solutions were prepared by DI water. The TOC was measured by a TOC analyzer (5000A, Shimadzu) based on the combustion-infrared method. The solution pH was recorded by a pH meter (420A, Orion). High-performance liquid chromatography (HPLC) was used to analyze the phenol and the aromatic intermediate compounds from the EC phenol degradation, including benzoquinone and hydroquinone (Shim and Park, 1997; Peiró et al., 2001). The HPLC (Agilent 1100) was equipped with a Zorbax column (Eclipse XDB-C8, ID = 4.6 mm, length = 150 mm, Agilent) and a UV detector used at working wavelengths of 212, 245, 260, and 290 nm. Methanol/water = 1/4 (V/V) was used as the mobile phase at a flow rate of 0.9 ml/min. Before each analysis, the sample was filtered through a 0.2-μm membrane filter (Osmonics). The injection volume was 50 μl.

Gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC/MS) were used for the measurement of the organic acids that were produced by the phenol electrolysis. To allow GC measurement of the non-volatile organic acids, the samples were esterified and then extracted following the procedure described elsewhere (Erbe and Bruckner, 2000; Wang et al., 2002; Peña-Alvarez et al., 2004). Esterification was performed by adding 3 ml of a sample and 2 ml of *n*-butanol together with 2 ml of concentrated HCl (37%) as catalyst in a 40-ml sealed bottle. The mixed solution was heated at 75 °C for 40 min. After cooling, 6 ml of hexane (HPLC grade, Fisher) was used to extract the esterified products from the solution. The extraction was repeated twice, and the extracted liquid was concentrated to 1 ml by a nitrogen flow before GC analysis. The GC (HP6890, Agilent) used a capillary column (HP-624, 25.0 m × 200 μm × 1.12 μm, Agilent) followed by detection with an MS (Netwaik 5973, Agilent). The temperature program began at 70 °C and increased at a rate of 20 °C/min up to 230 °C, with a holding time of 2 min for each increment. Helium was used as the carrier gas at a constant flow rate of 53.6 ml/min. The samples were injected in the splitless mode, and each injection was 1 μl. For quantification of a number of the intermediate organic acids, including maleic acid, succinic acid, and oxalic acid, another GC (HP6890, Agilent) equipped with a capillary column (HP-4, 30.0 m × 320 μm × 0.25 μm, Agilent) and a flame ionization detector (FID) was used. The temperature was increased from 70 °C at 10 °C/min up to 180 °C and then at 40 °C/min up to 260 °C with a holding time of 2 min for each increment. The helium carrier gas had a flow rate of 13.7 ml/min, and the sample injection procedure was the same as that described previously.

3. Results and discussion

3.1. Performance of selected anodes on phenol degradation

The three types of anodes, Ti/SnO_2-Sb, Ti/RuO_2, and Pt, performed considerably differently in the EC phenol degradation (Fig. 1A). The best result was obtained with the Ti/SnO_2-Sb anode, followed by the Pt anode and then the Ti/RuO_2 anode, although complete phenol removal was achieved by all of the anodes. The phenol was oxidised rapidly by the Ti/SnO_2-Sb anode, as its concentration decreased from around 490 mg/L to zero after 5 h of electrolysis. At the same current input rate

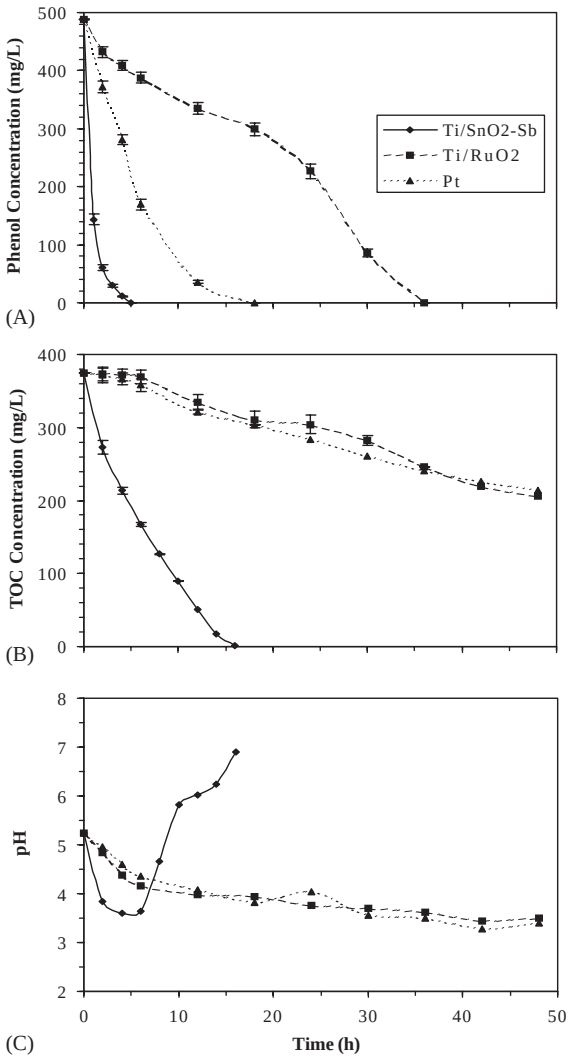


Fig. 1. Electrochemical degradation of phenol (490 mg/L) on anodes Ti/SnO_2-Sb, Ti/RuO_2, and Pt at a current intensity of 20 mA/cm^2. (A) Phenol degradation, (B) TOC removal, and (C) pH variation.

on the other two anodes the rates of phenol degradation were much slower. The time for complete phenol removal extended to about 18 h for the Pt anode and 36 h for the Ti/RuO_2 anode.

The three anode types had an even greater difference in the effectiveness of TOC removal (Fig. 1B). On the Ti/SnO_2-Sb anode, complete organic mineralization was achieved within 16 h. However, under the same current conditions with the Ti/RuO_2 and Pt anodes only 40% or less of the TOC was removed after a long treatment period of 48 h. The reproducibility of the EC experiments in terms of phenol and TOC degradation was satisfactory for each type of anode tested, with a low degree of variation observed in repeated test runs (Fig. 1). For the same voltage input of 4.6 V to the electrolysis cells, a different performance in phenol degradation was also recorded for the three different electrodes. With the Ti/SnO_2-Sb anode, a much lower charge consumption was used to achieve complete phenol and TOC removal than was used with the Ti/RuO_2 and Pt anodes.

The residual TOC in the solutions after phenol removal suggests the formation and accumulation of intermediate organic products, particularly with the Pt and Ti/RuO_2 anodes. The solution pH also changed during the electrolysis process (Fig. 1C). The pH dropped from the initial value of 5.3 to below 4.0 while the phenol was being electrochemically oxidised. It remained at around 3.5 with no sign of rising in the solutions that were treated by the Pt and Ti/RuO_2 anodes. In the Ti/SnO_2-Sb system, the pH began to increase after the phenol disappeared from the solution. The pH approached 7 when the TOC was completely removed after 16 h of electrolysis. The drop in pH was apparently caused by the formation of acidic substances from the phenol degradation. In combination with the TOC results, organic acids were probably one of the main intermediates produced by phenol electrolysis (Comninellis, 1994; Feng and Li, 2003; Houk et al., 1998; Tanaka et al., 2002; Comninellis and Pulgarin, 1991).

3.2. Intermediate products

The phenol solutions also exhibited colour changes during the electrolysis process. In the Ti/SnO_2-Sb cells, the liquid turned to yellow in the first 5 h of phenol oxidation. The yellow colour began to fade when the phenol concentration was reduced to zero, and the colour had almost disappeared about 4 h before the TOC was completely removed. For the Pt and Ti/RuO_2 anodes, however, the solution became dark yellow and turned to brown when the phenol had been totally removed. The colour did not fade even after another 24 h of electrolysis. It is generally believed that the yellow colour is caused by benzoquinone, which is produced by phenol oxidation (Comninellis and Pulgarin, 1991). The accumulation of benzoquinone was well detected by HPLC for the phenol solutions treated by all three types of anodes (Fig. 2). Hydroquinone, which is colourless, was found in an even higher quantity in all the experiments. Benzoquinone and hydroquinone are known as an active redox couple in equilibrium in an aqueous solution (Rieger, 1987). Their fractionation depends mainly on pH and other aquatic chemistry conditions (Shim and Park, 1997). The HPLC results indicate the transformation of the phenol by electrolysis to benzoquinone and hydroquinone, which were then both decomposed to other forms. Benzoquinone and hydroquinone were accumulated at a higher concentra-

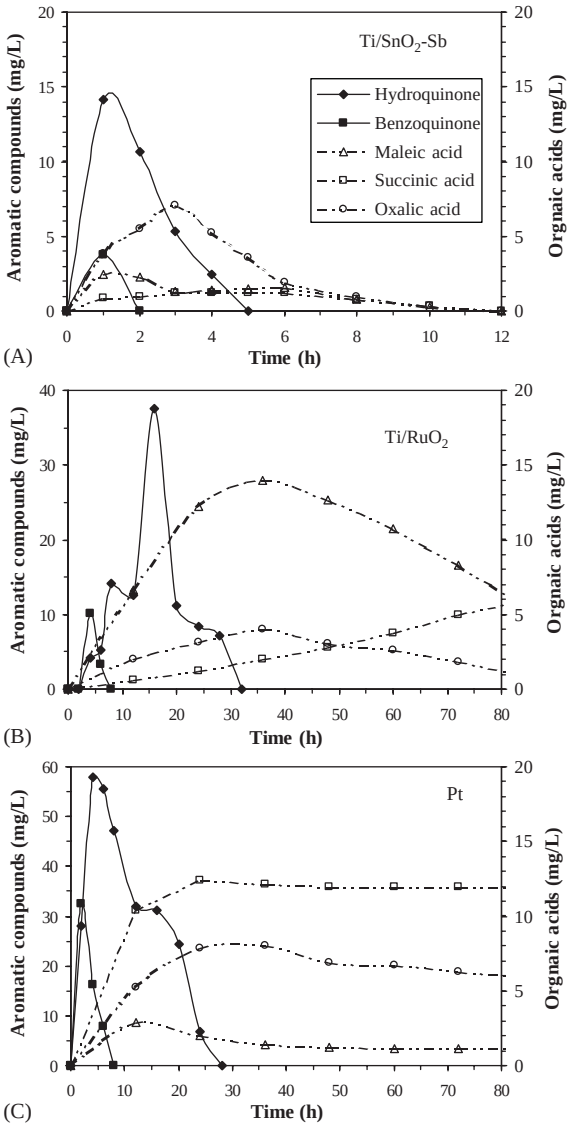


Fig. 2. Intermediate products of EC phenol (490 mg/L) degradation at a current intensity of 20 mA/cm^2 on anodes (A) Ti/SnO_2-Sb, (B) Ti/RuO_2, and (C) Pt.

tion level and for a much longer time in the solutions electrolyzed by the Ti/RuO_2 and Pt anodes than that electrolyzed by the Ti/SnO_2-Sb anode (Fig. 2).

Several carboxylic acids with two, three, and four carbon atoms were identified by GC/MS as important intermediates in the electrolyzed solutions, with maleic acid, succinic acid, and oxalic acid being found in dominant abundance. To quantify these non-volatile organic acids, the samples were esterified and extracted prior to GC determination. The results are presented only as the apparent concentrations in relation to the standards (100 mg/L) of the respective acids (Erbe and Bruckner, 2000; Hagen et al., 1999; Gonzalez-Bravo et al., 2000). In a comparative sense, however, there are notable differences between the three EC systems of different anodes in the formation and degradation of the intermediate organic acids. Oxalic acid was the main intermediate product with the Ti/SnO_2-Sb anode, and only a small quantity of maleic acid and succinic acid was detected (Fig. 2A). In agreement with the TOC data given in Fig. 1B, the organic acids were completely removed by electrolysis on the Ti/SnO_2-Sb anode. For the Ti/RuO_2 and Pt anodes, however, there was a greater accumulation of maleic acid and succinic acid during the EC process. The overall degradation of the organic acids by these two anodes was much slower than with the Ti/SnO2-Sb anode under the same experimental conditions.

As described above, a dark yellow to brown colour built up in the solutions that were treated by the Ti/RuO_2 and Pt anodes. Attempts using the HPLC to identify the substances that caused the colour failed to produce any sensible results. However, according to previous investigations, the colour is probably caused by the polymeric compounds produced by the EC oxidation of phenol (Gattrell and Kirk, 1993; Rajeshwar et al., 1994). The products of polymerization are so-called "synthetic humic acids" that consist of hydroquinone-benzoquinone monomeric units and that generally exhibit a dark brown colour (Feng et al., 1995). These amorphous polymers are formed by a radical reaction mechanism by phenate anions (Rodgers et al., 1999; Mengoli and Musiani, 1986). With the Ti/RuO_2 and Pt anodes, in addition to the brown build-up in the solutions, there were dark precipitates that were probably also formed by the polymeric compounds. For the Ti/SnO_2-Sb system, however, only a light yellow colour was visible during the EC process, which disappeared well before the TOC had been completely removed.

3.3. Pathways and mechanisms of EC phenol degradation

The mechanism of phenol degradation by EC oxidation has been the subject of several investigations (Rodgers et al., 1999; Feng and Li, 2003; Comninellis and Pulgarin, 1991; Gattrell and Kirk, 1993; Andreescu et al., 2003; Lund and Baizer, 1991; Iniesta et al., 2001). It is generally considered that phenol oxidation begins with an electron transfer that leads to phenoxy radical reactions (Lund and Baizer, 1991). Possible reactions related to phenoxy radicals include radical–radical coupling, radical disproportionation, radical elimination, and radical oxidation of cations. Radical reactions result in the formation of benzoquinone, which is believed to be an important intermediate of phenol oxidation (Tahar and Savall, 1999; Comninellis and Pulgarin, 1991; Iniesta et al., 2001). In the subsequent

stage, benzoquinone can be degraded with ring breakage to various carboxylic acids. Several mechanisms have been proposed for benzoquinone degradation. If benzoquinone is adsorbed onto the anode surface and gives up an electron, then the carbon that is double-bonded with the oxygen will be attacked by a neighbouring hydroxyl radical generated from water electrolysis. When this process is repeated at the para position, the ring could be opened and the benzoquinone would be broken down into small organic molecules such as carboxylic acids (Houk et al., 1998; Lund and Baizer, 1991). It has been suggested that the ring cleavage would result in the formation of maleic acid and another small organic compound such as ethene (Houk et al., 1998). The intermediate maleic acid has been experimentally proven (Johnson et al., 1999; Houk et al., 1998; Comninellis and Pulgarin, 1991). With continuous electrolysis, maleic acid would first be reduced to succinic acid at the cathode, followed by oxidation at the anode to malonic acid and then to acetic acid, and finally to CO_2 (Johnson et al., 1999; Feng and Li, 2003; Houk et al., 1998; Iniesta et al., 2001).

The present experimental findings in the removal of phenol and TOC, and in the formation of intermediate products, are in general agreement with the hypothesized reaction pathway of EC phenol degradation outlined above. Nonetheless, this pathway is apparently inadequate to explain the major differences between the three anodes in treating phenol under a similar EC condition. The theory would have considerable difficulties in accounting for the laboratory observations if the same reaction pathway were assumed for different anodes, including the much faster reaction kinetics with the Ti/SnO_2-Sb anode, the formation of oxalic acid, particularly in the liquid electrolyzed by the Ti/SnO_2-Sb anode, and the dark coloured polymeric products in the Ti/RuO_2 and Pt systems. Hence, the EC phenol degradation pathway theory needs to be modified to reconcile it with the experimental observations, although the main routes of the pathway can still be followed.

The major steps of the reaction pathway for EC phenol degradation are summarized in Fig. 3 with an emphasis on two modifications. The first is the inclusion of polymerization via phenoxy radicals that attack either benzoquinone or hydroquinone. Polymerization is hardly a reversible reaction, and the polymeric products are likely to be more recalcitrant to EC degradation than phenol. For benzoquinone and hydroquinone, ring cleavage (I) and polymerization (II) are two parallel processes that occur simultaneously. If the aromatic ring is broken rapidly, then there is little accumulation of benzoquinone and an insignificant formation of polymeric compounds, which is the case with the Ti/SnO_2-Sb anode. In contrast, if ring cleavage is rather slow, then polymerization becomes more significant, which is in fact the case with the Ti/RuO_2 and Pt anodes. Another pathway modification is the addition of a route from maleic acid to oxalic acid (III_B) in parallel with the conventional route of maleic acid reduction to succinic acid (III_A). For the Ti/RuO_2 and Pt systems, although the oxidation of maleic acid to oxalic acid might also take place, route III_A is still the dominant process. With the Ti/SnO_2-Sb anode, maleic acid is rapidly converted to oxalic acid following route III_B, whereas route III_A is relatively slower and hence less important. The intermediate oxalic acid is readily oxidised by anodic oxidation to CO_2 (Feng and Li, 2003).

The experimental results suggest that EC phenol oxidation on different anodes may follow different reaction pathways. It is apparent that different anode surfaces have different degrees of reactivity towards phenol degradation and its intermediate products. The exact catalytic role of the anode surface in organic oxidation is still under discussion. It is generally believed that organic compounds in aqueous solutions can be oxidised on an anode by direct electron transfer and indirect oxygen atom transfer (Rodgers et al., 1999; Chiang et al., 1995; Polcaro et al., 1999; Iniesta et al., 2001; Kirk et al., 1985). In the direct electron transfer process, organics are adsorbed on the anode surface and give up electrons to the anode, i.e.,

$$(\text{Organic})_{\text{ads}} - \text{ne}^- \rightarrow \text{Product}. \quad (1)$$

With the indirect oxygen atom transfer, it is generally considered that oxygen radicals, especially the hydroxyl radicals generated from water electrolysis, play a critical role in the EC oxidation mechanism of organic substances (Comninellis, 1994; Li et al., 2002; Iniesta et al., 2001; Simod et al., 1997). The formation of hydroxyl radicals on the anode surface can be expressed by Eq. (2), where M stands for the anode (Comninellis, 1994; Simod et al., 1997).

$$\text{M} + \text{H}_2\text{O} \rightarrow \text{M}[\bullet\text{OH}^-] + \text{H}^+ + \text{e}^-. \quad (2)$$

The hydroxyl radicals readily react with the organic molecules adsorbed on or in the vicinity of the anode to cause the oxidation reaction given below

$$\text{M}[\bullet\text{OH}^-] + \text{Organic} \rightarrow \text{Product}. \quad (3)$$

Meanwhile, the hydroxyl radicals will react with each other to form molecular oxygen to complete the electrolysis of the water molecules (Comninellis, 1994; Simod et al., 1997), i.e.,

$$2\text{M}[\bullet\text{OH}^-] \rightarrow 2\text{M} + \text{O}_2 + 2\text{H}^+ + 2\text{e}^-. \quad (4)$$

In organic wastewater treatment, anodic oxygen evolution actually causes a power loss, which reduces the overall current efficiency for both direct and indirect organic oxidation. Therefore, the use of an anode material with a high oxygen evolution potential is especially desirable since it can decrease the unwanted power loss to oxygen generation (Kötz et al., 1991;

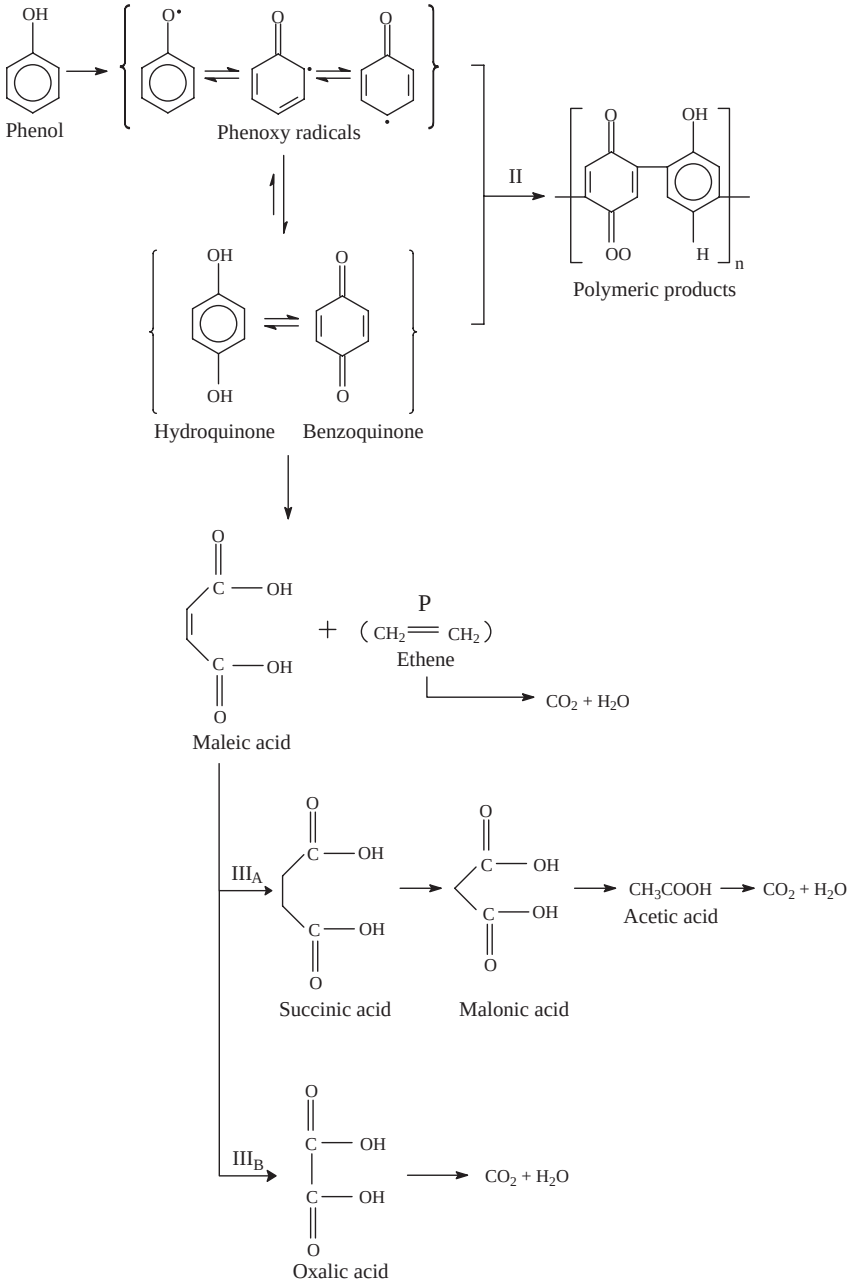


Fig. 3. Reaction pathway of electrochemical phenol degradation.

Stucki et al., 1991). According to the cyclic voltammograms (Fig. 4), the Pt and Ti/RuO_2 anodes had a lower oxygen evolution potential, with values of 1.4 and 1.1 V (vs the standard Ag/AgCl), respectively. The Ti/SnO_2-Sb anode, however, had a potential of 1.6 V. The high overpotential of the Ti/SnO_2-Sb anode suggests that the radical reaction forming molecular oxygen in Eq. (4) was probably restrained, which was favourable to organic oxidation by hydroxyl radicals. Hence, the difference in the oxygen evolution potential for the different anodes could have forced the EC phenol degradation through different pathways (Fig. 3).

Aromatic ring opening and maleic acid oxidation represent two limiting steps to complete EC phenol degradation. The high overpotential of the Ti/SnO_2-Sb anode would effectively extend the lifetime of the

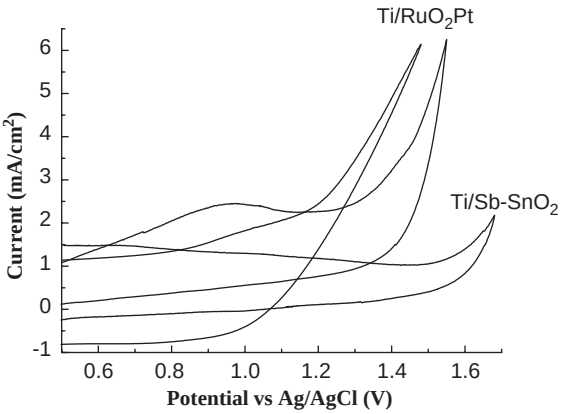


Fig. 4. Voltammograms of the anode materials Ti/SnO_2-Sb, Ti/RuO_2, and Pt obtained at a scan rate of 100 mV/s in 0.25 M Na_2SO_4 at 25 °C and pH = 6.

hydroxyl radicals on the anode, thus permitting more oxygen transfer from the radicals to the organic matter for oxidation (Eq. (3)). Without the strong oxidising power of free radicals, hydroquinone and benzoquinone would accumulate in the system, leading to the formation of polymeric products that are more refractory to EC oxidation. The generation of hydroxyl radicals would provide a sufficient non-selective oxidising capacity that could attack the aromatic rings more effectively and cause ring brokerage. As a result, the reaction step I would be enhanced and step II became less important. For the degradation of maleic acid, the formation of succinic acid by reduction is expected under normal circumstances (Johnson et al., 1999; Feng and Li, 2003; Feng and Johnson, 1991; Rajeshwar et al., 1994). However, with sufficient hydroxyl radicals formed on the anode, maleic acid could be oxidised directly to oxalic acid, which can be oxidised readily to CO_2. As a result, the reaction route III_B would become more predominant than route III_A, leading to much faster phenol degradation. Thus, the EC process at the Ti/SnO_2-Sb anode was mainly of the hydroxyl radical mechanism.

In contrast, the low overpotentials of the Pt and Ti/RuO_2 anodes would shorten the lifetime of the hydroxyl radicals, and hence hinder the oxygen transfer from the radicals for organic oxidation. The reaction steps I and III_B would become less important, whereas the slow routes of II and III_A would be more dominant in the pathway (Fig. 3). Thus, direct electron transfer reactions likely took place at the Pt and Ti/RuO_2 anodes leading to phenol oxidation. In addition, the Ti/SnO_2-Sb anode may have a better affinity with organic substances than the other two anodes. Better adsorption of the organic on the anode surface would improve electron transfer for direct organic oxidation, and allow a more effective indirect oxidation by the hydroxyl radicals generated on the anode.

4. Conclusions

Phenol could be readily mineralized at the Ti/SnO_2-Sb anode; however, its degradation was considerably slower at the Ti/RuO_2 and Pt anodes. The intermediate products of EC phenol degradation, including benzoquinone and organic acids, were subsequently oxidised rapidly by the Ti/SnO_2-Sb anode, but accumulated in the cells of Ti/RuO_2 and Pt. The surface property of the electrodes appeared to affect the kinetics of various steps of EC organic oxidation. More importantly, the anode could also mediate the pathway of organic degradation. Specific anode surface treatment such as the SnO_2-Sb coating provided the anode with an apparent catalytic function for rapid organic oxidation that was probably brought about by hydroxyl radicals generated from anodic water electrolysis. However, some anode materials, such as Ti/RuO_2 and Pt, were less favourable for use in the EC treatment of organic pollutants, because of their lack of the EC catalytic capacity and the production of intermediates more refractory to additional treatment. Based on the experimental study, a modified reaction pathway of EC phenol degradation was proposed. It is argued that under the electrocatalytic condition at the Ti/SnO_2-Sb anode the aromatic ring opening takes place rapidly. Maleic acid formed from ring cleavage can be oxidised directly to oxalic acid that can be readily mineralised by EC oxidation. However, at the Ti/RuO_2 and Pt anodes without significant catalytic functions, ring breakage becomes more difficult. The accumulation of intermediate aromatic compounds, such as hydroquinone and benzoquinone, will lead to the formation of more stable polymeric products. In addition, maleic acid will undergo a slow EC degradation process involving the formation of a number of intermediate organic acids, including succinic acid, malonic acid and acetic acid.

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