



Mechanism of the anodic oxidation of 4-chloro-3-methyl phenol in aqueous solution using Ti/SnO₂–Sb/PbO₂ electrodes

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ABSTRACT

Electrochemical oxidation of 4-chloro-3-methyl phenol (CMP) was examined using Ti/SnO₂–Sb/PbO₂ anodes. The physicochemical properties of the electrodes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. The degradation was studied by monitoring the total organic carbon (TOC) removal of CMP, and variation of the concentration of intermediates by high-performance liquid chromatography (HPLC), ion chromatography (IC) and gas chromatography/mass spectrometry (GC/MS). The mineralization of CMP is confirmed to be controlled by mass transfer or by both chemical reaction and mass transfer. Hydroxyl radicals ([•]OH) and active chlorine on the electrode surface had a dominant role in the electro-oxidation process. The chloride element in CMP was immediately driven away from parent substance by [•]OH attack, and then accelerated the ring cleavage of methyl-*p*-benzoquinone, which was formed during the anodic oxidation of CMP. Ultimately, the chlorine of CMP was mainly transformed to hypochlorite and chloride ion in aqueous solution. Additionally, formic acid and acetic acid were relatively stable products that were not electro-oxidized efficiently in our experiments. The degradation pathway of CMP is proposed on the basis of these results.

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1. Introduction

Electro-oxidation is in widespread use for the elimination of pollutants from water. Generally, the anodic oxidation process is dependent on the electrode material. Pt [1], carbon [2], boron-doped diamond (BDD) [3–5] and metal oxides such as PbO₂ [6–8], SnO₂ [8], RuO₂ [9], IrO₂ [10], and Ti–Ru–Sn ternary oxide are all in use as anodic materials [7]. PbO₂ and BDD, considered as “non-active” electrodes, are the most attractive electrodes because of their high oxygen overpotential. BDD anodes have the advantages of chemical and electrochemical stability, high current efficiency, long life, and a wide potential window for water discharge [11]. Nevertheless, the high cost and the difficulty of finding an appropriate substrate for deposition of a thin diamond layer limit the large-scale application of these electrodes. Tantalum, niobium and tungsten substrates are very expensive; and a silicon substrate is very brittle and has poor conductivity [12]. Recently, a PbO₂ anode has been considered to be practical for wide industrial applications.

PbO₂ is not expensive, the electrode is relatively easy to prepare, has low electrical resistivity, good chemical stability and has a large surface area [13]. Moreover, Ti/PbO₂ electrodes with a SnO₂ + Sb₂O₃ interlayer can increase the lifetime of the electrodes and the level of electrocatalytic activity [14].

The anode materials can influence the effectiveness of oxidation, degradation pathways and reaction mechanisms [15–18]. At the anode [18,19], the oxidation of organic pollutants may be attributed to (i) direct electrochemical oxidation on the anode surface, (ii) indirect electrochemical oxidation mediated by electrogenerated oxidants, such as peroxydisulfates (in the presence of SO₄²⁻) and active chlorine (in the presence of Cl⁻), and (iii) indirect electrochemical oxidation mediated by hydroxyl radicals [20–22]. Panizza and Cerisola [23] stated that the oxidation of synthetic tannery wastewater took place on the Ti/PbO₂ anode by direct electron transfer and indirect oxidation mediated by active chlorine. In contrast, Zhu et al. [22] suggested that at the Ti/SnO₂–Sb/PbO₂ anodes, hydroxyl radicals existed mainly as adsorbed hydroxyl radicals that reacted with organic molecules on the electrode surface.

Phenolic compounds are important contaminants that are discharged in wastewater streams from various industrial activities, such as coal conversion, wood preservation, foodstuff processing, metal casting and pulp and paper manufacturing [24]. Recently,

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anodic oxidation using dimensionally stable anodes (DSAs) has attracted a great deal of attention for the treatment of phenol-containing effluents, including olive mill wastewaters [10,25], textile wastewaters [26], and tannery wastewater [27].

Among the phenolic compounds, chlorinated phenols and cresols, which often occur in industrial wastewaters and solid waste leachates, are known to be toxic to humans as well as to aquatic life [28–31]. According to the mechanism involved in electro-oxidation of these chlorinated phenolic compounds, the evolution of chlorine is another problem. Many researchers have studied the dechlorination of chlorinated compounds [32–34]. Early studies reported that chloride was transformed into hypochlorite, which was either oxidized or combined with organic materials [8,20,35]. However, it was found that chloride ions were immediately driven away from 4-chlorophenol (PCP), and were not converted to hypochlorous acid (HClO) to oxidize organics [31]. Additionally, Iniesta et al. [6] showed that chloroform was the only halocompound detected at the end of the reaction in the electrochemical degradation of phenol when NaCl was present. Thus, adequate attention should be paid to the particular evolution of chlorine during the anodic oxidation process.

The biocide 4-chloro-3-methyl phenol (CMP) is a model pollutant representative of chloro-phenols frequently found in wastewater treatment plants and industrial landfill leachates [36]. To date, the mineralization of CMP by Fenton's reagent has been investigated [30], but the degradation of CMP by an electrochemical process has not been reported. In this work, the anodic oxidation of CMP using Ti/SnO₂-Sb/PbO₂ electrodes was investigated to explore the detailed mineralization site and evolution of the chlorine constituent of CMP, as well as the degradation pathway at a current density of 10 mA cm⁻².

2. Experimental

2.1. Reagents

All chemicals were of analytical grade and were used without purification. CMP was obtained from Shanghai Jingchun Medicine Co., Ltd. All other chemicals were purchased from Huadong Medicine Co., Ltd. All solutions were prepared with deionized, doubly distilled water.

2.2. Electrode preparation and characterization

Titanium plates (99.5%, 20 mm × 30 mm) were treated by the following procedures. The titanium sheets were degreased in absolute ethanol for 20 min, polished on 320-grit paper strips, and then etched in boiling aqueous 20% hydrochloric acid for 1 h, followed by thorough rinsing with deionized, doubly distilled water. The titanium substrate was now gray, and had lost the metallic sheen.

The SnO₂-Sb coating deposited onto the pretreated titanium substrate was prepared by electrodeposition of the inner coating layer and thermal deposition of the outer layer [37], which was used as substrate for the electrodeposition of PbO₂ films to improve the performance of the PbO₂ electrodes [16]. It should be noted that the electrode potential and electrodeposition time must be carefully controlled to ensure constant loading of PbO₂ during the electrodeposition process.

The surface morphology of the electrodes was characterized by X-ray diffraction (XRD, Thermo ARL SCINTAG X'TRA, 45 kV and 40 mA, Cu K α) and scanning electron microscopy (SEM, Philips XL-30). The XRD analysis (Fig. 1a) indicated that this PbO₂ was plattnerite. The morphology of the PbO₂ electrode was compact and presented a typical pyramid shape with an average grain size of ~8 μ m, as determined by SEM (Fig. 1b).

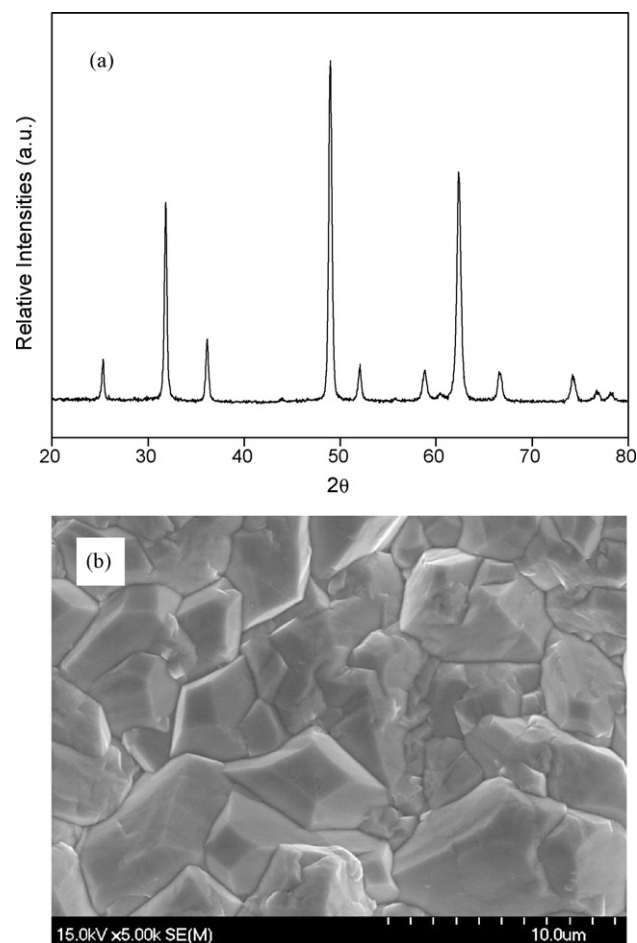


Fig. 1. XRD pattern (a) and SEM image (b) of the Ti/SnO₂-Sb/PbO₂ anode.

Cyclic voltammetry measurements were done at room temperature with a conventional three-electrode cell using a computer-controlled electrochemical workstation (CHI 660D, Shanghai Chenhua, China). The laboratory-made Ti/SnO₂-Sb/PbO₂ anode (10 mm × 10 mm) was used as the working electrode, a platinum sheet (15 mm × 20 mm) as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode in a separate compartment with a Luggin capillary.

To reduce the test time, the electrode stability was evaluated using the method of accelerated life test, which was done at a constant anodic current density of 1200 mA cm⁻² in a 9 M H₂SO₄ electrolyte at 90 °C. The potential of the working electrode was monitored periodically and the operational time at which the potential increased rapidly by 5 V above the initial value was taken to be the accelerated life of the electrode.

2.3. Bulk electrolysis

Electrochemical oxidation of CMP was done in a diaphragm cell with cooling jacket using a nickel foam substrate (99.2%, 20 mm × 30 mm) as the cathode, the Ti/SnO₂-Sb/PbO₂ electrode as the anode, and a Nafion-117 membrane as the cation exchange membrane. The distance between the anode and cathode was about 80 mm. A schema of the experimental setup is shown in Fig. 2. The anodic compartment held 80 mL of electrolyte containing 0.70 mM CMP and 0.25 M Na₂SO₄, which was stirred by a magnetic follower during the electrolysis process, while the cathodic compartment held 40 mL of 0.25 M Na₂SO₄. Electrolysis was done at a constant current density and temperature (25 ± 2 °C) for 8 h. Samples were

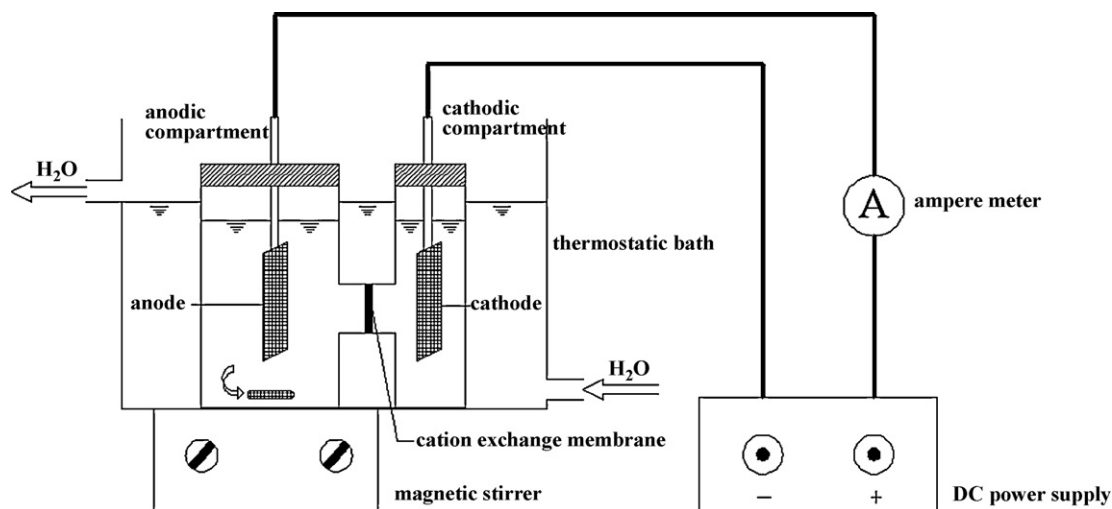


Fig. 2. Schema of the set-up used for the electrochemical oxidation of CMP.

collected from the anodic compartment at predetermined time-points for chemical analysis.

2.4. Analytical methods

The concentration of total organic carbon (TOC) was measured using a Shimadzu TOC-V_{CPH} analyzer. Chemical oxygen demand (COD) was measured by a titrimetric method using dichromate in an acidic solution as the oxidant [38]. On the basis of the COD values, the instantaneous current efficiency (ICE) was calculated as [39]

$$ICE = \frac{|(\text{COD})_t - (\text{COD})_{t+\Delta t}| FV}{8I\Delta t} \quad (1)$$

where $(\text{COD})_t$ and $(\text{COD})_{t+\Delta t}$ are the COD (mg L^{-1}) at times t and $t + \Delta t$ (s), respectively; F is the Faraday constant (96487 C mol^{-1}), V is the volume of the electrolyte (L), I is the current (A), and 8 is the equivalent mass of oxygen (g mol^{-1}).

The concentration of CMP and its degradation product methyl-*p*-benzoquinone in electrolyzed solutions were monitored with an Agilent 1200 Series high-pressure liquid chromatography system (HPLC) with an Eclipse XDBC-18 column ($150 \text{ mm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$ film thickness) and a DAD detector. The column temperature was 30°C . The concentration of CMP was determined by HPLC using a mobile phase of 1:1 (v/v) methanol/4% acetic acid at a flow rate of 0.5 mL min^{-1} . Acetonitrile/water/acetic acid (35:64:1, v/v/v) was used as the mobile phase at a flow rate of 0.5 mL min^{-1} to determine the concentration of methyl-*p*-benzoquinone. The UV detector was set at 280 nm , and the injection volume was $5 \mu\text{L}$.

Carboxylic acids, hypochlorite and chloride ions produced during electrolysis were analyzed with a Dionex model ICS 2000 ion chromatograph (IC) equipped with a dual-piston pump, a Dionex IonPac AS19 analytical column ($4 \text{ mm} \times 250 \text{ mm}$), an IonPac AG19 guard column ($4 \text{ mm} \times 250 \text{ mm}$), and a Dionex DS6 conductivity detector. Suppression of the eluent was achieved with a Dionex anion ASRS electrolytic suppressor (4 mm) in the autosuppression external water mode.

A Varian cp3800 gas chromatograph with a Varian Saturn 2000 mass spectrometer (GC/MS) was used to identify the reaction products. A wall coated open tubular (WCOT) fused silica series column ($30 \text{ m} \times 0.25 \text{ mm}$, $0.25 \mu\text{m}$ film thickness) was used and the temperature was held at 100°C for 1 min, then increased at a rate of $10^\circ\text{C min}^{-1}$ to 250°C , and held at that temperature for 25 min. The other experimental conditions were: EI impact ionization 70 eV , carrier gas helium, injection temperature 280°C , and source temperature 100°C .

3. Results and discussion

3.1. Voltammetry measurements

Fig. 3 shows the cyclic voltammograms of the Ti/SnO₂-Sb/PbO₂ electrode in the solution with/without 0.70 mM CMP. During one cyclic sweep, an anodic current peak at $\sim 1.35 \text{ V}$ and a cathodic current peak at $\sim 0.90 \text{ V}$ were observed in a blank solution, representing the oxidation and reduction of Pb(IV)/Pb(II)/Pb(0) couples [40,41]. There was no significant effect on the shape of the cyclic voltammogram when CMP was added to the blank solution, meaning that the direct electron transfer did not occur in the process of oxidation. Thus, the degradation must be caused by indirect electrochemical oxidation.

3.2. Electrode stability

Good stability is an important attribute to be considered in the choice of an electrode. An accelerated life test was used to evaluate electrode stability, and the results showed that the laboratory-prepared electrode was stable for about 175 h under accelerated conditions. However, the real lifetime of the electrode would be much longer and would rely on the test conditions, including

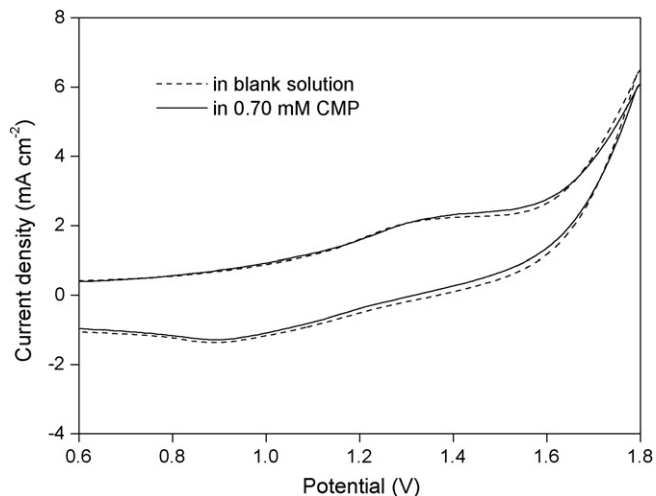


Fig. 3. Cyclic voltammograms of the Ti/SnO₂-Sb/PbO₂ electrode at a scan rate of 50 mV s^{-1} .

current density, pH and temperature of the electrolyte. A rough estimation was derived from the method described by Hine et al. [42], which gives a simple relationship between the electrode service life (SL) and the current density (i) [18,42]:

$$SL \sim \frac{1}{i^n} \quad (2)$$

where n ranges from 1.4 to 2.0. Given that n is equal to an average of 1.7 for the electrode, its service life with a current density of 100 mA cm^{-2} in strongly acidic solutions was estimated to be approximately 1.6 years.

3.3. Preliminary analysis of process dynamics

The effect of a specific electrical charge on the TOC reduction of CMP is shown in Fig. 4. The mineralization efficiency increased with the increase of specific electrical charge. Also, no obvious improvement in TOC removal was found when compared with the mineralization results for the current densities of 20 and 30 mA cm^{-2} . Therefore, the optimal current density for our experiments was 10 mA cm^{-2} . On the basis of these results for current density optimization, the effect of the initial concentration of CMP (0.70–3.50 mM) on TOC removal using Ti/SnO₂-Sb/PbO₂ anodes at a current density of 10 mA cm^{-2} was investigated and the results are shown in Fig. 5. Interesting results were obtained at the Ti/SnO₂-Sb/PbO₂ electrode. It was evident that the removal efficiency of TOC increased with increasing initial concentration of CMP and reached the highest value when the initial concentration of CMP was 2.10 mM, and then decreased. Generally, the overall steps for degradation of organic compounds principally involve mass transport of organic compounds from the bulk of the solution toward the surface of the anode, adsorption of organic compound onto the catalytic sites of the anode, and the reaction between hydroxyl radical and adsorbed organic molecules [43].

The Ti/SnO₂-Sb/PbO₂ anode, considered as a “non-active” electrode, does not participate in the direct anodic reaction of organics and does not provide any catalytic active site for their adsorption from the aqueous medium [44]. In this regard, it is unreasonable that the mineralization of CMP was controlled by the adsorption process. To explore the rate-limiting step, the inset in Fig. 5 shows the amount of TOC removal as a function of the electrolytic oxidation time at different initial concentrations of CMP (0.70–3.50 mM) using Ti/SnO₂-Sb/PbO₂ anodes at a current density of 10 mA cm^{-2} . At various time-points, the results show that the removal of TOC

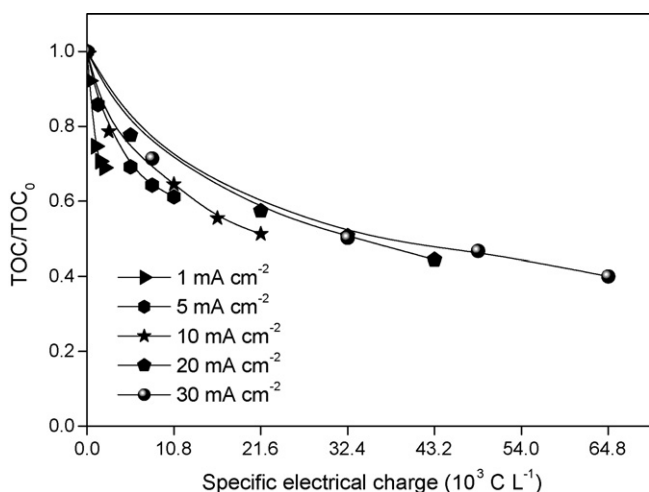


Fig. 4. Effect of current density on TOC removal with the initial concentration of CMP of 0.70 mM.

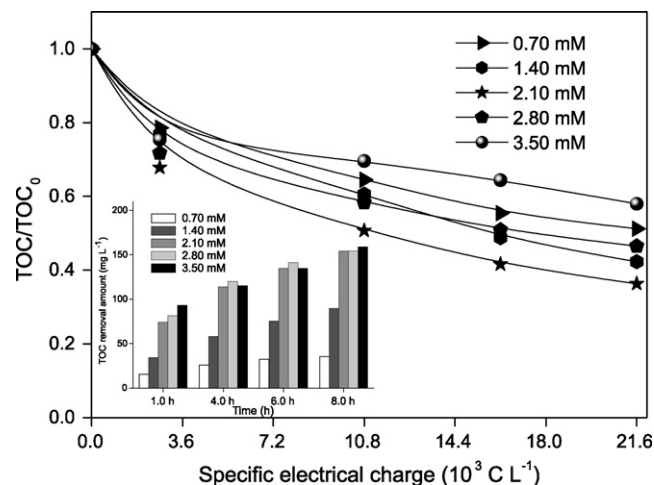


Fig. 5. Effect of the initial concentration of CMP on TOC/TOC₀ and the amount of TOC removal (inset).

increased as the concentration increased from 0.70 to 2.10 mM, and an invariant could be obtained in later stages (i.e. at higher concentrations), which meant that the overall process was not controlled by chemical reaction. In addition, as mentioned above (Fig. 4), the mineralization efficiency increased sharply at first and then slowly with increasing current density, suggesting that the mass transfer could not be neglected in our experiments. In other words, the mineralization of CMP was controlled by mass transfer, or at least, by the combination of mass transfer and chemical reaction.

Fig. 6 shows the COD- and TOC-time curves for anodic oxidation of 0.70 mM CMP at a current density of 10 mA cm^{-2} . The TOC disappearance is always less than the COD reduction, reflecting the fact that the reaction by-products are resistant to degradation. According to the COD values, the variation of ICE with reaction time is shown in the Fig. 6inset. The ICE for the Ti/SnO₂-Sb/PbO₂ anode decreased dramatically from 20% at 1 h to 6.5% at 8 h, demonstrating that the intermediates are much more difficult to oxidize during the electrochemical treatment. Combined with the intermediate anions identified in Fig. 7, we conclude that this anode was more suitable for decomposition of CMP than other organic acids.

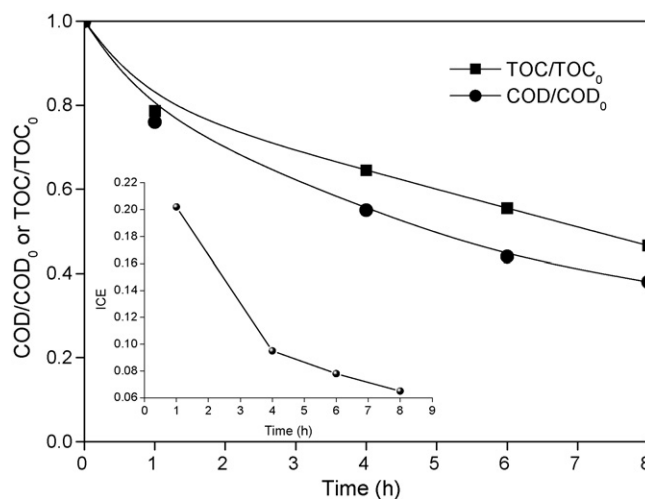


Fig. 6. The COD- and TOC-time curves for anodic oxidation of CMP and the variation of ICE for the Ti/SnO₂-Sb/PbO₂ electrode (inset).

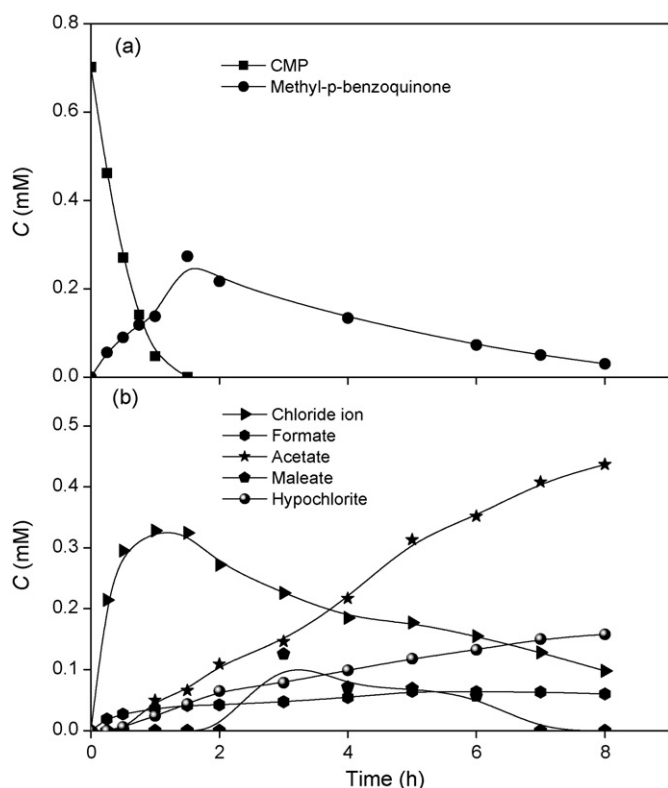


Fig. 7. Variation of the concentration of related organic intermediates and anions during CMP degradation detected by HPLC (a) and IC (b).

3.4. Identification of the reactive species

To discriminate the actual reactive species mediated in the process, iodide ion was used to scavenge hydroxyl radicals [45]. The TOC removal of CMP was strongly inhibited in the presence of KI (7.0 mM), as shown in Fig. 8. This result indicates that electrogenerated oxidants on the anode surface rather than direct electrochemical oxidation has a dominant role for TOC removal. Additionally, peroxydisulfates ($S_2O_8^{2-}$) can be formed in the presence of sulfates (SO_4^{2-}), and some of them can be decomposed to hydrogen peroxide and other oxidants [46]. However, when 0.25 M Na_3PO_4 instead of 0.25 M Na_2SO_4 was used as the supporting

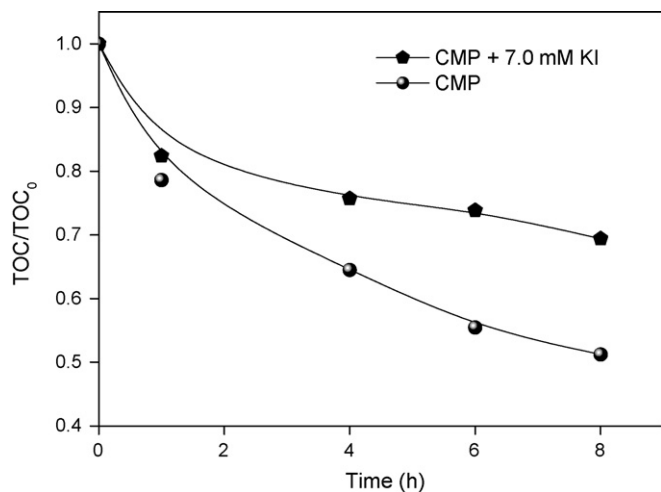


Fig. 8. Effect of iodide ions on TOC removal with the initial concentration of CMP of 0.70 mM at a current density of 10 mA cm^{-2} .

electrolyte in electrochemical oxidation of CMP in a separate experiment, no obvious difference of TOC removal could be observed (data not shown). This behavior indicated that the electrogenerated oxidants formed by SO_4^{2-} should not be responsible for TOC removal. Since only outer-sphere reactions and water oxidation are possible with this kind of anode [44], hydroxyl radicals produced from water discharge and active chlorine are subsequently involved in the TOC removal of CMP. But it is important to note that chlorine driven away from CMP could accelerate the ring cleavage of methyl-*p*-benzoquinone formed during the anodic oxidation, which will be discussed below.

3.5. Fate of the chlorine in CMP

The substrate removal efficiency (complete removal after 90 min reaction) was greater than the TOC removal efficiency (~49% removal after 8 h reaction) for 0.7 mM CMP in the electrolysis system, which indicated that part of the substrate was degraded to soluble intermediates rather than oxidized completely to CO_2 and H_2O [47]. Additionally, electron-withdrawing groups such as element chlorine are expected to interact with active species in an end-on manner due to electrostatic attraction between the head-group and the positive charge on the anode surface. Thus, the disappearance rate of CMP should be faster than that of PCP, since methyl, as an electron-donating group, would further increase the electron density on the *ortho*-chlorine substituent, and consequently enhance the interaction between chlorine and hydroxyl radicals. The results shown in Fig. 9 confirmed the above deduction. In this way, in the anodic oxidation of CMP, the first step was the release of the chloride ion from the aromatic ring to form phenolics or quinones. As for the dechlorination mechanism, in previous studies dealing with other chloro-phenolics, it was usually suggested that the predominant chlorine removal mechanism was the hydroxyl substitution on the phenolic ring structure (*ipso*-substitution) [30,48]. Our results were in accordance with this fact, as discussed above.

To elucidate the evolution of the chlorine and to propose the degradation pathway of CMP, the evolution of the main intermediates during the anodic oxidation of CMP was detected by HPLC and IC (Fig. 7). The existence of some intermediates was further confirmed by GC/MS (Table 1). After dechlorination, the primary product formed during the anodic oxidation was methyl-*p*-benzoquinone, which reached a peak concentration at about 90 min and then began to decrease. The quinone structure formed

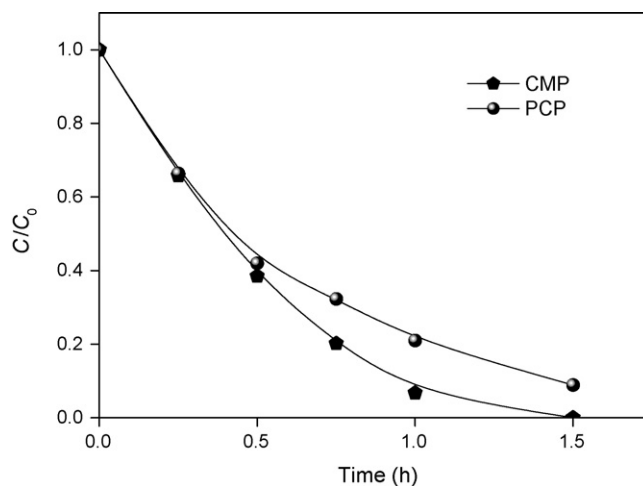
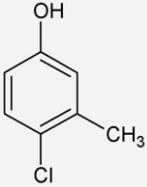
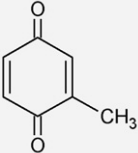



Fig. 9. Comparison of anodic oxidation of CMP and PCP using $Ti/SnO_2-Sb/PbO_2$ as the electrode at a current density of 10 mA cm^{-2} .

Table 1Intermediates identified by GC/MS: initial concentration of CMP 0.70 mM; current density 10 mA cm⁻²; temperature 25 °C.

Symbol	Compounds	Structural formula	Sample time (min)				
			15	30	60	240	480
D ₁	4-Chloro-3-methyl phenol		✓	✓	✓		
D ₂	2-Methylbenzo-1,4-quinone		✓	✓	✓	✓	
D ₃	(2Z)-But-2-enedioic acid				✓	✓	✓
D ₄	Acetic acid	CH ₃ COOH		✓	✓	✓	✓

was much more stable than CMP itself [49], which was consistent with the results shown in Fig. 10a. It was shown that methyl-*p*-benzoquinone was removed completely after 6 h, and the addition of 0.7 mM NaCl promoted the removal of methyl-*p*-benzoquinone significantly, indicating that chloride ions can accelerate the ring cleavage. The anodic reaction of chloride ions first formed chlorine molecules and/or hypochlorite ions [23,50], and then attacked the C–C bonds leading to the ring cleavage of methyl-*p*-benzoquinone.

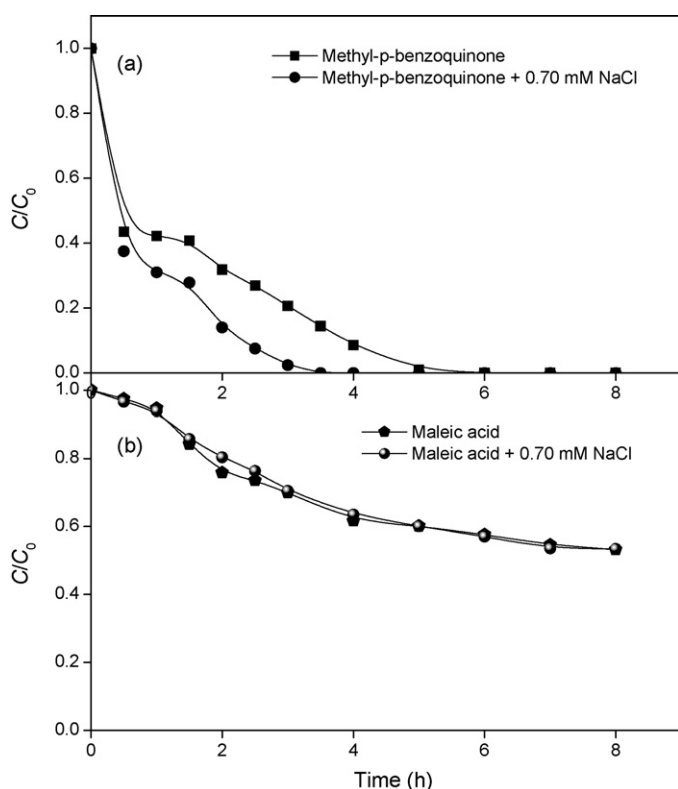


Fig. 10. Effect of chloride ions on the removal of 0.70 mM methyl-*p*-benzoquinone (a) and 0.70 mM maleic acid (b).

Afterward, smaller organic acid molecules were generated, as shown in Fig. 7. The concentration of maleic acid began to increase at 2 h, reached a peak at about 3 h, and then decreased. The removal of residual organic compounds might also be promoted by the formation of hypochlorite ions in the final part of the electrolysis [30]. Hence, the effect of chloride ions on the removal of maleic acid was investigated. In contrast to previous reports, the result (Fig. 10b) showed that the addition of NaCl had little effect on the degradation of maleic acid.

As shown in Fig. 7, hypochlorite was detected in aqueous solution throughout the electrolysis of CMP, which was formed mainly by the anodic oxidation of chloride ion. Eventually, after a reaction time of 8 h, ~14% of the elemental Cl was transformed to Cl⁻, and ~23% was translated into hypochlorite. In this case, the total content of Cl⁻ and hypochlorite accounted for ~37% of the initial chlorine in CMP, which may be ascribed to the fact that some of the chlorine would have been degassed gradually in the form of chlorine gas and/or chloroform [20].

3.6. Degradation pathway of CMP

On the basis of the results presented above, a proposed pathway of CMP (D₁) degradation is shown in Fig. 11. Chlorine atoms were released from the aromatic ring preferentially by indirect electrochemical oxidation to form benzene derivatives such as S₁, which could react with hydroxyl radicals and yield the aromatic by-product methyl-*p*-benzoquinone (D₂). The C–C bonds of compound D₂ were cleaved by the action of •OH, chlorine and/or hypochlorite ions to form carboxylic acids such as butene diacid (D₃) and formic acid (D₅, detected by IC). D₃ could be further oxidized by •OH, yielding acetic acid (D₄) and oxalic acid (S₂). D₄ and D₅ remained in solution and could not be oxidized easily under the experimental conditions used in this work, which was verified by the concentration variation during 8 h electrolysis as shown in Fig. 7. S₂ was not converted into D₅ but was oxidized directly to carbon dioxide and water without the accumulation of other stable organics. This was supported by the fact that D₅ and other intermediates were not detected by IC during the anodic oxidation of S₂ in a separate experiment.

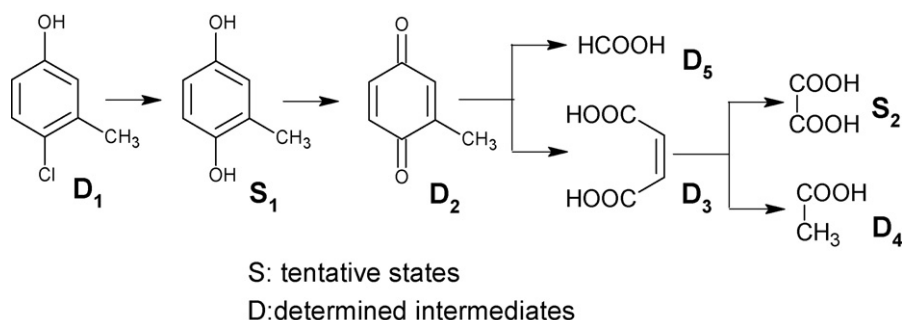


Fig. 11. Possible degradation pathway of CMP at the Ti/SnO₂-Sb/PbO₂ anodes.

Taking the mass balance of the carbon into account, we compared the TOC estimation derived from the intermediates detected by HPLC and IC with that detected by the TOC analyzer. The results indicated that approximately 50% of the carbon-containing substances were not identified. Thus, further work is required to identify more details of the mechanism.

4. Conclusion

Electrochemical oxidation using a Ti/SnO₂-Sb/PbO₂ anode appears to be an attractive alternative for the mineralization of CMP. More work is needed to determine accurately the mechanisms involved in the degradation process reported here. We believe that with further investigation and improvement this electrode will be worthy of further application in the degradation of other chlorinated phenols and cresols in wastewater.

Acknowledgments

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