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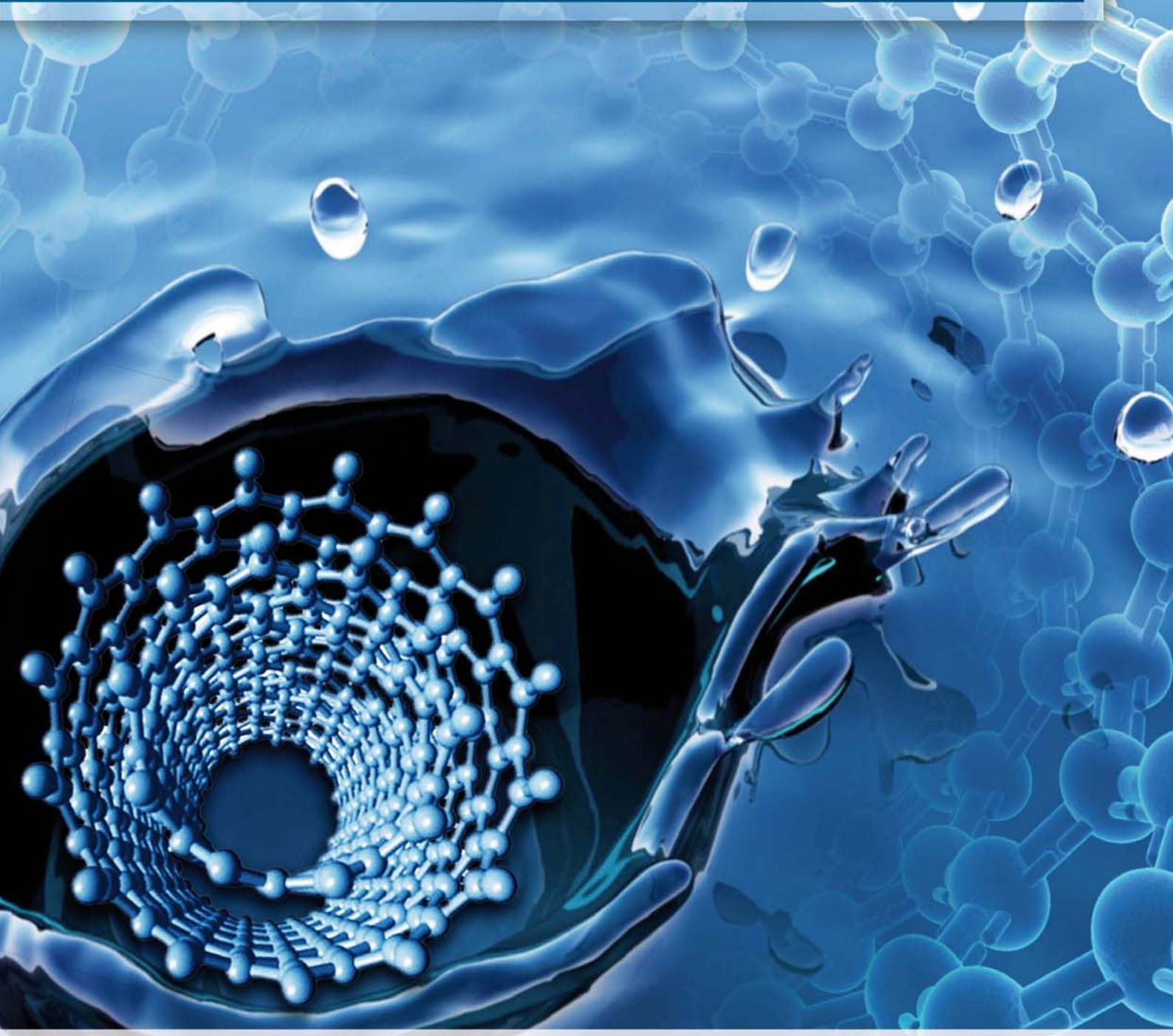

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# A high activity of Ti/$SnO_2$-Sb electrode in the electrochemical degradation of 2,4-dichlorophenol in aqueous solution

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**Abstract**

Electrochemical degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution was investigated over Ti/$SnO_2$-Sb anode. The factors influencing the degradation rate, such as applied current density (2–40 mA/cm$^2$), pH (3–11) and initial concentration (5–200 mg/L) were evaluated. The degradation of 2,4-DCP followed apparent pseudo first-order kinetics. The degradation ratio on Ti/$SnO_2$-Sb anode attained > 99.9% after 20 min of electrolysis at initial 5–200 mg/L concentrations at a constant current density of 30 mA/cm$^2$ with a 10 mmol/L sodium sulphate ($Na_2SO_4$) supporting electrolyte solution. The results showed that 2,4-DCP (100 mg/L) degradation and total organic carbon (TOC) removal ratio achieved 99.9% and 92.8%, respectively, at the optimal conditions after 30 min electrolysis. Under this condition, the degradation rate constant ($k$) and the degradation half-life ($t_{1/2}$) were 0.21 min$^{-1}$ and (2.8 ± 0.2) min, respectively. Mainly carboxylic acids (propanoic acid, maleic acid, propanedioic acid, acetic acid and oxalic acid) were detected as intermediates. The energy efficiencies for 2,4-DCP degradation (5–200 mg/L) with Ti/$SnO_2$-Sb anode ranged from 0.672 to 1.602 g/kWh. The Ti/$SnO_2$-Sb anode with a high activity to rapid organic oxidation could be employed to degrade chlorophenols, particularly 2,4-DCP in wastewater.

**Key words**: 2,4-dichlorphenol; Ti/$SnO_2$-Sb electrode; electrochemical degradation; total organic carbon
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## Introduction

Chlorophenols are a group of toxic organic compounds used as wood preservatives, antirusting agents and pesticides, listed by the United States Environmental Protection Agency (US EPA) as priority pollutants (Keith et al., 1979). As a kind of intermediate of chloro-pesticides, 2,4-dichlorophenol (2,4-DCP) has dreadful toxicity and is extremely harmful to human and animal's endocrine system (Topalov et al., 2000; Zhang et al., 2005). Recently, various types of methods have been designed to remove 2,4-DCP from wastewater, such as physical, chemical and microbial methods. However, because of high toxicity and low endurable concentration, it is difficult to remove 2,4-DCP completely to match the standard environmental consent. Lately, advanced oxidation processes (AOPs) have been considered as leading processes in wastewater treatment for their high degradation efficiency to oxidize organic contaminants by the generation of hydroxyl radicals (·OH). The AOPs, including photoelectrocatalysis (Qu and Zhao, 2008), UV (Ultraviolet)/Fenton (Du et al., 2005), photocatalysis and catalytic ozonation (Gu et al., 2010; Lei et al., 2007) etc., are radical based oxidation processes. They have received significant awareness in wastewater treatment.

Among the various AOPs, electrochemical technology over the last decades is proved to be of greater advantage due to its powerful oxidative capability, amenability to automation, environmental compatibility, and cost effectiveness to degrade toxic or biorefractory organic pollutants (Rajeshwar and Ibanez, 1997; Panizza, 2010; Niu et al., 2012; Lin et al., 2012, 2013). In the electrochemical treatment, electrodes with high stability, high activity, and low cost are important for a successful organic oxidation process (Rodrigo et al., 2001; Flox et al., 2009). The composition and structure of coatings on the electrode surface are the main factors that affect the electro-catalytic characteristics and stability of electrodes. A few experiments have been conducted regarding efficiency of the electrode in electrochemical degradation of phenolic compounds particularly 2,4-DCP. Previous reports indicated that phenolic compounds could be degraded over BDD-

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$TiO_2$, Ti/$IrO_2$, Ti/$RuO_2$, Pt and Ti/$SnO_2$-Sb electrodes. The reaction mechanism was supposed to be electron transfer from 2,4-DCP to BDD-$TiO_2$ and Ti/$SnO_2$-Sb anode. However, other anodes including Ti/$IrO_2$, Ti/$RuO_2$ and Pt were found to be unable to remove 2,4-DCP from aqueous solution (Comninellis, 1994; Feng and Li, 2003; Qu and Zhao, 2008). Although the BDD-$TiO_2$ electrode has better performance of chemical and electrochemical stability, long life, and high oxygen evolution potential, its high cost and mainly the difficulties to find a suitable substrate for depositing the diamond layer limit the large-scale application of the BDD electrode (Qu and Zhao, 2008; Panizza and Cerisola, 2009). Recently, dimensionally stable anodes, typically titanium including different coating, are found to have a varying degree of success. However, traditional electrodes, such as graphite and nickel, also show a poor current efficiency in organic degradation (Rodgers et al., 1999). Especially Sb doped Ti-based $SnO_2$ anode, $SnO_2$-Sb, has many advantages, such as cost efficiency, easy preparation, long life time and high oxygen evolution over-potentials (Schümann and Gründler, 1998; Polcaro et al., 1999; Comninellis and Pulgarin, 1993; Adams et al., 2009), which has been widely used in industrial and pharmaceutical applications.

In the present study, the influencing factors including initial concentration, current density and initial pH were assessed for 2,4-DCP degradation in aqueous solution. Removal of total organic carbon (TOC) and the degradation intermediates were determined in the electrochemical degradation process. The energy efficiency and the activity of the model electrode (Ti/$SnO_2$-Sb) was also focused during the degradation of 2,4-DCP.

## 1 Materials and methods

### 1.1 Reagents

Analytical grade 2,4-DCP was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH), ammonium acetate ($CH_3COONH_4$), and perchloric acid ($HClO_4$) were obtained from Sinopharm (Beijing, China). Sodium sulfate ($Na_2SO_4$) was used as support electrolyte. Water used in the experiments was ultrapure. The pH of solution was adjusted to desired range by using diluted hydrochloric acid (HCl) or NaOH.

### 1.2 Preparation of Ti/$SnO_2$-Sb electrode and characterization

The electrode was prepared from 1.0 mm thickness genuine titanium plates with 12 cm × 5 cm dimensions. The plates were treated with NaOH solution (5%, *m*/*m*) followed by oxalic acid (10%, *m*/*m*) to make uniform surface roughness. According to previous report (Lin et al., 2012), Ti/$SnO_2$-Sb electrode was prepared by a slightly modified sol-gel technique. Ethylene glycol was merged with citric acid and agitated at 60°C until full dissolution, and the solution was then heated to 90°C with continuous stirring. Proper combination of $SnCl_4{\cdot}4H_2O$ and $SbCl_3$ was added to the solution at the molar ratio of 140:30:9:1 for citric acid:ethylene glycol:$SnCl_4{\cdot}4H_2O$:$SbCl_3$. The above solution was maintained at 90°C for 30 min to attain sol-gel. Then, the complete solution was uniformly applied to coat the surface of Ti plates followed by dip-coating method. Finally, Ti plates were dried at 140°C in an oven and then sintered for the coating thermal decomposition at 500°C for 10 min in a muffle furnace. The above process was repeated 24 times, and the electrode films were ultimately annealed for 2 hr at 500°C. To characterize the above electrode in our experiments, scanning electron microscopy (SEM; S4800, Hitachi, Japan) study was employed.

### 1.3 Electrochemical experiments

Electrochemical properties of the electrodes were measured by CHI 660D electrochemical workstation with a conventional three-electrode cell (Shanghai Chenhua Instrument Co. Ltd., China). The observable electric potential (OEP) of the electrode was measured with the linear sweep voltammetry (LSV) technique in 0.5 mol/L $H_2SO_4$ solution.

Electrochemical cell used in this study was made up of organic glass, Ti/$SnO_2$-Sb electrode used as anode, and Ti electrode (dimensions: 12 cm × 5 cm; thickness: 1 mm) used as cathode. Both the anode and cathode were a projected electrode surface area of 60 $cm^2$. To investigate the influencing parameters, exactly a volume of 25 mL of 2,4-DCP solution was used to conduct the electrochemical experiments including the effects of pH, current intensity and different 2,4-DCP concentrations. However, these parameters were changed in the corresponding condition experiments. In the effect of pH, the solution was adjusted from 3.0 to 11.0. The solution pH was determined by a microprocessor pH meter (pH211; Eutech Co., USA). The electric current was provided by a DC power supply with constant current control mode. At first, the initial 2,4-DCP concentration (5, 10, 50, 100 and 200 mg/L) was investigated using this electrochemical setup. Constant plate distance (0.5 cm) was adopted for all the experiments and each sample containing 25 mL of 2,4-DCP and $Na_2SO_4$ (10 mmol/L) solution in a quartz reactor for better analysis.

### 1.4 Analytical techniques

The concentration of 2,4-DCP was determined by a high performance liquid chromatography (HPLC; Ultimate 3000, USA). The separation was carried out by a reversed phase column (C18 column) at the flow rate of 1 mL/min and column temperature of (30 ± 2)°C. TOC in aqueous solution was observed by Analyzer multi N/C UV (Analytic Jena, Germany) according to the 800°C combustion catalytic oxidation method. TOC removal ratio (*R*) was

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then calculated as follows:

$$R = (1 - C_{TOC}/C^0_{TOC}) \times 100\% \quad (1)$$

where, $C_{TOC}$ and $C^0_{TOC}$ (mg/L) are the value of TOC in aqueous solution and initial TOC value of 2,4-DCP, respectively.

Intermediate products from the degradation of 2,4-DCP were examined by gas chromatography-mass spectrometry (GC-MS; QP2010SE; Shimadzu, Japan) equipped with a DB-5 column (30 m × 0.25 mm ID, 0.25 μm film thickness) (J&W, USA). The ion source temperature was 230°C. The injector temperature was set at 280°C. Helium was served as carrier gas at a constant flow of 1.0 mL/min (He, 99.999%).

## 2 Results and discussion

### 2.1 Characterization

Ti/$SnO_2$-Sb electrode was characterized by a scanning electron microscope (SEM; S4800, Hitachi, Japan). The related SEM photograph is shown in **Fig. 1**. The results showed the presence of spherical smooth objects coated by sol-gel and randomly arranged over the Ti/$SnO_2$-Sb electrode. The size of the particle was in the range of 5 μm. The result in **Fig. 1** also showed an identical surface morphology of the plate which influences a uniform degradation of 2,4-DCP.

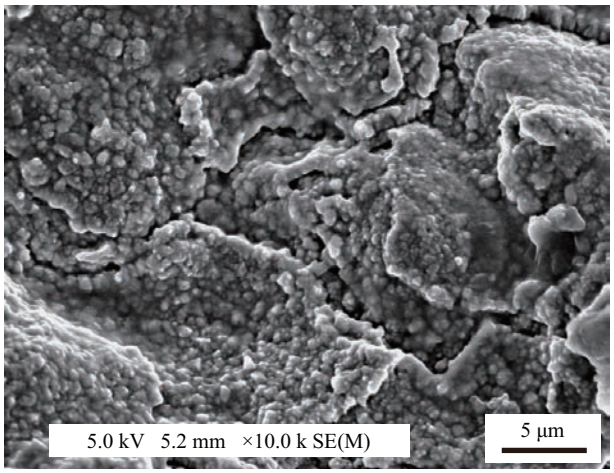


**Fig. 1** SEM pattern and the particle size of Ti/$SnO_2$-Sb electrode.

### 2.2 Effect of initial 2,4-DCP concentration

As shown in **Fig. 2**, the degradation ratio of initial 2,4-DCP concentrations (5–200 mg/L) achieved > 99.9%, after 20 min electrolysis, indicating that the Ti/$SnO_2$-Sb electrode has a powerful performance at the different ranges of concentration in the electrochemical process. However, the degradation rate constants ($k$) were 0.21 and 0.26 $min^{-1}$ for 2,4-DCP initial concentrations of 100 and 200 mg/L, respectively, and the respective half-life ($t_{1/2}$) values were (2.8 ± 0.2) and (2.3 ± 0.1) min (**Table 1**).

As shown in **Table 1**, the pH value of the solution decreased significantly after electrolysis. Previous report found that the sharp decrease of pH was apparently caused by the formation of acidic substances from the phenol degradation (Comninellis, 1994; Feng and Li, 2003; Comninellis and Pulgarin, 1993). However, our results signified that the concentration of acidic substances generated by 2,4-DCP degradation had slightly effect on the change of solution pH value.

### 2.3 Effect of initial pH

The effect of initial pH values ranging from 3 to 11 on 2,4-DCP degradation is shown in **Fig. 3**. A high degradation efficiency (99.9%) was observed at all pH conditions after 20 min electrolysis. The $k$ value at initial pH of 3 ($k$, 0.31 $min^{-1}$) was about 2 times higher than that at pH 11 ($k$, 0.18 $min^{-1}$), and the respective $t_{1/2}$ value ranged from (1.9 ± 0.1) to (3.3 ± 0.1) min, indicating that the degradation process was more favorable in acidic solution. It has also been reported that the decreasing pH value increases the

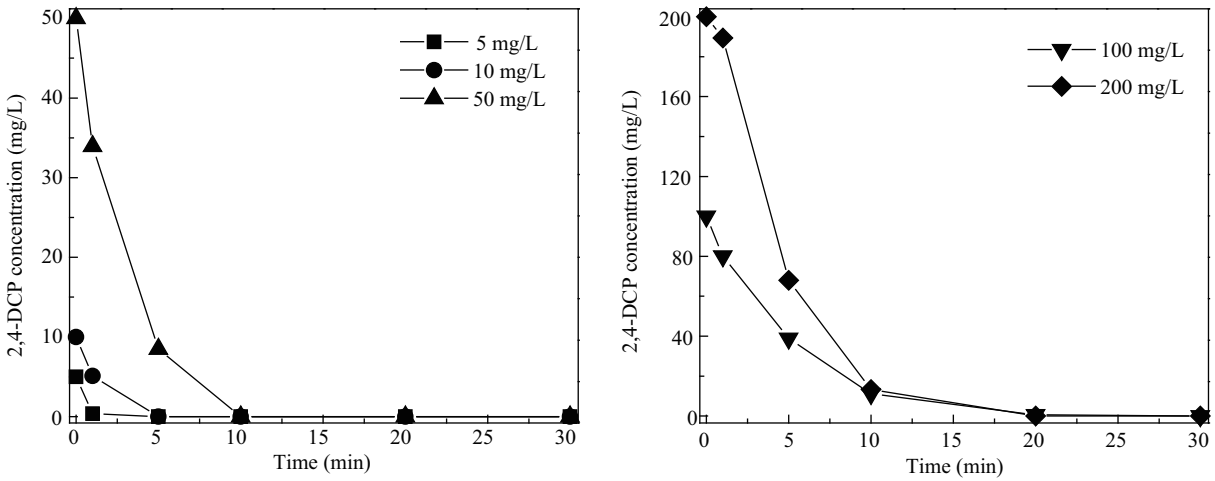


**Fig. 2** Concentration of 2,4-DCP varies as a function of electrolysis time at initial concentrations of 5, 10, 50, 100 and 200 mg/L. Conditions: initial pH value was 6; constant current density 30 mA/$cm^2$; plate distance 0.5 cm; 10 mmol/L $Na_2SO_4$ at room temperature. $n$ = 3, error bars negligible.

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**Table 1** Electrochemical degradation of 2,4-DCP over Ti/$SnO_2$-Sb electrode at different experimental parameters

| Parameter | | Reaction time ($t$, min) | Removal rate (%) | Initial-final pH during reaction | Rate constant ($k$, $min^{-1}$) | Half-lives ($t_{1/2}$, min) | $R^2$ |
|---|---|---|---|---|---|---|---|
| Initial concentration ($C_0$, mg/L) | 5 | 1 | > 99.9 | 6.0–4.6 | – | – | – |
| | 10 | 5 | > 99.9 | 6.0–4.3 | – | – | – |
| | 50 | 10 | > 99.9 | 6.0–3.6 | – | – | – |
| | 100 | 20 | > 99.9 | 6.0–4.1 | 0.21 | 2.8 ± 0.2 | 0.990 |
| | 200 | 20 | > 99.9 | 6.0–3.4 | 0.26 | 2.3 ± 0.1 | 0.971 |
| pH ($C_0$ = 100 mg/L and 30 mA/$cm^2$) | 3.0 | 20 | > 99.9 | 3.0–2.6 | 0.31 | 1.9 ± 0.1 | 0.978 |
| | 5.0 | 20 | > 99.9 | 5.0–2.8 | 0.24 | 2.5 ± 0.1 | 0.978 |
| | 7.0 | 30 | > 99.9 | 7.0–3.0 | 0.08 | 7.2 ± 0.2 | 0.997 |
| | 9.0 | 20 | > 99.9 | 9.0–3.4 | 0.20 | 2.9 ± 0.1 | 0.997 |
| | 11.0 | 20 | > 99.9 | 11.0–10.3 | 0.18 | 3.3 ± 0.1 | 0.966 |
| Current density (mA/$cm^2$) ($C_0$ = 100 mg/L) | 2 | 30 | > 99.9 | 5.8–3.3 | 0.15 | 4.0 ± 0.1 | 0.915 |
| | 5 | 20 | > 99.9 | 5.8–3.0 | 0.16 | 3.6 ± 0.1 | 0.993 |
| | 10 | 20 | > 99.9 | 5.8–2.9 | 0.22 | 2.6 ± 0.1 | 0.987 |
| | 30 | 20 | > 99.9 | 5.8–3.1 | 0.31 | 1.9 ± 0.1 | 0.945 |
| | 40 | 20 | > 99.9 | 5.8–3.0 | 0.31 | 1.9 ± 0.1 | 0.914 |

Supporting electrolyte ($Na_2SO_4$) concentration 10 mmol/L.

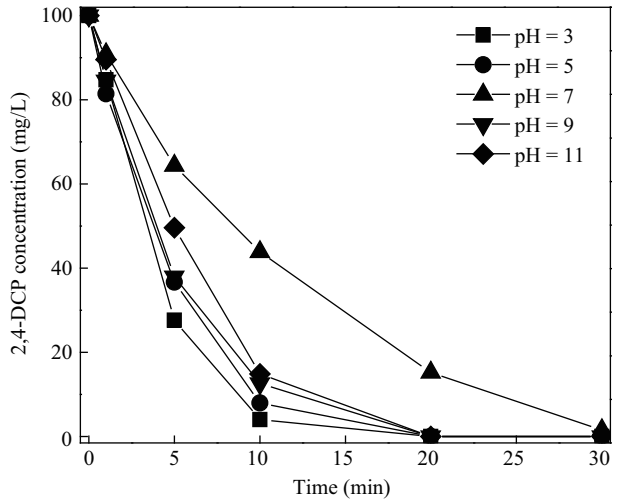


**Fig. 3** Concentration of 2,4-DCP (100 mg/L) varies as a function of electrolysis time at initial pH value of 3, 5, 7, 9 and 11. Conditions: plate distance 0.5 cm; constant current density 30 mA/$cm^2$; 10 mmol/L $Na_2SO_4$ at constant room temperature. $n$ = 3, error bars negligible.

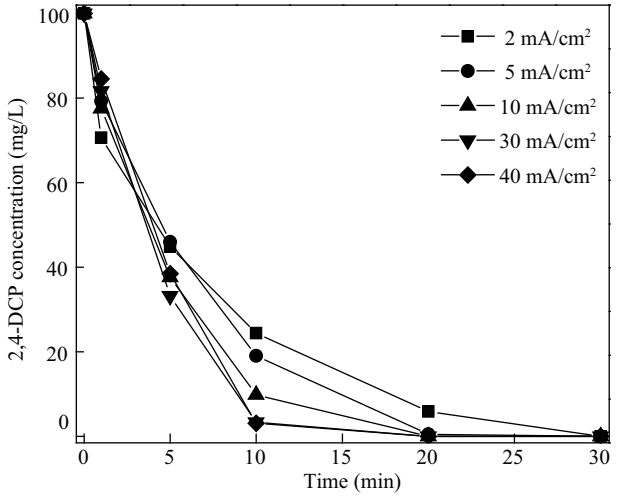


**Fig. 4** Concentration of 2,4-DCP (100 mg/L) varies as a function of electrolysis time at constant current densities of 2, 5, 10, 30 and 40 mA/$cm^2$. Conditions: plate distance was 0.5 cm; initial pH value 5.8; 10 mmol/L$Na_2SO_4$ at room temperature. $n$ = 3, error bars negligible.

oxygen over-potential (Zhao et al., 2007; Zhou et al., 2005). Therefore, at pH of 3, the low pH value inhibits the oxygen evolution reaction, leading to the enhancement of 2, 4-DCP degradation efficiency to some extent.

### 2.4 Effect of current density

The electron transfer potential and hydroxyl radical generation may govern the 2,4-DCP degradation efficiency in aqueous solution. However, the above abilities, particularly hydroxyl radical generation merely depends on the applied current density. The effect of applied current density (2–40 mA/$cm^2$) on the degradation rates of 2,4-DCP (100 mg/L) by Ti/$SnO_2$-Sb anode was investigated. **Figure 4** depicts that the degradation rate of 2,4-DCP increases with the increasing applied current density. The degradation rate of 2,4-DCP achieved > 99.9% at applied current densities of 5, 10, 30 and 40 mA/$cm^2$ after 20 min electrolysis. The reaction followed pseudo first-order kinetics. The $k$ values of 2,4-DCP degradation were 0.15 to 0.31 $min^{-1}$ for the current density of 2–40 mA/$cm^2$, respectively, and the corresponding $t_{1/2}$ values varying from (4.0 ± 0.1) to (1.9 ± 0.1) min are shown in **Table 1**. In addition, the TOC removal ratio attained 92.8% at 30 mA/$cm^2$ with the energy efficiency of 0.744 g/kWh, suggesting the efficiency of 2,4-DCP degradation over Ti/$SnO_2$-Sb anode is relatively high.

### 2.5 Energy efficiency

The energy efficiency and corresponding electrolysis time in the electrochemical degradation of 2,4-DCP (5–200 mg/L) over Ti/$SnO_2$-Sb anode are depicted in **Table 2**. The energy efficiency in the electrochemical degradation process varies from 0.672 to 1.602 g/kWh at 5–200 mg/L initial concentrations of 2,4-DCP, respectively.

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**Table 2** Energy efficiency and electrolysis time for 2,4-DCP degradation by different voltages

| Current (A) | Concentration (mg/L) | Volume (L) | Electrolysis time (min) | Voltage (V) | Energy efficiency (g/kWh) |
|---|---|---|---|---|---|
| 1.8 | 5 | 0.025 | 1 | 6.2 | 0.672 |
| 1.8 | 10 | 0.025 | 5 | 6.0 | 0.277 |
| 1.8 | 50 | 0.025 | 10 | 5.6 | 0.744 |
| 1.8 | 100 | 0.025 | 20 | 5.6 | 0.744 |
| 1.8 | 200 | 0.025 | 20 | 5.2 | 1.602 |

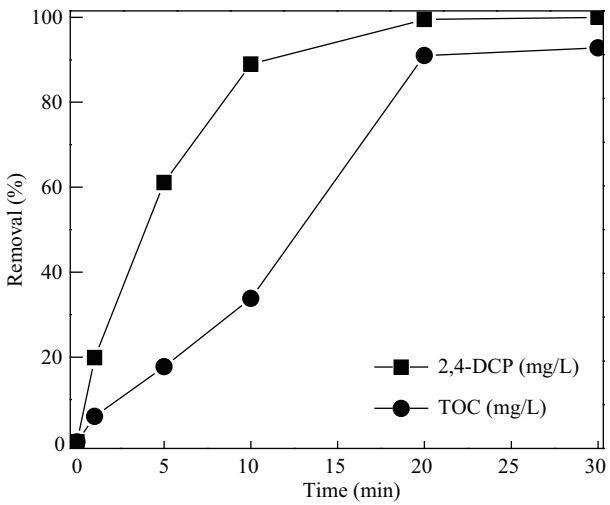


**Fig. 5** Concentration of 2,4-DCP versus total organic carbon removal ratio as a function of electrolysis time at constant current density 30 mA/cm$^2$. Conditions: initial concentration 100 mg/L; plate distance 0.5 cm; initial pH value 6; 10 mmol/L $Na_2SO_4$ at room temperature.

## 2.6 Electrochemical degradation mechanisms of 2,4-DCP

The concentration of 2,4-DCP was removed rapidly by the Ti/$SnO_2$-Sb anode at a constant current density of 30 mA/cm$^2$ after 20 min electrolysis. However, other report indicated that the time for complete phenol degradation was 18 hr for the Pt anode and 36 hr for the Ti/$RuO_2$ anode (Li et al., 2005). In the present study, the TOC removal efficiency on the Ti/$SnO_2$-Sb electrode reached at 92.8% after 30 min electrolysis at a constant current density of 30 mA/cm$^2$ (**Fig. 5**). Thus, the electrochemical technology in terms of 2,4-DCP degradation and TOC removal rate was highly suitable for Ti/$SnO_2$-Sb type of anode with favorable energy efficiency (0.744 g/kWh).

A minor quantity of TOC remaining in the aqueous solutions after complete degradation (99.9%) of 2,4-DCP indicates that the intermediate products with the Ti/$SnO_2$-Sb anode were formed and accumulated. However, pH changed slightly during the electrolysis process (**Table 1**). A little drop in pH may be caused by the formation of acidic substances from 2,4-DCP degradation. In combination with the TOC results, organic acids were probably the main intermediates produced by phenol electrolysis (Comninellis, 1994; Feng and Li, 2003; Tanaka et al., 2002).

To detect the intermediates during electrochemical degradation of 2,4-DCP, GC-MS analysis was performed, and mainly oxalic acid followed by maleic acid, propanoic acid, propanedioic acid and acetic acid were identified. In agreement with the TOC removal and 2,4-DCP degradation results, the organic acids were completely removed by electrolysis on the Ti/$SnO_2$-Sb anode, while some unknown acids accumulated during the electrochemical process. Different anodes have different degrees of reactivity towards organic degradation and its intermediate products. The exact catalytic function of the anode surface in 2,4-DCP degradation is still under discussion. It is commonly assumed that organic compounds in aqueous solution can be oxidized on an anode by direct electron transfer and indirect oxygen atom transfer (Kirk et al., 1985; Chiang et al., 1995; Polcaro et al., 1999; Rodgers et al., 1999; Iniesta et al., 2001). During the direct electron transfer process, organic compounds are adsorbed on the surface of anode and give up electrons to the anode. However, in the indirect oxygen atom transfer, oxygen radicals mainly ·OH generate from water electrolysis and play a vital role in the electrochemical process. The hydroxyl radicals readily react with the organic molecules adsorbed on the surface of anode to enhance the oxidation process, while ·OH will further react with each other to form molecular oxygen to complete the electrolysis of the water molecules (Comninellis, 1994; Iniesta et al., 2001). The whole reaction can be expressed as:

$$M + H_2O \longrightarrow M[\cdot OH] + H^+ + e^- \quad (2)$$

$$M[\cdot OH] + \text{Organic pollutants} \longrightarrow \text{Products} \quad (3)$$

$$2M[\cdot OH] \longrightarrow 2M + O_2 + 2H^+ + 2e^- \quad (4)$$

where, M stands for the anode.

In the above circumstance, high oxygen evolution by anode mainly reduces the efficiency of current activity for organic reduction process (Kötz et al., 1991). The high over-potential bearing Ti/$SnO_2$-Sb anode (1.5 V) shows that the formation of molecular oxygen by radical reaction possibly restrained, which was favorable to organic oxidation by ·OH (Reaction (4)). The high over-potential of the Ti/$SnO_2$-Sb anode can effectively extend the lifetime of ·OH on the anode, thus allowing more oxygen transfer from the radicals to organic matter for oxidation (Reaction (3)). The current study suggests that maleic acid may be

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oxidized directly to oxalic acid, which can be oxidized readily to $CO_2$, due to the formation of ·OH on the Ti/$SnO_2$-Sb anode.

## 3 Conclusions

High efficiency electrochemical degradation of 2,4-DCP was achieved over Ti/$SnO_2$-Sb anode as a model electrode. The degradation rate of 2,4-DCP achieved 99.9% after 20 min electrolysis at higher initial concentrations of 100 and 200 mg/L, and the degradation rate constant ($k$) values were 0.21 and 0.26 $min^{-1}$, respectively. The reaction followed pseudo first-order kinetics and the $k$ value of 2,4-DCP significantly increased with increasing current density and decreasing pH value. The higher TOC removal ratio (92.8%) and 2,4-DCP degradation ratio (99.9%) was achieved after 30 min electrolysis at a constant current density of 30 mA/$cm^2$. The aliphatic carboxylic acids (i.e., propanoic acid, maleic acid, propanedioic acid, acetic acid and oxalic acid) were identified as the main intermediates after 7 min. However, the other degradation products were not found prominently because of the high activity of Ti/$SnO_2$-Sb anode and rapid degradation rate of 2,4-DCP. This result provides an insight that Ti/$SnO_2$-Sb anode is highly fruitful for the efficiently electrochemical technology to degrade 2,4-DCP at mild conditions with appropriate energy consumptions.

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