



Preparation and characterization of Ti/SnO₂–Sb₂O₃–Nb₂O₅/PbO₂ thin film as electrode material for the degradation of phenol

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ABSTRACT

In this work, a novel electrode of titanium substrate coated with mixed metal oxides of SnO₂, Sb₂O₃, Nb₂O₅ and PbO₂ was successfully prepared using thermal decomposition and electrodeposition. The surface morphology and the structure of the prepared thin film were characterized by scanning electronic microscopy (SEM) and X-ray diffraction (XRD), respectively. Experimental results showed that the structure of the prepared electrode might be described as a Ti/SnO₂–Sb₂O₃–Nb₂O₅/PbO₂ thin film and its surface was mainly comprised pyramidal-shape β-PbO₂ crystals. The modified electrode had higher oxygen evolution potential than that of other PbO₂ modified electrodes. Electrocatalytic oxidation of phenol in aqueous solution was studied to evaluate the potential applications of this electrode in environmental science. The phenol removal efficiency in an artificial wastewater containing 0.50 g/L phenol could reach 78.6% at 20 °C and pH 7.0 with an applied electricity density of 20 mA/cm² and treatment time of 120 min. When 21.3 g/L chloride was added to this wastewater, the removal efficiency could reach to 97.2%.

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1. Introduction

Phenols are aromatic compounds with one or more hydroxyl group attached to the aromatic ring and are produced as wastes in a variety of industries, such as petroleum refineries, chemical synthesis, dyes, plastics, coke plants, pulp and paper industry, textiles, detergents, pesticide and herbicide synthesis, and pharmaceuticals [1,2]. The oxidation removal of phenolic compounds has been of particular interest because of their abundances in industrial effluents [3]. Aqueous wastes containing aromatic compounds are recalcitrant and toxic to microorganisms in conventional biological treatment reactions [4,5]. Many methods have been reported for removal of these toxic organic wastes including chemical oxidation [6], photocatalytic degradation [7–9], peroxide/UV-induced decomposition [10], supercritical water oxidation [11,12], and sonochemical degradation [13]. Electrochemical degradation is another alternative method for degrading toxic organic wastes. Moreover, electrolysis can be used as a pre-treatment technology in detoxification of bio-treatment [14]. As an environmental friendly and promising method, it offers some advantages in terms of compatibility, energy efficiency, low-volume application, versatility and

amenability to automation. To date many environmental scientists have focused on the development of stable anodes for removal of persistent organic pollutants by electrochemical oxidation [15]. Traditional electrodes, such as graphite and nickel, show poor current efficiency in organic degradation [16]. Phenols can be oxidized rapidly at the Pt anode but they can inactivate the Pt anode due to the deposition of oligomers on the anode. Since the discovery of dimensionally stable anodes (DSA), the electrochemical degradation of phenols has been quite successful. As such, much work has focused on finding and preparing new DSA anodes for electrochemical applications.

Report on applying PbO₂ as a substitute of Pt electrode in perchlorate industry can be dated back to 1930s', but the study and preparation of Ti-based PbO₂ electrode began only 20 years ago. PbO₂ was regarded as an excellent metal oxide electrode and was widely used in electrochemical oxidation because of its lower cost compared to noble metals, good conductivity, chemical stability in corrosive media, as well as high over-potential for oxygen evolution reaction [17,18]. With more research in applying PbO₂ electrode to the field of water processing, the understanding and knowledge of this type of electrode has become more thorough. A lead oxide/titanium modified electrode has been developed for the efficient removal of *o*-nitrophenol from aqueous solutions by electrochemical oxidation [19]. Samet et al. used Nb-doped PbO₂ anodes in acidic medium for 4-chloroguaiacol degradation [20]. Tahar and Savall described the phenol oxidation on PbO₂ electrodes

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using different metal substrates (Ti, Ta, and Pb) with varying composition of electrolysis baths [21]. Andrade et al. studied phenol electrooxidation in H_2SO_4 medium using pure PbO_2 or F-, Co- and Co/F-doped PbO_2 electrodes in filter-press cells [22]. Ni–Nb–Pt–Sn alloys were applied to oxidation of phenols in acidic aqueous solutions [23]. Recently some modified electrodes composed of binary and ternary oxide mixtures have also been investigated and the electrochemical performance was enhanced [24]. SnO_2 thin films show some advantages of good electrical conductivity, excellent chemical and corrosion resistance [25]. An interlayer of Sn-doped PbO_2 into Ti substrate and a RuO_2 coating with IrO_2 base electrode could also enhance the conductivity of the electrode and improve catalytic characteristics [14].

The aim of this work is to increase the electrochemical activity and stability of Ti/ PbO_2 electrode by doping with some metal oxides such that the modified electrode can be used to remove phenol from wastewater. This modified electrode with a Ti/ SnO_2 – Sb_2O_3 – Nb_2O_5 / PbO_2 thin film was prepared by thermal decomposition and electrochemical deposition technique. Both the surface- and inter-layers of the thin film were fully characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD). The electrochemical properties of this electrode were studied by cyclic voltammetry. Moreover, the electrocatalytic characteristics of the prepared thin-film electrode for degradation of phenol from an artificial wastewater were investigated. Our work demonstrates that the electrochemical performance can be further enhanced by the addition of chloride in the wastewater sample.

2. Experimental

2.1. Reagents

Chromatographic grade phenol (purity $\geq 99\%$) was obtained from Sigma-Aldrich (St. Louis, USA). All other chemicals and reagents used in this study were of analytical reagent grade. Distilled water was used throughout the work.

2.2. Electrode preparation

2.2.1. Titanium surface treatment

To prepare for a good adhesive metal oxide film, the titanium substrate was pretreated according to the following procedures before anodization. Firstly, a titanium sheet ($3\text{ cm} \times 1.8\text{ cm}$) was polished by 320-grit paper strips with water as lubricant followed by 1 mm siliceous paste blasting. Then the titanium sheet was cleansed with water and acetone to remove solid particles and grease. Secondly, the sheet was rinsed by a 50 g/L sodium hydroxide solution and then a hot 1:1 (v/v) acid solution of HNO_3 and H_2SO_4 . Finally the sheet was washed with copious amounts of water. Since a smooth surface with no oxides or scales is required for a uniform and well adhered deposit, the treated titanium (Ti) substrate was immersed in a boiling aqueous solution of oxalic acid (15%) until the TiO_2 on the Ti substrate was dissolved completely.

2.2.2. Coating SnO_2 – Sb_2O_3

In this step, 20.0 g SnCl_4 , 2.0 g Sb_2O_3 and 13.2 mL of concentrated HCl were dissolved in 50 mL isopropanol and then diluted to 100 mL with isopropanol. The treated Ti sheet was dipped in this solution for 5 min, and then dried at 130°C for 15 min. This was repeated three times and the Ti sheet was annealed at 480°C for 60 min in a tube furnace with an influx of oxygen for tin and antimony oxides (SnO_2 – Sb_2O_3) to grow on the pretreated

Ti substrate. Thus, this interlayer of the modified electrode was obtained.

2.2.3. Electrochemical deposition Nb_2O_5 – PbO_2

Afterwards, PbO_2 was deposited galvanostatically on the SnO_2 – Sb_2O_3 interlayer of the Ti substrate by electrochemical anodization in a saturated PbO (140 g/L) NaOH solution for 120 min at 40°C with a constant anodic current density of 20 mA/cm^2 and another titanium sheet as the cathode. Then, PbO_2 and Nb_2O_5 was further deposited galvanostatically on the electrode by the same method with another electroplating solution containing 1.0 g Nb_2O_5 in 100 mL of 35% $\text{Pb}(\text{NO}_3)_2$ for 120 min at 40°C with a constant anodic current density of 80 mA/cm^2 . The modified electrode was thus obtained.

2.3. Electrochemical removal of phenol

The electrolysis of aqueous solutions containing phenol was carried out in a 100-mL one-compartment Pyrex glass cell. The anode (Ti/ SnO_2 – Sb_2O_3 – Nb_2O_5 / PbO_2 modified electrode) was supported vertically and parallel to the stainless steel cathode. The distance between the cathode and the anode was 3 cm. 50 mL of sample solution was used in each experiment. The electrical current was provided by a direct current power supply (YB-1720A, Jiangsu Lvyang Electronic Instrument Group Co., Ltd., China). The current and potential measurements were carried out by a digital multimeter (MF-500, Shanghai No. 4 Electronic Meter Factory, China).

2.4. Analysis

The morphologies of the middle and surface layers of the modified electrode were examined by a scanning electron microscope (Jeol, JSM-5900 LV, Japan). Structural analysis of the middle and surface layers of the modified electrode was also confirmed by an X-ray diffractometer (X'pert Pro MPD, Philips, The Netherlands). The X-ray diffraction (XRD) patterns were taken for 2θ angles from 10° to 90° at a scan rate of $0.02^\circ/\text{s}$. The accelerating voltage and the applied current density were 35 kV and 20 mA/cm^2 , respectively.

Amperometric measurements were performed in an unstirred solution using an electrochemical analyzer (CHI618B, Shanghai Chenhua Instrument Co., Ltd., China). A three-electrode system was used in this experiment with the modified Ti/ SnO_2 – Sb_2O_3 – Nb_2O_5 / PbO_2 electrode as the working electrode, a saturated calomel electrode as the reference electrode and a platinum wire electrode as the counter electrode. The background current was allowed to decay to a steady value before the phenol solutions were added. After that the increase in phenol oxidation current was measured as the response current. Unless otherwise stated, the temperature was kept at 20°C during the whole measurement process.

Two main parameters were measured to evaluate the electrochemical phenol removal efficiency: the remaining phenol concentration (mg/L) and the chemical oxygen demand (COD) ($\text{mg O}_2/\text{L}$). The COD of the solution was determined during the electrolytic process by a closed reflux titrimetric method. A Waters 2690 high-performance liquid chromatograph equipped with a photodiode array detector (Milford, MA, USA) was used to separate and identify the products and intermediates after phenol oxidation. The separation column was a Nucleisil C_{18} ($4 \times 250\text{ mm}$, $5\ \mu\text{m}$) column and the mobile phase was acetonitrile:water (60:40) at a flow-rate of 1.0 mL/min . In addition, an UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) was used to measure the absorbance of phenol and its intermediate products.

The instantaneous current efficiency (ICE) for the anodic oxidation of phenol was calculated from the COD [26]:

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

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

3. Results and discussion

3.1. Characterization of Ti/PbO₂ modified electrode

Fig. 1 shows the morphologies of the interlayer and surface layer of a fresh modified Ti/SnO₂–Sb₂O₃–Nb₂O₅/PbO₂ electrode under various magnifications. Fig. 1(a) and (b) visualizes the structure of orderly crystallites on the interlayer and different crystal structures can be seen. Most of the small rectangular crystals were SnO₂ and the larger cubical crystals were Sb₂O₃. These two oxides were further confirmed by the XRD data (vide infra).

Fig. 1(c) and (d) displays the morphology of the surface layer of the modified Ti/SnO₂–Sb₂O₃–Nb₂O₅/PbO₂ electrode which is uniform and of typical pyramidal shape. The average grain size was about 6 μm. The size of PbO₂ crystals was smaller than that of Ti/Sb–SnO₂/PbO₂ electrode undoped niobium oxide reported by Kong and co-worker [27]. The average grain size of PbO₂ decreased with the addition of niobium oxide because the doped rare earth oxide provided a new center for PbO₂ to nucleate and hindered the growth of PbO₂ [28]. On the other hand, some crystallites have orthorhombic crystal structures as shown in Fig. 1(d), which is attributed to Nb₂O₅.

Fig. 2 shows the phase behavior of the interlayer of the modified Ti/SnO₂–Sb₂O₃–Nb₂O₅/PbO₂ electrode. The peaks at $2\theta = 26.6, 33.9,$

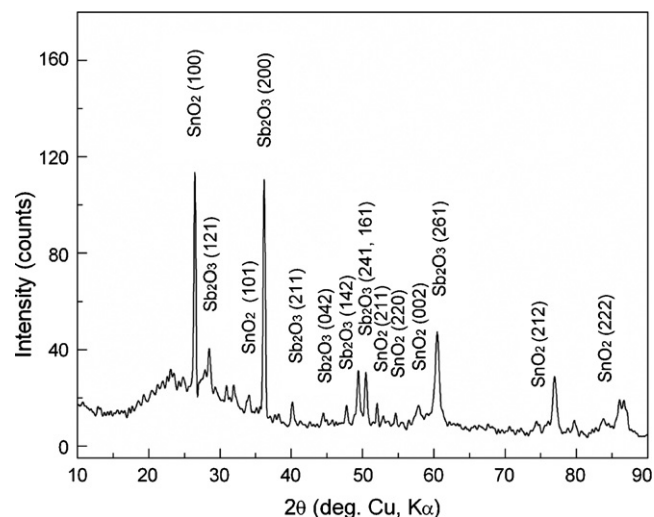


Fig. 2. XRD pattern of the electrode interlayer.

51.7, 54.7, 57.8, 74.4 and 83.8 are regarded as the attributive indicator of tetragonal cassiterite tin(IV) oxide. However, a few peaks were at slightly different positions from the characteristic peaks of pure SnO₂ crystal. This observation was caused by the solid solution in SnO₂, which was formed by antimony and tin oxides on electrode interlayer. Some peaks ($2\theta = 28.4, 36.6, 40.3, 44.2, 48.1, 50.1, 50.5,$ and 60.3) of Sb₂O₃ are also presented in the XRD pattern, further confirming that two kinds of crystals are present at the interlayer which are consistent with the SEM images (vide supra).

Generally, orthorhombic α -PbO₂ and tetragonal β -PbO₂ are found in PbO₂. The conductivity of β -PbO₂ is about one order of magnitude higher than that of α -PbO₂, indicating that the conductivity of PbO₂ can be enhanced by increasing the β -PbO₂

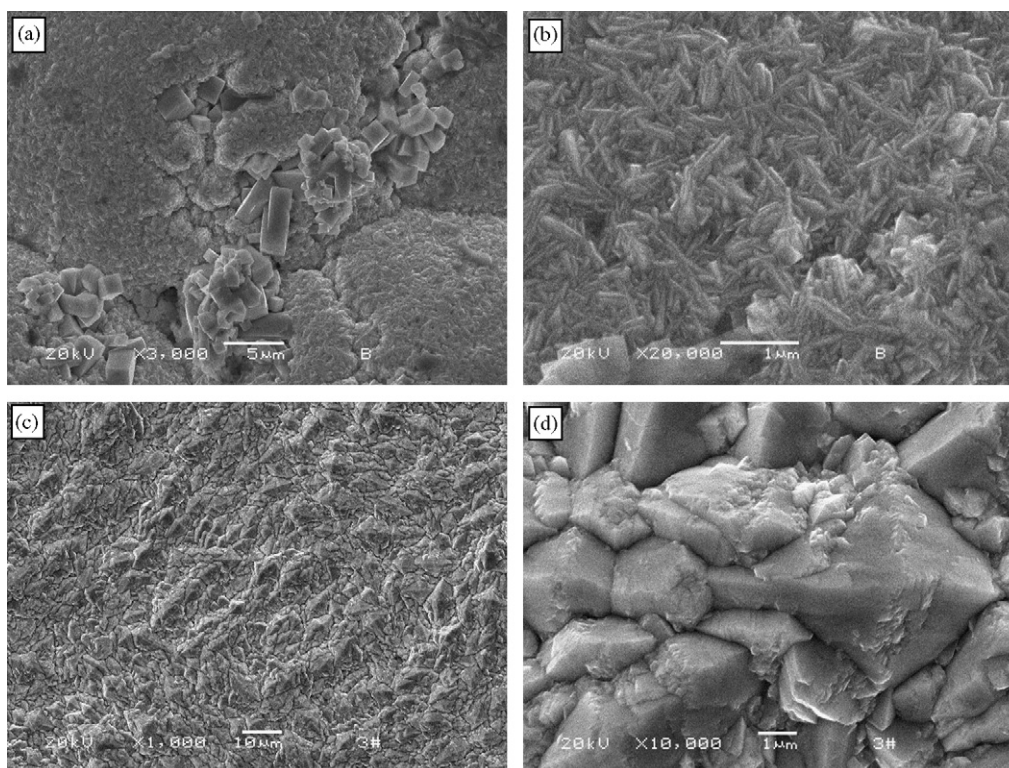


Fig. 1. SEM images of electrode interlayer (a and b) and surface layer (c and d). (a–d) With 3000, 20,000, 1000 and 10,000 \times magnification, respectively.

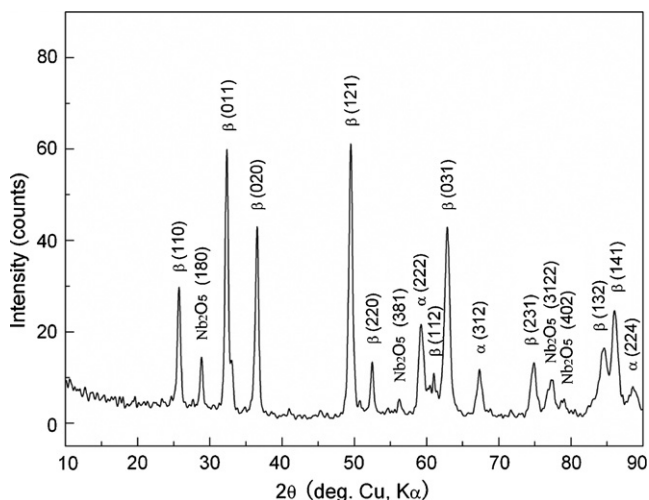


Fig. 3. XRD pattern of the electrode surface layer.

content. Thus, β - PbO_2 is the preferred electrode material when PbO_2 is used [29]. Fig. 3 displays the strong main diffraction peaks at $2\theta = 25.4, 32.0, 36.2, 49.1, 52.1, 62.3, 74.4, 84.1$ and 85.8 which show that the surface layer of the thin modified $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5/\text{PbO}_2$ electrode consists mainly of β - PbO_2 with little α - PbO_2 . At the same time, some weak peaks ($2\theta = 28.4, 56.4, 77.8$ and 78.8) infer the presence of orthorhombic Nb_2O_5 . This further confirms the orthorhombic crystallite in the SEM images in Fig. 1(d) is Nb_2O_5 . However, no diffraction peaks of tin and antimony oxides are observed indicating that the Pb-Nb coating of the surface layer was uniform and thus the minute tin and antimony oxides were undetected by XRD. In summary, a thin layer of $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5/\text{PbO}_2$ has been successfully coated on the Ti electrode.

It is well-known that prior to the formation of a PbO_2 coating on a Ti plate by the electrochemical deposition method, a TiO_2 insulative layer will simultaneously deposit on the Ti plate attributing to the osmosis of nascent oxygen produced on the anode. This can result in PbO_2 coating leaching from the Ti plate and affect its electrochemical activity and life-time. However, as the energy gap of SnO_2 is 3.7 eV at ambient temperature, it has good chemical stability and electrochemistry stability [30]. Consequently, the compact SnO_2 layer may effectively slow down the diffusion of nascent oxygen toward the matrix and prevent the formation of TiO_2 on the Ti substrate. In addition, the SnO_2 layer can resist oxidation such that the diffusion of oxygen toward matrix is minimized. As a consequence, devitalization of the electrode can be avoided and the life-time of the electrode will be lengthened. Theoretically, the formation of a solid solution from an oxides mixture depends on the ionic radius difference of the elements. The ionic radii of $\text{Ti(IV)}, \text{Sn(IV)}, \text{Sb(V)}$ and Pb(IV) are 0.068, 0.069, 0.060 and 0.084 nm, respectively. The difference in ionic radii of Ti(IV) and Pb(IV) is 21% which is larger than the Hume–Rothery limit for successful substitution, i.e., 15% [31]. This suggests that it is difficult to form solid solution between the mixture of TiO_2 and PbO_2 . However, the maximum difference among $\text{Ti(IV)}, \text{Sn(IV)}$ and Sb(V) is 14%, this explains why the oxide mixture of $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_5$ can exist as solid solution. When this solid solution layer is in between the Ti matrix and the surface layer, it can strengthen the adhesive force of the surface layer which is favorable for improving the conductivity of this semiconducting material. A certain amount of Sb(V) doped in the SnO_2 crystal lattice can provide more electrons in the conduction band so that the resistance is decreased [32]. But over-doping can destroy the crystal lattice and decrease the conductance of SnO_2 . At the

same time, SnO_2 in tin and Sb mesosphere can regulate the deposition potential of gas [14]. In addition, Nb_2O_5 doped in the β - PbO_2 crystal lattice can roughen the thin-film surface and then enlarge the surface area of the electrode material; as a result, the absorption of reactant is enhanced [33]. At the same time, Nb doped in the electrode films can improve the microcrystal structure or short-range atomic bonding, resulting in an increase in electrical conductivity and improved hydrophilicity. Moreover, the doped-Nb as a donor increases electrical conductivity and improved hydrophilicity [34]. Thus, hydroxylation takes place easily on the electrode surface when water is in the vicinity, which favors the formation of hydroxyl group free radical and thus increases the electrocatalytic oxidation.

3.2. Voltammetry measurements

It is well-known that anodic oxygen evolution actually causes a power loss in organic wastewater treatment, 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. Fig. 4 displays the cyclic voltammograms of 7.5 g/L Na_2SO_4 electrolyte (pH 7.0) without and with 5.0 mg/L phenol at 20°C at a scan rate of 50 mV/s. The modified $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5/\text{PbO}_2$ electrode had a higher oxygen evolution potential of 1.8 V (vs. SCE) which is higher than that of other PbO_2 or Ti-based modified electrodes, such as 1.6 V for β - PbO_2 [14], 1.6 V for $\text{Ti/SnO}_2\text{-Sb}$ [2], and 1.4 V for $\text{Ti/RuO}_2\text{-Sb}_2\text{O}_5\text{-SnO}_2$ [31]. This indicates that the formation of molecular oxygen in the radical reaction during the electrochemical oxidation was probably restrained by our $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5/\text{PbO}_2$ modified electrode, which is favorable to organic oxidation by hydroxyl radicals [35].

A well-defined anodic peak current corresponding to the oxidation of phenol is obtained at about 1.48 V (vs. SCE) as shown in Fig. 4b. However, the anodic current peak of phenol decreased and shifted to higher potential with the continuous potential scan. The oxidation peak for phenol almost disappeared in the fifth cycle (not shown here), indicating that the resulting semiconducting product formed on the modified Ti/PbO_2 electrode surface subsequently reduces the rate of electron transfer at the electrode. Similar phenomena were observed for other phenolic compounds including phenol [36], bisphenol A [37] and polyphenol [38]. It is

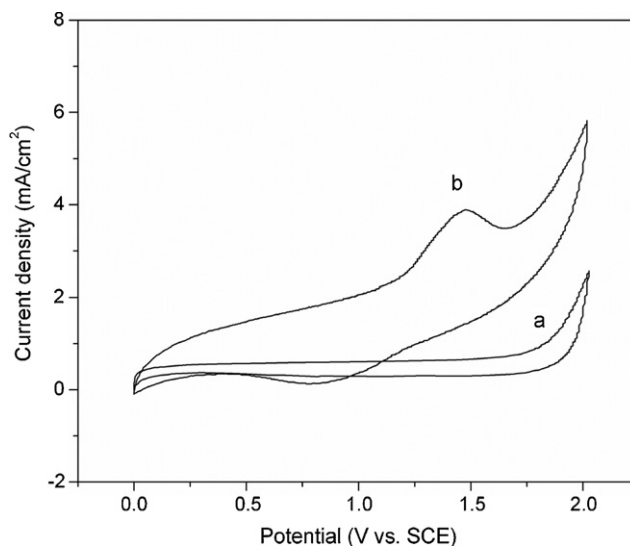


Fig. 4. Cyclic voltammograms obtained in 7.5 g/L Na_2SO_4 electrolyte (a) and 7.5 g/L Na_2SO_4 electrolyte containing 5.0 mg/L phenol (b) at pH 7.0, 20°C and a scan rate of 50 mV/s.

well-known that the direct oxidation of phenolic compounds via one- and two-electron transfers generates the intermediate products of phenoxy radical and quinone, respectively. Oxidation of phenolic compounds to quinone can be suppressed by low applied over-potentials. The production of the electropolymerized phenol film on the modified Ti/PbO₂ electrode surface might also attribute to the dimerization of the phenoxy radical, and/or a free radical multistep-growth polymerization with the monomer or the oxidized monomer initiated by phenoxy radicals [39]. The electrode activity could never be recovered by just washing with aqueous or any organic solvent. However, it could be restored by an anodic polarization process in aqueous solution at the water decomposition potential (>2.5 V) with the same supporting electrolyte. Alternatively, this can be achieved by switching the polarity of the electrodes similar to the wastewater treatment process. In this case, the surface polarization process may lead to the complete destruction of polymeric product adsorbed on the electrode surface by generating large amounts of •OH. Probably this hydroxyl radical will oxidize the polymeric product into some smaller organic molecules [15]. It is also observed that the anodic oxidation peak of phenol returned to its initial position after anodic polarization. Nevertheless, no such passivation behavior was observed during the electrolysis process for our phenol degradation since the experiments were conducted in the water decomposition potential.

3.3. Electrical degradation of phenol

Factors affecting the phenol removal efficiency and the intermediate products were studied by electrolysis. In this study, 7.5 g/L Na₂SO₄ was used as the supporting electrolyte, Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ modified electrode and stainless steel were used as the anode and cathode, respectively. At the same time, the function of chloride ions in the degradation solution was also studied.

The solution containing phenol was electrolyzed with our laboratory-made Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ modified electrode. The initial concentration of phenol was 0.50 g/L. Fig. 5A shows the degradation efficiency of phenol (pH 7.0) under different current densities at 20 °C. The removal efficiency of phenol increased with the current density but leveled off at about 30 mA/cm². In addition, the effect of current density (0–50 mA/cm²) on ICE and COD residual of electrocatalytic degradation of phenol solution (0.50 g/L) were investigated with the initial COD of 250 mg/L. Our results

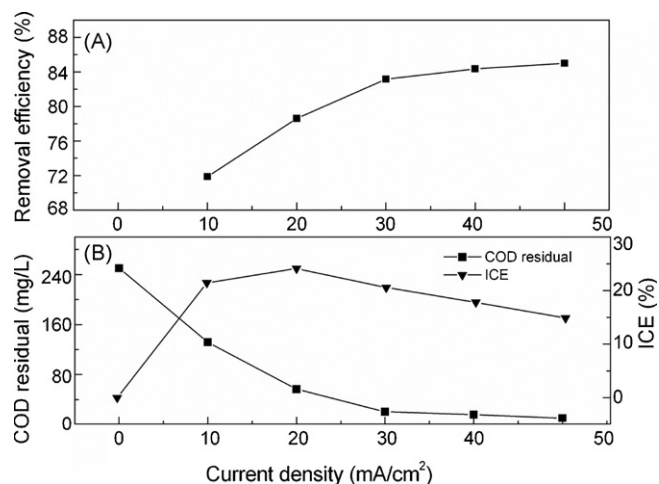


Fig. 5. Effect of applied current density on phenol removal efficiency (A) and COD removal and ICE (B).

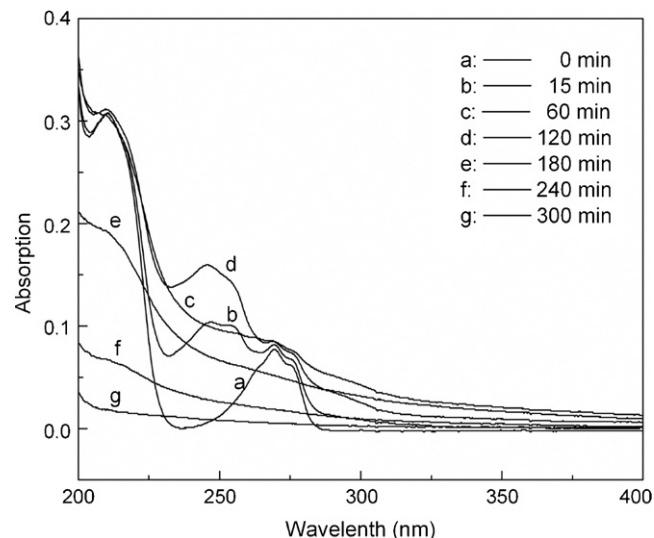


Fig. 6. UV absorption spectra of the phenol degradation solution at different electrolysis times.

show that higher current density resulted in higher phenol removal efficiency. In addition, COD removal increased with the increase of the applied current density as depicted in Fig. 5B. However, the highest instantaneous current efficiency (ICE) was at 20 mA/cm² when the current density changed from 0 to 50 mA/cm². In view of electric energy efficiency, 20 mA/cm² was chosen as the optimal condition in most of our experiments.

The UV absorption spectrum of the sample varied very much after different periods of electrolysis as shown in Fig. 6. This indicates that the Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ modified electrode was very effective for phenol degradation and can entirely degrade the artificial wastewater containing relatively high concentration of phenol. Fig. 6 also shows the disappearance of the characteristic peak ~270 nm of phenol during the electrolysis, inferring that the aromatic ring of phenol was possibly open. The electrolysis at different stages of electrochemical reactions produced various carboxylic acids. Almost no organic substrates remained in the electrolyte when the Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ modified electrode was selected as the anode, and lower absorbency was detected at 220–300 nm. These results show that the oxidation efficiency from phenol to benzoquinone is high, relating to the facile aromatic rings opening on the Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ anode. However, much more organic compounds still remained in the electrolyte when Ti/RuO₂, and Ti/Sb-Sn-RuO₂ were employed as the anodes [14], and this means that these two anodes had relative poor oxidation ability for organic compounds. Our Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ electrode has faster and higher phenol removal efficiency than that of pure β-PbO₂ electrode. This might be the result of the improved conductivity of the Sb-doped SnO₂ interlayer and the enhanced catalytic capability by doping Sb and Nb into the coating. Fig. 7 displays the HPLC analysis of the intermediate species produced during the electrolytic decomposition of phenol. The major intermediate products were benzoquinone, pyrocatechin, resorcin, hydroquinone, fumaric acid, maleic acid, and oxalic acid. However, when the electrolytic decomposition of phenol lasted for 240 min, these intermediate species were not detected by the UV-vis absorption and HPLC methods as they were further converted to carbon dioxide and water similar to the results reported in literature [26]. The removal efficiency of phenol of an artificial wastewater containing 0.50 g/L phenol (pH 7.0) could reach 78.6% after electrolysis at 20 °C and 20 mA/cm² for 120 min.

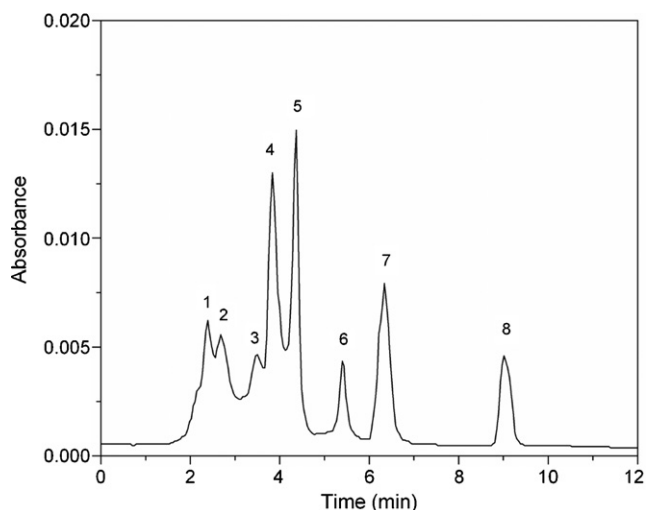


Fig. 7. Chromatogram of intermediate species produced during the electrolytic decomposition of 0.50 g/L phenol (pH 7.0) at current density of 20 mA/cm², 30 min of electrolysis and 20 °C. (1) Oxalic acid, (2) maleic acid, (3) fumaric acid, (4) hydroquinone, (5) resorcin, (6) catechol, (7) benzoquinone, and (8) phenol.

The effect of chloride on the removal of phenol was studied as shown in Fig. 8. The phenol removal efficiency increased with increasing chloride concentration for 120 min of electrolysis. Such observation indicates that the catalytic activity of the Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ modified electrode can be improved. The removal efficiency could reach 97.2% when 21.3 g/L chloride was added to the solution as the electrogenerated Cl₂ and ClO⁻ ions might play a major role in the electrocatalytic oxidation of phenol [19].

In order to verify the reproducibility of the electrode preparation, the experiments were repeated in triplicate. The phenol removal efficiencies of three individual electrodes were 97.2, 98.5 and 92.1% under optimal electrolysis conditions with chloride in the solution. Good reproducibility of the current efficiency was obtained for the three electrodes with a relative standard deviation (R.S.D.) of 3.4%. Furthermore, the electrode maintained an integrated surface and stable current efficiency after 20 h of operation under optimal electrolysis conditions. Analysis of the treated solutions revealed that no obvious metal dissolution occurred during the electrolysis.

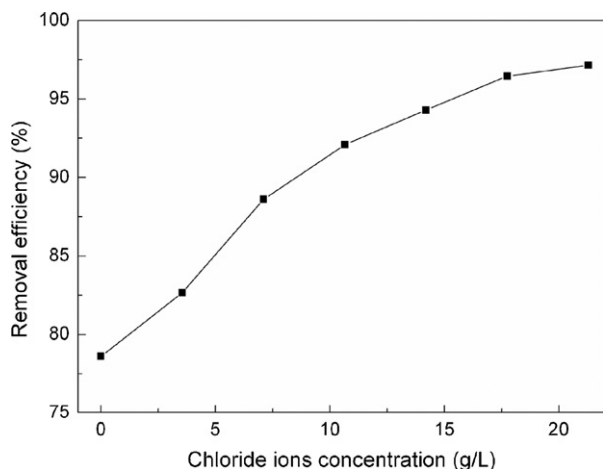


Fig. 8. Effect of chloride concentration on the removal of 0.50 g/L phenol (pH 7.0) at current density of 20 mA/cm², 120 min of electrolysis and 20 °C.

4. Conclusion

The pyramidal-type SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ multiple oxides were successfully prepared on a Ti substrate by the thermal decomposition and galvanostatical deposition methods. XRD distinctively identified the presence of crystalline structures of SnO₂, Sb₂O₃, Nb₂O₅ and PbO₂ on the modified electrode. The as-prepared electrode film possesses large rough surface which is considered an advantage for electrocatalytic applications. The electrode was electrochemically active for the oxidation of phenol. The removal efficiency of phenol reached 78.6% for an artificial wastewater containing 0.5 g/L phenol (pH 7.0) at 20 °C and a current density of 20 mA/cm². The phenol removal efficiency could reach 97.2% when the wastewater contained 21.3 g/L chloride, indicating that the chloride ions can improve the catalytic activity of the modified electrode. In essence, our developed Ti/SnO₂-Sb₂O₃-Nb₂O₅/PbO₂ electrode can be an effective anodic material for phenol degradation and is promising for the electrooxidation of other organic compounds in aqueous media.

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