Electrochemical Oxidation of Bisphenol A on Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ Anode for Waste Water Treatment

B. Xue, Y. Zhang and J.Y. Wang

School of Petrochemical Engineering, Shenyang University of Technology, Box 33, 30 Xueyuan Road, 111003, Liaoyang, Liaoning, P. R. China

Abstract

The electrochemical oxidation of bisphenol A on Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ electrode was studied by cyclic voltammetry in this paper. The electrochemical behaviour of the electrode in sodium sulfate solution and in the mixture solution of sodium sulfate and bisphenol A has been studied. The experimental results of cyclic voltammetry showed that acidic media was suitable for efficient electrochemical oxidation of bisphenol A. Some electro-generated reagent formed in the electrolysis process and bisphenol A could be oxidized by the electro-generated reagent. The Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ electrode was used as the anode and the electrolysis experiment was carried out under the optimized conditions. The electrolysis process was monitored by UV-visible spectrometry and high performance liquid chromatography (HPLC) and the chemical oxygen demand (COD) was determined by the potassium dichromate method. The mechanism of bisphenol A be oxidized was studied primarily by the cyclic voltammetry and UV-visible spectrometry. The results of electrolysis experiment demonstrated the possibility that the electrode was used as an anode for electrochemical treatment of bisphenol A contained in the waste water.

Keywords: Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ electrode; bisphenol A; cyclic voltammetry; electrochemical oxidation; waste water treatment.

1. Introduction

The use of direct and indirect electrochemical oxidation for the treatment of aqueous wastes has undergone rapid development in recent years [1-3]. This technology can be successfully applied in the treatment of waste water containing non-biodegradable organics [4-5]. The electrochemical activity of each organic compound depends on the anode material used. In fact, while spontaneously, the oxidation reaction by oxygen transfer is characterized by low rate constants when carried out on traditional
electrode materials such as Au, Pt, C \cite{7-8}. It is now thought that the step preceding the transfer of an oxygen atom in the oxidation mechanism of organic substances in aqueous solution is the discharge of the water molecule leading to an adsorbed hydroxyl radical \cite{9,10}. The use of an anode material with a high oxygen evolution potential favors the oxygen transfer. Lead dioxide fulfills this criteria.

Ti/PbO₂ is a kind of material of metal oxide anode, which has been used in electrolysis industry as a dimension stable anode (DSA) for its good characters of stability, higher oxygen evolution potential, conductivity, corrosion resistance and longer service life \cite{11}. In recent years, the improvement for Ti/PbO₂ electrode has been reported \cite{12-14}. The researchers reported that the middle layers of SnO₂-SbOₓ between the PbO₂ layer and the Ti substrate, that is SnO₂/Sb₂O₃ or SnO₂/Sb₂O₅, made the electrode be improved obviously, and the electrocatalytic activity, the electrochemical stability and the service life of the electrode was improved evidently.

Bisphenol A, or 2,2-bis(4-hydroxyphenyl)propane, is one of the widely used organic compounds. It is well known that 2,2-bis(4-hydroxyphenyl)propane has estrogenic activity \cite{15}, the purification of waste water containing phenolic compounds is a longstanding problem owing to the low rate of biodegradation and high toxicity of such phenol derivatives.

The goal of the present work is aimed at studying the electrochemical oxidation of bisphenol A on Ti/SnO₂-Sb₂O₅/PbO₂ anode in order to evaluate the potential application of this electrode to the electrochemical treatment of bisphenol A contained in waste water.

2. Experimental

2.1 Preparation of Ti/SnO₂-Sb₂O₅/PbO₂ electrode

The Ti/SnO₂-Sb₂O₅/PbO₂ anodes were prepared by deposition of the SnO₂-Sb₂O₅ layer by spray pyrolysis technique on Ti with high temperature oxidation and then the PbO₂ layer was electro-deposition on the surface of the middle-layer \cite{16}.

2.2 Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out by using a three-electrode cell (50 ml) at room temperature. Meshy Ti/SnO₂-Sb₂O₅/PbO₂ electrode of 2.0 cm² area was used as working electrode, a platinum wire electrode was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. To increase the reproducibility of the polarization measurements, the electrode was electrochemically preconditioned before use and in polarizing the electrodes the preconditioning was conducted for 30 minutes in 1.0 mol/L H₂SO₄ solution under anodic current density of 50mA/cm². The cyclic voltammograms were determined and recorded with a CHI 620 Electrochemical Workstation (CH Instruments, USA) controlled by a computer. A 0.1 mol/L Na₂SO₄ solution was used as supporting electrolyte for the cyclic voltammetric study, and the pH was adjusted by adding appropriate amount of H₂SO₄ or NaOH solution.

2.3 Electrolysis

A DC voltage-stabilized power supply RXN-303A was used for the electrolysis experiments, and the electrolysis experiments were carried out in constant current density condition. The cell for electrolysis is a flow through cell which dimension is 6.0cm × 6.0cm × 2.0cm, and the tank for waste water sample is a 2.0L narrow-mouthed bottle. Meshy Ti/SnO₂-Sb₂O₅/PbO₂ electrode which dimension 6.0cm × 5.0cm was used as the anode, and a stainless steel electrode with the same dimension was used as the cathode.
Preconditioning of the anode was conducted in polarizing the electrodes for 30 min in 1.0 mol/L H₂SO₄ solution under anodic current density of 50mA/cm². The potential was constant during each electrolysis, indicating that neither appreciable deterioration of the electrode nor passivation phenomena took place. 0.02 mol/L Na₂SO₄ solution was used as supporting electrolyte for the electrolysis studies, and the pH was adjusted by adding appropriate amount of H₂SO₄ or NaOH standard solution.

2.4 Analytical procedures

UV-visible spectra of bisphenol A were measured and recorded by using a TU-1900 UV-visible spectrophotometer. The concentration of bisphenol A was determined by HPLC[22] by using a HPLC series 200 (Perkin-Elmer company). Chemical oxygen demand (COD) was determined by the potassium dichromate method. All the chemicals were analytical-reagent grade and all solutions were prepared by using distilled water.

3. Results and discussion

3.1 Cyclic voltammetry

The cyclic voltammetric experiments were performed at a sweep rate of 100mVs⁻¹ and the scanning potential range was from 0.0 to 1.8V. The cyclic voltamograms obtained in 0.1 mol/L Na₂SO₄ solution (blank solution, curve a) and in 1.0×10⁻⁴ mol/L bisphenol A + 0.1 mol/L Na₂SO₄ solution (curve b) are shown in Fig.1.

![Figure 1](image_url) The comparison of cyclic voltamograms in blank and bisphenol A solutions. Curve a: absence of bisphenol A solution; curve b: bisphenol A 1.0×10⁻⁴ mol/L.

Comparing the cyclic voltamograms curve a and b in Figure 1, it can be seen that, the anodic current in the potential range of more than 0.6V is larger in the bisphenol A solution than that in blank solution. In the experimental condition, the oxygen evolution potential starts from about 1.5V. In the potential range of oxygen evolution, the anodic current in the bisphenol A solution is enlarged faster than that in blank solution. It is reasonable to assume that bisphenol A can be oxidized fast on the electrode surface by the electro-generated reagent and the evolution oxygen, and the oxidizing reaction accelerats the mass transfer rate of the electro-generated reagent, such as peroxodisulphate[6] and oxygen, from the electrode surface to the substrate solution.
3.2 The influence of pH and concentration of bisphenol A on the oxidizing reaction

The influence of pH on the reaction of bisphenol A being oxidized on the Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ anode was investigated within the pH range from 2.0 to 6.0. The cyclic voltammetric experiments were performed at a sweep rate of 100 mVs$^{-1}$ in a 0.1 mol/L Na$_2$SO$_4$ solution and 5.0×10$^{-5}$ mol/L bisphenol A, within the potential range from 0.0 to 1.8V. The voltammetric curves obtained are shown in Figure 2. It can be seen from Figure 2 that, when the potential of anode less than the oxygen evolution potential, the anode current was the biggest under the pH of electrolysis solution was 4. While the potential of anode was more than the oxygen evolution potential, the anode current under the pH condition of 4 was bigger than the other pH conditions but at pH=2 condition. It can be reasonable resulted that bisphenol A was oxidized easily on the Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ anode at the pH condition of 4, the result was consistent with the results of electrolysis experiments. The influence of the bisphenol A concentration on the oxidizing reaction on the Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ anode was investigated in the concentration range from 1.0×10$^{-7}$ mol/L to 1.0×10$^{-4}$mol/L bisphenol A. The cyclic voltammetric experiments were performed at a sweep rate of 100mVs$^{-1}$ in a 0.1 mol/L Na$_2$SO$_4$ solution at pH 4.0, and within the scanning potential range from 0.0 to 1.8 V. The result of experiments showed that the fouling was formed in concentrated bisphenol A solution, and the fouling formation by the production of incomplete oxidization of bisphenol A. Fortunately, the fouling can be oxidized completely in a higher potential condition, such as in the oxygen evolution potential condition, and the further oxidation reaction can make bisphenol A be mineralized completely, which can be illuminated by the changing rule of the anodic current.

![Fig.2 Cyclic voltammograms in different pH conditions in bisphenol A solution](image)

3.3 Electrolysis for the degradation of bisphenol A

To test the possibility of using Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ anode for electrochemical incineration of bisphenol A, electrolysis experiments in constant current conditions were carried out. The Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ electrode with a area of 30.0 cm$^2$ was used as the anode, and a stainless steel with the same area was used as the cathode. The factors which influence the oxidation of bisphenol A, such as current density, electrolyte, pH value, space between the anode and cathode were optimized, and the optimum electrolyte condition was adopted in the electrolysis experiments. The space between the anode and cathode was 10 mm, the concentration of the support electrolyte, Na$_2$SO$_4$, was 0.02 mol/L, the pH was 4.0, the current density was 40 mA/cm$^2$, and the initial concentration of bisphenol A was 1.0×10$^{-4}$ mol/L. The concentration was monitored real timely by HPLC. The electrochemical oxidation of bisphenol A was a complex process, the UV-visible spectra were recorded in the electrolysis of bisphenol A and they were
shown in Fig. 3. It can be observed from Fig. 3 that, bisphenol A was rapidly degraded by electrochemical oxidation, and some intermediate products were formed in the process of electrolysis, and finally, the intermediate products were destroyed almost completely.

The chemical oxygen demand (COD) was monitored with potassium dichromate method in the process of bisphenol A being degraded and the result was shown in Fig. 4. It can be seen from Fig. 4 that the COD decreased nearly directly with the electrolysis time during the first 80 min. With further electrolysis, the rate of COD being removed was gradually slow with the increasing of electrolysis time. These results indicated that the oxidation reaction was a kinetic-controlled in the first 80 min and then was a diffusion-controlled when the organic pollutant was in a small concentration in the electrolysis time which was longer than about 80 min. The curve of COD being removed shows that under the above experimental conditions, bisphenol A could be degraded effectively.

![UV-Visible spectra of bisphenol A at different electrolysis time](image1)

**Fig.3.** UV-Visible spectra of bisphenol A at different electrolysis time

![Ratio of COD removed vs Electrolysis time](image2)

**Fig.4.** The COD removed during the electrolysis

4. Conclusions

The research of the electrochemical behavior of bisphenol A on the Ti/SnO$_2$-Sb$_2$O$_3$/PbO$_2$ anode shows that bisphenol A could be oxidized directly on the surface of the electrode, and pH=4 is a suitable condition for the efficient electrochemical oxidation of bisphenol A. Bisphenol A could be oxidized by
the electro-generated reagent not only in the substrate solution but also on the anode surface under the experimental conditions. The fouling formed by the production of incomplete oxidation of bisphenol A on the surface of the electrode could be oxidized completely at a higher potential, and the further oxidation reaction could make bisphenol A oxidized completely. The electrolysis experimental results demonstrate that it is possible to use Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ as an anode for electrochemical treatment of waste water containing bisphenol A.

References


**Bin Xue** is presently a teacher and a research scientist at School of Petrochemical Engineering, Shenyang University of Technology. Professor Xue’s main research areas include catalysis and environment engineering. He has published more than 20 journal papers science 1995.