Electrochemical degradation of aqueous bisphenol A using Ti/SnO₂-Sb/Ce-PbO₂ anode

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Abstract: The electrochemical degradation kinetics and energy consumption of aqueous bisphenol A (BPA) were investigated using Ti/SnO₂-Sb/Ce-PbO₂ anode. The electrochemical degradation of BPA followed the pseudo-first-order kinetics. Different influence factors, i.e. current density, BPA initial concentration and Na₂SO₄ concentration, on the degradation kinetics and energy consumption were evaluated. The optimal degradation kinetic rate and energy consumption were 0.067 min⁻¹ and 9.96 Wh/L, respectively. Electrochemical oxidation process was effective in the degradation of aqueous BPA.

1. Introduction
Bio-refractory compounds have been largely produced from the industries, and also be released to the environment. These compounds have been widely detected in waters during the last decades. Bisphenol A (BPA), a well-known endocrine chemical, is often used in the production of polycarbonate, epoxyresin and plastics [1]. BPA have been widely detected in the natural environments. BPA can induce feminization phenomena [2]. Meanwhile, BPA can cause prostate cancer, cardiovascular disease, birth defects, hormonal imbalance, and liver enzyme abnormalities [3, 4]. However, biological and chemical processes can not degrade BPA effectively. Therefore, it is quite urgent to search for effective methods to degrade BPA.

Advanced oxidation processes (AOPs) can effectively oxidize the recalcitrant organic pollutants because of the produced hydroxyl radical (·OH). Hydroxyl radical can react with many organic pollutants non-selectively, even at ambient temperature and pressure [5, 6]. Among AOPs, electrochemical oxidation process is an ideal technique for aqueous organic contaminants degradation because of its unique advantages, i.e. strong oxidation property, mild reaction conditions, and environmental compatibility [7, 8]. Electrochemical oxidation process was already applied in the elimination of many organic pollutants (i.e. dyes, antibiotics, pesticides and perfluorinated compounds) [9-12]. In principle, BPA can be effectively degraded in the electrochemical oxidation process by the produced ·OH.

In the present study, the degradation of BPA in aqueous solution was investigated in electrochemical oxidation process with Ti/SnO₂-Sb/Ce-PbO₂ anode. The influence factors, e.g. applied current density, BPA and Na₂SO₄ concentration, on BPA degradation were investigated. The energy consumption during BPA degradation in electrochemical oxidation process was also studied based on different influence factors.
2. Experimental Sections

2.1. Materials
Bisphenol A, Na₂SO₄, SnCl₂•5H₂O and SbCl₃ were obtained from J&K chemical. Pb(NO₃)₂ and Ce(NO₃)₃•6H₂O were purchased from Aladdin. Ti/SnO₂-Sb/Ce-PbO₂ electrode was prepared following sol-gel and electrodeposition methods, as clearly described in the previous work [13].

2.2. Experimental Setup and Procedures
The degradation experiments were carried out in an electrochemical oxidation system. Ti/SnO₂-Sb/Ce-PbO₂ with the effective size of 5 cm × 5 cm worked as the anode, while two stainless-steel plates worked as cathodes. The total volume of solution was 100 mL with Na₂SO₄ as supporting electrolyte. All experiments were carried out at 25 ± 1 °C.

2.3. Analyses
The concentration of BPA was measured by using UPLC (ACQUITY H-class, Waters), and the PDA detector was at 254 nm. The separation process was used an Xbridge BEH C18 column (2.1 mm × 50 mm, 1.7 μm, Waters). An isocratic flow of 30% water and 70% methanol was used as the mobile phase with a flow rate of 0.2 mL/min. BPA degradation was fitted with the pseudo-first-order kinetic model.

3. Results and Discussion

3.1. Effects of Current density
The influence of applied current density on the electrochemical degradation of BPA was investigated, and the result is clearly shown in Figure 1. BPA degradation performance was enhanced with higher current density, which was consisted with other contaminants degradation in the electrochemical oxidation process [13]. BPA degradation process follows pseudo-first-order reaction kinetic. The kinetic rate constant ($k$) values were 0.033, 0.067, 0.101 and 0.124 min⁻¹ at the current density of 4, 6, 8 and 10 mA/cm², respectively, as shown in Table 1. The production of free radicals is higher at larger current density, which is the main reason of enhanced $k$ value. The energy consumption ($E_{EO}$) was calculated following the method in the previous work [14], and the results are listed in Table 1. The $E_{EO}$ values were 11.6, 9.96, 10.3 and 11.7 Wh/L at the current density of 4, 6, 8 and 10 mA/cm², respectively. A higher current density can cause greater competing reactions. The lowest energy consumption was found at current density of 6 mA/cm², which was chosen as the ideal current density in the following experiments.

![Figure 1. BPA degradation efficiencies with different current densities. Experimental conditions: BPA concentration of 10 mg/L, 10 mM Na₂SO₄ and pH without adjusted.](image-url)
### Table 1. Kinetics and energy cost for the electrochemical degradation of BPA.

| Parameters | $k$ (min$^{-1}$) | $t_{1/2}$ (min) | Average voltage (V) | $E_{EO}$ (Wh/L) |
|------------|------------------|-----------------|---------------------|-----------------|
| $j$ (mA/cm$^2$) | 4 | 0.033 | 21.0 | 5.0 | 11.6 |
| | 6 | 0.067 | 10.4 | 5.8 | 9.96 |
| | 8 | 0.101 | 6.96 | 6.8 | 10.3 |
| | 10 | 0.124 | 5.59 | 7.6 | 11.7 |
| Na$_2$SO$_4$ (mM) | 5 | 0.060 | 11.6 | 7.6 | 14.6 |
| | 10 | 0.067 | 10.3 | 5.8 | 9.96 |
| | 20 | 0.079 | 8.78 | 4.8 | 6.98 |
| | 40 | 0.090 | 7.70 | 4.3 | 5.49 |
| BPA (mg/L) | 10 | 0.067 | 10.3 | 5.9 | 9.96 |
| | 20 | 0.044 | 15.8 | 5.9 | 15.4 |
| | 30 | 0.037 | 18.7 | 5.8 | 18.0 |
| | 40 | 0.033 | 21.0 | 5.8 | 20.2 |

### 3.2. Effects of Na$_2$SO$_4$ concentration

The effect of Na$_2$SO$_4$ concentration on BPA degradation is shown in Figure 2. BPA degradation performance slightly enhanced with the higher Na$_2$SO$_4$ concentration, while the $k$ values were 0.060, 0.067, 0.079 and 0.090 min$^{-1}$ at Na$_2$SO$_4$ concentration of 5, 10, 20 and 40 mM, respectively. The conductivity of solution was enhanced with higher Na$_2$SO$_4$ concentration, which could be proved by the decrease of cell voltage as shown in Table 1. The $E_{EO}$ value decreased with higher Na$_2$SO$_4$ concentration, which might be helpful to BPA degradation. However, the total degradation performance should be evaluated in consideration of the water quality. In some kinds of water, the conductivity might be not very high. Thus, a high Na$_2$SO$_4$ concentration might not be applicable for the degradation of BPA in all kinds of water. Na$_2$SO$_4$ concentration of 10 mM was chosen as the optimal condition in the following experiment.

![Figure 2. BPA degradation efficiencies with different Na$_2$SO$_4$ concentration. Experimental conditions: BPA concentration of 10 mg/L, current density of 6 mA/cm$^2$ and pH without adjusted.](image)

### 3.3. Effects of BPA concentration

BPA degradation performance with its different initial concentration is shown in Figure 3. The $k$ values were 0.067, 0.044, 0.037 and 0.033 min$^{-1}$ at the BPA concentration of 10, 20, 30 and 40 mg/L, respectively. A higher initial concentration inhibited its degradation. The yield of formed free radicals was almost equal at the same current density. Therefore, a smaller part of BPA was degraded by the free radicals at higher concentration. Furthermore, more degradation intermediates were produced at
higher BPA concentration, which could slow down the degradation of BPA. Higher energy consumption was found at higher BPA initial concentration, as clearly shown in Table 1.

![Figure 3. BPA degradation efficiencies with different BPA concentration. Experimental conditions: current density of 6 mA/cm², 10 mM Na₂SO₄ and pH without adjusted.](image)

4. Conclusion
In this study, aqueous BPA was effectively degraded in electrochemical oxidation process using Ti/SnO₂-Sb/Ce-PbO₂ anode. The degradation process follows pseudo-first-order reaction kinetics. When the current density was 6 mA/cm², Na₂SO₄ concentration was 10 mM and BPA concentration was 10 mg/L, the optimal degradation kinetic rate and energy consumption was 0.067 min⁻¹ and 9.96 Wh/L, respectively. The higher current density and Na₂SO₄ concentration were in favor of degradation kinetic rate, but not of energy consumption.

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