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Electrochemical Degradation of 4, 4'-(propane-2, 2-diyl) diphenol in Water with $CeO_2/\beta\text{-}PbO_2/Ti$ Electrode

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Ti-base $CeO_2/\beta\text{-}PbO_2$ composite electrodes were prepared by using electro-deposition and its morphology and crystal structure and electrochemical characterization of composite electrodes were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry and the accelerated life testing. The efficiency of electrocatalytic degradation of 4,4'-(propane-2,2-diyl)diphenol (BPA) by using composite electrodes as anode were examined as a function of initial solution pH, applied voltage and supporting electrolyte concentration were investigated. The results showed that $CeO_2/\beta\text{-}PbO_2/Ti$ electrode had an excellent corrosion resistance and excellent catalytic performance higher catalytic activity in electro-chemical degradation of 4, 4'-(propane-2, 2-diyl) diphenol in water. The removal efficiency of COD_{Cr} could be reached 95.7% after 1.5 h electrolysis at NaCl concentration of 0.020 mol/L, 4,4'-(propane-2,2-diyl)diphenol initial concentration of 20 mg/L, applied voltage of 20 V, electrode spacing of 7 cm and electrolyte pH of 5. The reaction mechanism and kinetics of $CeO_2/\beta\text{-}PbO_2/Ti$ composite electrodes electrochemical degradation 4, 4'-(propane-2, 2-diyl) diphenol mainly caused by the OH radical attacking parent molecules and the degradation followed pseudo-first-order kinetics.

Keywords: $CeO_2/\beta\text{-}PbO_2/Ti$ electrodes; 4, 4'-(propane-2, 2-diyl) diphenol; electrochemical degradation

1. INTRODUCTION

4,4'-(propane-2,2-diyl)diphenol(BPA) is a major component in the production of polycarbonate (PC) and epoxy resin (EP) which are widely used as plastic food containers, water bottles and baby bottles [1]. During the manufacturing process or the degradation of these products, BPA can be released into the environment to pollute surface water [1-2]. Thus, humans may ingest trace mounts of BPA and some studies showed that the potential risks of BPA include reproduction dysfunctions, neuro-chemical effects and behavioral effect [3]. Therefore, it is necessary to find an efficient approach to degrade BPA so as to minimize its contamination.

Electro-chemical methods are frequently used to treat wastewater and the application of electro-chemical method to remove organic pollutants has some advantages compared with biological and chemical method [4-5]. In recent decades, a lot of electrode materials have been examined to improve the effectiveness of oxidation efficiency, such as graphite [6], platinum [7], RuO_2 [8], PbO_2 [9-10] and BDD electrodes [11-12]. Moreover, electro-chemical technique is a suitable method for degradation of organic pollutants due to its environmental compatibility, simple operation and high efficiency [13]. β-PbO_2 electrodes has been extensively studied owing to its high electrical conductivity, low cost and a strong ability to produce hydroxyl radicals, high over-potential for oxygen evolution[12]. However, pure β-PbO_2 electrode coatings could easily flake away from the base [13]. To solve this problem, many researches had focused on modification of PbO_2 anodes. Xue et al [14] used Ti/SnO_2-Sb_2O_5/PbO_2 electrode to electrochemical oxidize 4, 4'-(propane-2, 2-diyl) diphenol and found it could be oxidized directly on the surface of the electrode, and pH=4 is a suitable condition for the efficient electrochemical oxidation of BPA. Ntsendwana et al [3] reported that electro-chemical detection of 4, 4'-(propane-2, 2-diyl) diphenol using graphene-modified glassy carbon electrode and found that the detection limit of this method was as low as 4.689×10^{-8} mol/L.

The aim of this work was to increase the electro-catalytic performance and stability of β-PbO_2 electrode by doping with metal oxide through electro-deposition technique. The morphology and crystal structure and electro-catalytic characterization of composite electrodes were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry and the accelerated life testing. And composite electrodes was selected as electrode for electro-catalytic degradation of BPA simulated wastewater, the influence of parameters such as initial solution pH, applied voltage and supporting electrolyte concentration were investigated. Furthermore, the degradation kinetics and mechanisms of BPA were also discussed.

2. EXPERIMENTAL SECTION

2.1. Materials and instruments

4,4'-(propane-2,2-diyl)diphenol (BPA, Sinopharm Chemical Reagent Co., Ltd.), tertiary butanol, cerium oxide, silver sulfate (Tianjin Damao Chemical Reagent Factory), lead dinitrate, ammonium iron sulfate, mercuric sulfate, sodium chloride and oxalic acid (Shantou Xilong Chemical Reagent Factory), potassium dichromate (Shanghai Surui Chemical Reagent Co, Ltd.), sulfuric acid and phosphoric acid (Shanghai Zhengqi Chemical Reagent Co. Ltd.), all of chemical were analytical grade reagent and used as received.

DC Power Supply (WYK-1503, Jiangsu Powerware Electric Manufacturing Co., Ltd.), pH meter (DELTA-320, Mettler Toledo Instrument Co., Ltd.), Electrochemical workstation (CHI 660C, Shanghai Zhenhua Instrument Co., Ltd.), Scanning electron microscopy (Acquity UPLC LCT Premier TM XE, Waters, UV–vis absorbance spectra(UV-175, Shimadzu), Atomic absorption spectrometer (WFX-130A, Beijing Rayleigh Analytical Instrument Co. Ltd) and XRD (DX-2700, Shanghai precision instruments and meters Co., Ltd.).

Products were analyzed by the Finnigan MAT ITD 800 GC/MS spectrometer (Finnigan Mat Itd). AHP-5 (5% diphenyl and 95% dimethylpolysiloxane) silicon capillary column (30 m × 0.25 mm, thickness 0.25 μm) was used in gas chromatography. Column temperature was programmed to rise from 100 to 300 ^{0}C at 15 ^{0}C /min. Injector was heated at 250 ^{0}C. Ionization source was electron impact (EI) with an electron energy 70 *eV* and was maintained at 200 ^{0}C. Helium was used as carrier gas with a flow rate of 1.0 mL/min.

2.2. Electrode preparation

2.2.1. Titanium plate pretreatment

Titanium plates with the size of 5 cm × 10 cm × 0.2 cm and the effective area of 5 cm × 5 cm. Ti plates were thoroughly polished with sand paper, followed by acetone cleaning for about 10 min in an ultrasonic bath to remove sand particles. After these physical treatments, the Ti plates were submerged in 40% NaOH for 20 min to remove organic compounds absorbed on the surface. Then, Ti plates were stewed in 10% oxalic acid solution for 2 h until oxalic acid titanium formed on Ti plate’s surface. After these pretreatment, Ti plates were stored in 1% oxalic acid solution [15-16].

2.2.2.CeO_2/β-PbO_2/Ti electrode preparation

The Ti plate stored in 1% oxalic acid solution was rapidly inserted into electrodeposition solution which consisted of 0.1 mol/L nitric acid, 5 mmol/L cerium oxide and 0.5 mol/L lead nitrates. The cathode was Ti plate with the same area. The applied current density was 20 mA/cm^2 and different thickness CeO_2/β-PbO_2/Ti obtained by different time [17].

2.2.3. Electrochemical performance of CeO_2/β-PbO_2/Ti electrode

The electrolysis of aqueous solutions containing BPA was carried out in an electrochemical cell with an effective volume of 360 mL (12 cm × 6 cm × 5 cm). The CeO_2/β-PbO_2/Ti was employed as the working electrode. In all cases, Ti plate with the same area was used as the cathode. The electrolytic cell was made by PTFE material and experimental setup adopted opposite side for electrode and cathode. COD_{Cr} in solution before and after electrolyzing were chosen as the parameter to evaluate the process of electro-catalytic degradation. The COD_{Cr} removal efficiency was calculated by the following formula:

$$COD_{Cr}(\%) = (1 - \frac{[COD_{Cr}]}{[COD_{Cr}]_0}) \times 100\%$$

Where $[COD_{Cr}]_0$, $[COD_{Cr}]$ were the COD_{Cr} value at the initial and the given time, respectively and COD_{Cr} was measured by the dichromate method.

3. RESULTS AND DISCUSSION

3.1. Characterization of CeO_2/β-PbO_2/Ti electrode

3.1.1. SEM characterization

The surface morphology and composition of the CeO_2/β-PbO_2/Ti electrode was characterized by SEM. Fig.1 showed the SEM images of β-PbO_2/Ti electrode (a) and CeO_2/β-PbO_2/Ti electrode (b) with magnification of 3000 times. The β-PbO_2/Ti electrode had a uniform and typical pyramidal shape. When CeO_2 was introduced to the electrode, the morphology of electrode was more regular, with better oriented crystals of higher size [18], and the electrode surface was more porous. It was suggested that introducing CeO_2 to Ti plate could effectively improve its structure [15]. Therefore, it will provide better electro-activity in the electro-catalytic degradation of BPA.

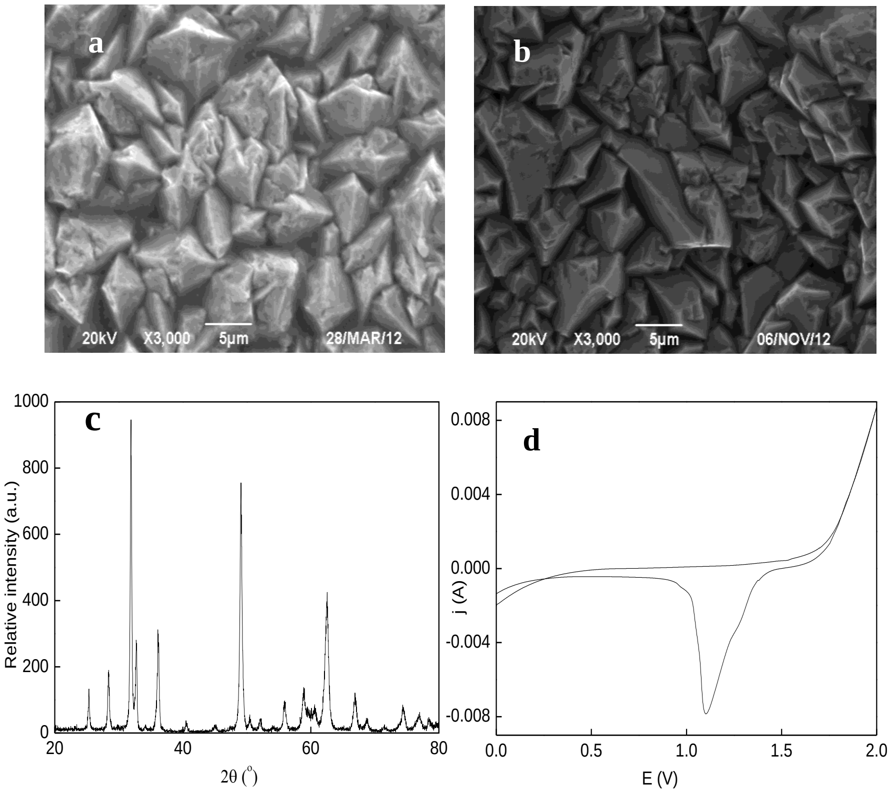

Figure 1. Characterization of electrode analysis by SEM pattern β-PbO_2 (a) and CeO_2/β-PbO_2 (b), XRD images of CeO_2/β-PbO_2 (c), cyclic voltammetry curve of Co_3O_4/β-PbO_2 (d).

3.1.2. XRD characterization

The composition structures of electrode and the composition were identified by XRD and the analysis was performed using DX-2700 X ray diffractometer analyzer, copper electrode target, graphite monochromator, tube voltage of 40 kV, scanning rate of 6°/min and sampling interval of 0.02°. Fig.1c showed the XRD patterns of the electrode of $CeO_2/\beta\text{-}PbO_2/Ti$ electrode. Three diffractive peaks at 25.4º, 32º, 49.1º were observed. After adding CeO_2, the electrode crystallization was mainly unchanged and it was still the $\beta\text{-}PbO_2$. But the diffractive peaks became higher by adding CeO_2 into electrode [16].

3.1.3. Cyclic voltammetry curve

Typical cyclic voltammograms of $CeO_2/\beta\text{-}PbO_2/Ti$ electrode in 0.5 mol/L H_2SO_4 solution containing 20 mg/L BPA were shown in Fig.1d. The curves were recorded from 0 V to 2.0 V with a scan rate of 100 mV/s. Fig.1d showed that $CeO_2/\beta\text{-}PbO_2/Ti$ electrode had a higher oxygen evolution potential of 1.8 V. This high oxygen evolution indicated oxygen formation was not easily took place on $CeO_2/\beta\text{-}PbO_2/Ti$ electrodes [19-21]. In the reversed potential scan, a reduction peak between 1.0 and 1.4 V. Reduction peak may correspond to the generation of Pb^{2+} from PbO_2 Pb^{4+} to Pb^{2+} and Ce^{4+} to Ce^{3+} at about 1.28V[15, 18, 22]. There was no oxidation peak appeared in Fig.1d, suggesting that BPA can not be decomposed by direct electrochemical oxidation on this electrode surface, the results was in good agreement with Liu et al [16,21]. Therefore, the BPA degradation must be achieved via indirect oxidation, mediated by active radical (such as OH·) and intermediate products produced in electrolytic process [19-20].

3.1.4. Corrosion resistance characterization of $CeO_2/\beta\text{-}PbO_2/Ti$ electrode

To characterize electrode corrosion resistance, the $CeO_2/\beta\text{-}PbO_2/Ti$ electrode and $\beta\text{-}PbO_2/Ti$ electrode were used as anode, respectively and the voltage were 100 V. 20 mg/L BPA in 0.1 mol/L sulfuric acid was continuously electrolyzed for 12 h. As measured by flame atomic absorption spectrophotometer, Pb concentration in electrolytic solution was 0.084 mg/L and 0.013 mg/L after the electrolysis, respectively. Thus the $CeO_2/\beta\text{-}PbO_2/Ti$ electrode corrosion rate was calculated to only 0.05％/d in strong acidic conditions. It was suggested that $CeO_2/\beta\text{-}PbO_2/Ti$ electrode had excellent corrosion resistance. In addition, soluble Pb concentration was much lower than the provisions of the maximum permissible emission concentration (1.0 mg/L) by GB8978-1996 of China. Therefore, secondary pollution problem can be neglected.

3.1.5. Accelerated lifetime test

Anti-corrosion performance of $CeO_2/\beta\text{-}PbO_2/Ti$ electrode was investigated by using accelerated lifetime test with current density of 2.0 A/cm^2 in the medium of 1.0 mol/L H_2SO_4 solution at 60 ℃.

The volume of the electrolyte was 250 mL. At the beginning of electrolytic, the potential of cell was about 5 V. The service life of the CeO_2/β-PbO_2/Ti electrode was defined as the operation time when the anodic potential increased by 10 V [19, 23].

CeO_2/β-PbO_2/Ti electrode displayed excellent activity under accelerated life test conditions up to 120 h and the result was shown in Fig.2. And then, a sharp potential increase was observed. In order to assess the actual life, a rough evaluation could be made using the method by Hine et al [24]. It could be obtained electrode lifetime was 7.21 year [15].

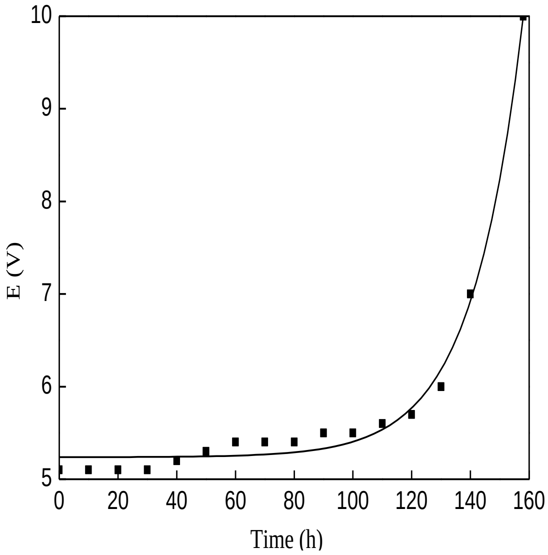

Figure 2. Cell potential variation with time in accelerated life test for CeO_2/β-PbO_2/Ti electrode (H_2SO_4, 1 mol/L; T, 60℃ and current density, 2 A/cm^2)

3.2. Electrochemical degradation of BPA aqueous solution using CeO_2/β-PbO_2/Ti electrode

3.2.1. Effect of supporting electrolyte

The influence of the types of supporting electrolyte on COD_{Cr} removal efficiency was shown in Fig.3a at BPA concentration of 20 mg/L, applied voltage of 20 V and plate spacing of 7 cm for 1.5 h electrolysis. Supporting electrolytes were K_2HPO_4, Na_2SO_4 and NaCl, respectively.Fig.3a showed that chloride ions have a significant effect on the COD_{Cr} removal efficiency due to the formation of strong oxidant [Cl_2, ClO_2 and ClO^-] and the COD_{Cr} removal efficiency could be above 95.7% [25]. Polcaro et al[26] reported that the electro-degradation of dichloroaniline with BDD electrode, lead to lower mass transfer limitations and can explain the faster degradation, for both metabolites, observed when NaCl was the electrolyte.

$2Cl^- - 2e^- \rightarrow Cl_2$ (1)

$Cl^- + 2OH\cdot - 2e^- \rightarrow ClO\cdot + H_2O$ (2)

$Cl_2 + H_2O \leftrightarrow HOCl + Cl^- + H^+$ (3)

HClO species was more dominant when the pH of solution was about 6 [27] and its oxidation potential was greater than Cl_2 [28]. Therefore reaction (3) had been advantageous particularly in the electrochemical application of BPA degradation.

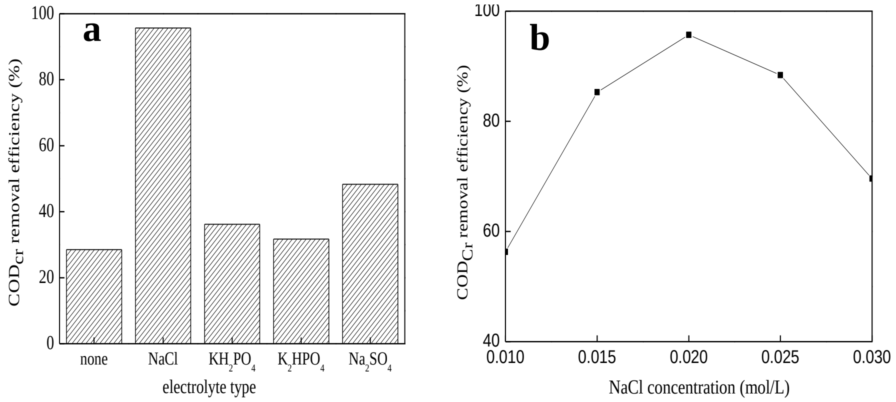

Figure 3. Effect of (a) supporting electrolyte type and (b) supporting electrolyte concentration on BAP COD_{Cr} removal efficiency (BPA 20 mg/L, applied voltage 20 V and electrolysis time 1.5 h).

3.2.2. Effect of NaCl supporting electrolyte concentration

It was important to investigate the effect of electrolyte concentration since actual wastewater usually contains certain amount of salts. Fig.3b showed the effect of NaCl concentration on COD_{Cr} removal efficiency during the electro-degradation of BPA at BPA concentration of 20 mg/L for 1.5 h electrolysis. Proper NaCl concentration could improve the performance and effectiveness of the electrochemical process. When NaCl concentration was 0.020 mol/L, the COD_{Cr} removal rate reached maximum. The addition of NaCl to BPA would increase the production of oxidants, such as Cl_2, HOCl and ClO^- [29]. However, when NaCl concentration was more than 0.020 mol/L, COD_{Cr} removal efficiency was decline and it was because that the excess electrolyte concentration may lead to the occurrence of side reaction [30].

3.2.3. Effect of electro-catalytic time

When NaCl supporting electrolyte concentration of 0.020 mol·L^{-1} and applied voltage of 20 V for 1.5 h electrolysis, the relationship between electro-catalytic time and the degradation efficiency of COD_{Cr} was shown in Fig.4a. The $[COD_{Cr}]/[COD_{Cr}]_0$ of BPA aqueous solution decreased with the increase of electrolysis time and scope of variety became smaller and smaller. It was because that the BPA concentration was high at the initial stage, and the influence of system by concentration polarization was not significant. Therefore, BPA can spread to the electrode surface and react with strong oxidizing free radicals, and then BPA concentration became less and less[31].

3.2.4. Effect of initial BPA concentration

Effect of initial concentration of BPA on the $[COD_{Cr}]/[COD_{Cr}]_0$ of BPA aqueous solution was shown in Fig.4b at NaCl supporting electrolyte concentration of 0.020 mol/L and applied voltage of 20

V for 1.5 h electrolysis. The results showed that with the increase of the BPA initial concentration, the COD_{Cr} removal decreased. At low initial concentration, the electro-catalytic reaction was faster than diffusion, the BPA was expected to be degraded completely [32]. When the initial concentration increased, more organic substances were transferred to the surface of electrode and the COD_{Cr} degradation efficiency would decrease with increased initial concentration of BPA [33]. This might be explained that the ratio of hydroxyl radical and other reactive species to BPA concentration decreased with the increase in initial concentration [31]. And the decrease in rate of COD_{Cr} degradation could lead to the possible fact that the competitive consumption of hydroxyl radical for oxidizing the intermediate compounds [34].

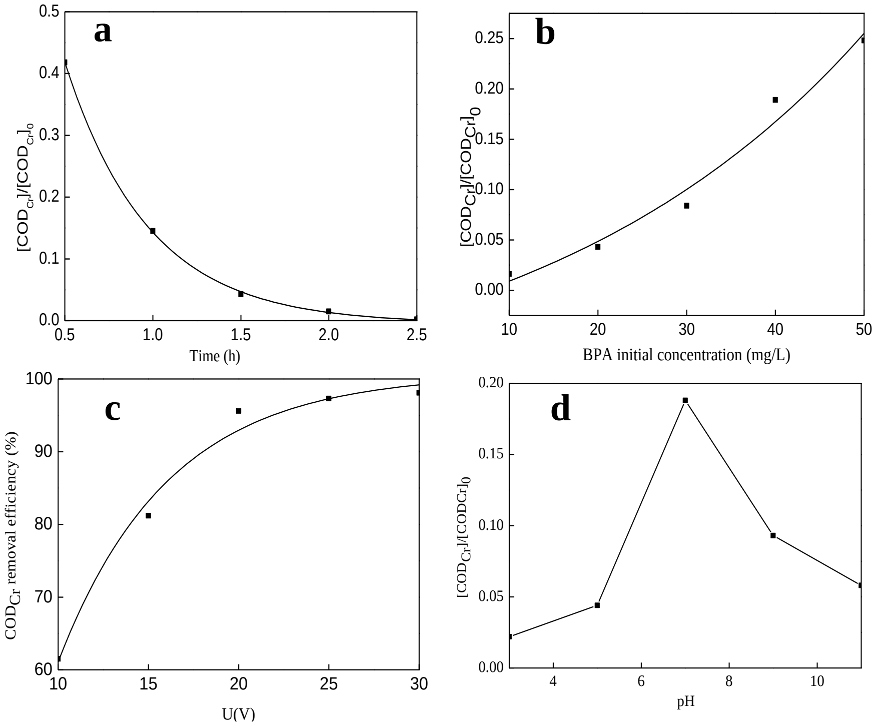

Figure 4. Effect of various electro-catalytic degradation factors on BPA removal efficiency (a) electrolysis time, (b) initial concentration of BPA, (c) applied voltage, (d) initial solution pH.

3.2.5. Effect of electrolysis voltage

Fig.4c presented the effect of electrolysis voltage on COD_{Cr} removal efficiency at BPA concentration of 20 mg/L for 1.5 h electrolysis. From Fig.4c, with the electrolysis voltage increased, the degradation efficiency of COD_{Cr} gradually increased. As the voltage increased, the current in the electrolytic system strength was enhanced and the number of hydroxyl radical had a corresponding increasing, so the degradation rate was increased. However, if the voltage was too high, it might lead to the increase of the energy consumption.

3.2.6. Effect of initial pH value

Initial pH value was another important factor that influenced the degradation reaction and crucial importance in the electro-catalytic degradation process. Fig.4d showed the effect of initial pH on $[COD_{Cr}]/[COD_{Cr}]_0$ of BPA at BPA concentration of 20 mg·L^{-1} and applied voltage of 20 V within 1.5 h of the reaction. It was noted that initial pH strongly affected electro-catalytic degradation efficiency. The COD_{Cr} removal was higher in acid or alkaline conditions, which lower removal was observed at neutral pH value. Ma et al [29] reported that the COD removal reached 96.43% at pH=3 and lower removal at higher pH value. In the acid condition, a large number of hydrogen ions can effectively suppress the occurrence of secondary reaction, accelerate the degradation of BPA. Ju et al [35] studied the electro-catalytic degradation of BPA on a Ti-based PbO_2-ionic liquids electrode and concluded that more BPA existed in the form of anion under the higher pH and could facilitate the degradation of BPA. Kaneco et al [36] concluded that more hydroxide ions would exist in the solution at a higher pH inducing the generation of more hydroxyl radical, which subsequently enhanced the degradation rate of BPA. However, the COD_{Cr} removal efficiency was higher in acid than in alkaline conditions. It was because that the oxidation potential of hydroxyl radical was higher in acid condition (+2.85V) than in alkaline condition (+2.02V) [37-38]. And in the acid condition, a large number of hydrogen ions can effectively suppress the occurrence of secondary reaction, accelerate the degradation of BPA.

3.3. BPA degradation product analysis

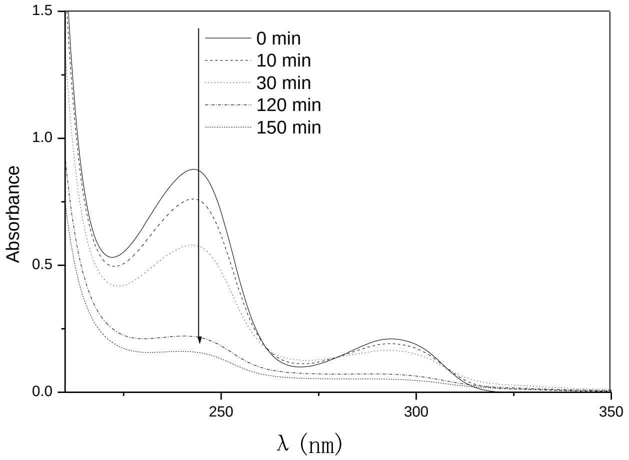

Figure 5. The ultraviolet absorption spectrum of BPA (BPA 20 mg/L, NaCl 0.020 mol/L and applied voltage 20 V).

The UV absorption spectrum of the BPA degradation solution after different periods of electrolysis was shown in Fig.5. It was indicated that the $CeO_2/\beta\text{-}PbO_2/Ti$ electrode was very effective for BPA degradation and could entirely degrade the simulative wastewater containing BPA. There were two obvious absorption peaks at 243 and 294 nm and the absorption peaks decreased with the increase of electrolysis time. When electrolysis time reached 150 min, these two peaks almost totally disappeared. The main organic degradation products identified by GC–MS analysis were 1,2-dichloropentane (64%), Heptanoic acid (26%) and 1,2-dichloroethane (10%). In addition, the total organic carbon (TOC) had decreased by 68.6%, which indicated that most of the organic carbon converted into CO_2.

3.4. Analysis of BPA possible degradation dynamics

The removal of BPA was mainly due to the contribution of hydroxyl radical [16], and hydroxyl radical was produced from H_2O at β-PbO_2 surface [39]. Under the conditions of other same parameters, with the initial concentration of BPA increased, the COD_{Cr} and organic molecules at the anode surface increased. It will lead to the decrease of hydroxyl radical production, and affect the degradation reaction rate. Therefore, the concentration of OH radical was related to BPA initial concentration and *k* $[\cdot OH]^m$ can be rewritten as $k''C_0^p$:

$$k' = k[\cdot OH]^m = k''C_0^p \tag{4}$$

Where C was BPA concentration after electrolyzing for *t* min, (mg/L); [OH·] was OH radical concentration, (mg/L); *k* was reactions kinetic parameters; m and n were reaction order; m was reaction order.

BPA removal rate equation can be simplified to equation (5):

$$-\frac{dC}{dt} = -kC^n[\cdot OH]^m = k^{'}C^n \tag{5}$$

Where n was reaction order.

According to formula (5), equation (6) can be obtained：

$$\ln k' = \ln k'' + p\ln C_0 \tag{6}$$

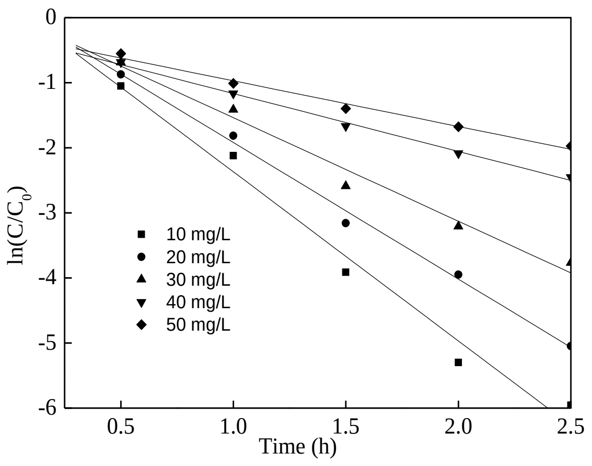

Figure 6. The kinetic fitting curve of BPA removal efficiency (NaCl 0.020 mol/L and applied voltage 20 V).

When n=1, the first order kinetics curve fitting of different BPA concentration was shown in Fig.6.The higher of fitting correlation coefficients (R=0.996±0.05) indicated that BPA degradation followed apparent pseudo-first-order reaction process.

p and k" were obtained by fitting k' with C_0 (Fig.7). The correlation coefficient of 0.97 suggested that equation (5) was tenable and OH radical concentration associated with BPA concentration was feasible. p=-0.845，k"=4.04×10^{-3} (mg/L·s) can be obtained according to the slope and intercept of the straight line. Therefore, BPA removal rate equation can be expressed as:

$$-\frac{dC}{dt} = 4.04\times10^{-3}C_0^{\ -0.845}C \qquad (7)$$

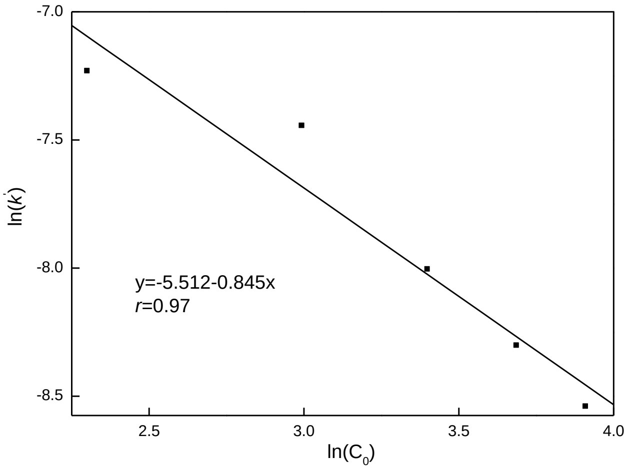

Figure 7. Effect of initial concentration of BPA on concentration of hydroxyl radicals

4. CONCLUSIONS

(1)The electro-catalytic degradation of BPA on CeO_2/β-PbO_2/Ti electrode was carried out successfully. SEM and XRD and cyclic voltammetry curve showed CeO_2/β-PbO_2/Ti electrode had a good structure and electro-catalytic performance.

(2)When the supporting electrolyte was NaCl, BPA initial concentration was 20 mg/L, applied voltage was 20 V, plate spacing was 7 cm and solution initial pH was 5, COD_{Cr} removal efficiency reached up to 95.7% for 1.5 h electrolysis. The BPA electro-catalytic degradation was mainly caused by OH radical and other strong oxidation reactive species. The degradation followed pseudo-first-order reaction process.

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