Int. J. Electrochem. Sci., 13 **(2018)** 7141 – 7156, doi: 10.20964/2018.07.76

**International Journal of
ELECTROCHEMICAL
SCIENCE**
www.electrochemsci.org

Electrochemical Degradation of Bisphenol A Using Different Modified Anodes Based on Titanium in Aqueous Solution

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Received: 24 March 2018 / *Accepted:* 16 May 2018 / *Published:* 5 June 2018

Electrochemical degradation of bisphenol A (BPA) was researched by using Ti/SnO_2-SbO_2/PbO_2, Ti/Ti_4O_7, Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes in aqueous solution. The electrochemical degradation conditions were acquired by investigating the effect of different working factors, such as current densities (5-40 mA/cm^2), initial pH (3.4-12.0) and different plate distance (0.5-3 cm). The best performance of BPA degradation and COD removal was obtained with anodes of Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2, the Ti/RuO_2-IrO_2 anode exhibited a moderate capability to degrade BPA, and Ti/RuO_2 showed the lowest efficiency in BPA degradation. Samples were separated by high performance liquid chromatography (HPLC), and the intermediates products were identified with mass spectrometry (MS). The pathways and mechanisms of the electrochemical degradation of BPA process were researched and it could be divided into the following three steps. First, the BPA was believed to be attacked by •OH radical generated from water electrolysis and then decomposed into one-ring aromatic compounds. Subsequently, these one-ring aromatic compounds could be oxidized and converted to short chain aliphatic acids. Finaly, all the intermediate compounds were mineralized into CO_2 and H_2O. The Ti/Ti_4O_7 anode had the highest oxygen evolution potential of 2.4 V, for the Ti/SnO_2-SbO_2/PbO_2 anode it was 1.6 V, the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes had similar oxygen evolution potentials of 1.1 V and 1.2 V, respectively. By comparing the different electrodes, the Ti/Ti_4O_7 anode have high oxygen evolution potential and a good performance of organic degradation, it is strong potential material for effective electrochemical degradation of BPA and other similar structure of organic pollutants in wastewater.

Keywords: Bisphenol A (BPA); Electrochemical degradation; Ti/Ti_4O_7; Hydroxyl radical; Mechanism;

1. INTRODUCTION

In recent years, much industrial wastewater containing refractory organic pollutants, such as aromatic hydrocarbons, phenolic compounds and pesticides, due to its toxicity and hard biodegradation, have become an intractable environmental problem and potential hazard towards human and animal health. BPA is an abroad raw material which applied in many chemical goods, such as phenolic resin, flame retardant and epoxy resins [1, 2, 3]. However, the BPA and its derivative can spill over from chemical goods through the hydrolytic cleavage of the ester bond under basic or acidic conditions, which we can found in a variety of environmental media, such as air, soil, drinking water, wastewater, food and drinks [4]. Although we cannot know clearly the content of BPA in the nature environment, it is well proved that the low content of BPA continuous exposure on the environment could cause male infertility, immune system disorders, heart disease. There has researched that BPA concentration of 120-300 mg/L can be dissolved in water and 3.0-3.5 mg/L was discovered in freshwater Rainbow Trout [5]. Taking into account the serious adverse effects of BPA on human health and the environment, there is an urgent need to find an effective method to remove it [6].

The electrochemical degradation is a kind of advanced oxidation technology, which has been widely used in sewage treatment in recent years. Electrochemical degradation is suitable for low-volume applications and has good environmental compatibility [7]. The electrode surfaces can generate strong oxidizing active substances to remove pollutants. Advanced oxidation technology (AOP) is applied to a variety of optics, acoustics, electricity, magnetism and other physics [8, 9]. The sonochemical reaction was carried out to improve the efficiency through increasing the formation of ▪OH radical. Organic pollutants can be degraded into CO_2 and H_2O through electrochemical process of a direct anodic oxidation or an indirect oxidation [10, 11]. The electrocatalytic degradation of BPA was induced by ▪OH radical and other oxidative species [12]. The degradation products mainly consisted of small straight chain compounds, CO_2 and H_2O. It is a prospective technology, electrochemical oxidation is applied effectively to degrade complex structure of organic pollutants due to its simple operation, low energy consumption, environment friendly and safety [13]. Electrochemical degradation of BPA and acid green dye were studied by using composite electrodes [14, 15]. AOP have been successfully used for the depuration of domestic sewage and industrial wastewater [16].

The TiO_2 electrode was abroad applied for electrochemical degradation of stubborn organic pollutants such as dyestuff because of its favorable electrochemical performance, high stability and high oxygen evolution potential [17, 18]. Many researches used TiO_2 electrodes which coated TiO_2 films on the surfaces of conductive substrates for photoelectrocatalytic degradation of organic pollutants [19, 20].

Interestingly, the electronic properties of TiO_2 can be drastically transformed by establishing oxygen deficiencies within the crystalline lattice what is called Magnéli-phase titanium oxides with a generic formula of Ti_xO_{2x-1} ($4 \leq x \leq 10$) [21]. Especially, Ti/Ti_4O_7 electrode showed the highest conductivity of $\approx$1500 S/cm [22]. Ti_4O_7 electrode has attracted much attention due to its high oxygen evolution potential, thermal stability and good corrosion resistance [23, 24]. In recent years, many kinds of metal oxide electrodes, such as SnO_2, PbO_2, IrO_2 and TiO_2, have been widely used in the electrochemical degradation of organic pollutants [25]. The different styles of metal oxide layers have different oxygen evolution potential. Researchers successfully introduced a new porous Ti/SnO_2-Sb_2O_3/PbO_2 electrode prepared by using porous Ti as the matrix [26]. Those studies showed that porous Ti were an important matrix in changing the capability of PbO_2 electrodes compared with traditional plane of Ti matrix [27, 28]. Li et al [29] applied electrodes based on RuO_2 and IrO_2 in chlorine-alkali industry and Toshihide Arikawa et al [30] used the mixed RuO_2/IrO_2 anode to remove pollutants in sulfuric acid media. In general, a desirable electrode should have the properties of high stability, high activity and high oxygen evolution potential.

In this experiment, four different electrodes of Ti/Ti_4O_7, Ti/RuO_2-IrO_2, Ti/SnO_2-SbO_2/PbO_2 and Ti/RuO_2 were applied for BPA degradation. The electrochemical degradation conditions were acquired by investigating the effects of different working factors, such as current densities (5-40 mA/cm^2), initial pH (3.4-12.0) and different plate distance (0.5-3 cm). The change of pH during the BPA degradation were caculated by pH meter. Four different titanium-based materials have different oxygen evolution potential which can influence the production of hydroxyl radicals effectively. Those intermediate compounds during BPA degradation by using different electrodes were identified with HPLC and MS.

2. MATERIALS AND ANALYTICAL METHODS

2.2. Preparation of four types electrode

There were four different electrodes of Ti/SnO_2-SbO_2/PbO_2, Ti/Ti_4O_7, Ti/RuO_2 and Ti/RuO_2-IrO_2 which were applied for BPA degradation. A Pt grid was used as the counter electrode. Tissot et al. have used Ti and Pt mesh, Pt/Ti, SnO_2/Ti and carbon fiber electrodes as the anodes for electrochemical removal of BPA [31]. Ti/RuO_2-IrO_2 and Ti/RuO_2 were two of the most widely used electrochemical electrodes, and the Ti/SnO_2-SbO_2/PbO_2 and Ti/Ti_4O_7 anodes were selected for electrocatalysis in organic oxidation. Ti/SnO_2-SbO_2/PbO_2, Ti/Ti_4O_7, Ti/RuO_2-IrO_2 and Ti/RuO_2 electrodes were cut into square plates (2.5×4 cm). The Ti/RuO_2-IrO_2, Ti/RuO_2 and Ti/SnO_2-SbO_2/PbO_2 electrodes were prepared by Baoji ZhiMing special metal co., LTD. The Ti/Ti_4O_7 anode was purchased from Magneli Materials LLC, USA. The TiOx particles were incorporated into the plasma stream by using argon as a carrier gas. It was sprayed onto the Ti substrate by plasma melting to form a roughened surface [32].

2.3. BPA electrolysis

All of chemicals in this experiment were reagent grade. Bisphenol A (reagent grade $\geq$ 99%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (shanghai, China). A 100-mL glass beaker was used as a container for degradation of BPA. All water solution in this experiment was used for ultrapure water. The pH values of solution were adjusted by adding 0.1M H_2SO_4 or 0.1M NaOH solutions. All of the current density and voltage in this experiment were written down. Electrochemical degradation was provided with a voltage instrument which was regarded as the power source.

In this experiment, 70 ml of 25 mg/L BPA solution was kept in glass beaker with 0.1 mol/L Na_2SO_4 as the electrolyte. All anodes were tested with different current densities (5, 10, 20 and 40 mA/cm^2), plate distance (0.5, 1.0, 2.0 and 3.0 cm) and different pH value (3.4, 5.1, 8.2 and 12.0), separately. The samples of the electrolysis were collected from the solution at different time for testing the BPA concentration. Electrolysis was conducted with constant stirring at 450 rpm. The electrolysis testing temperature was set at 303 K. The results of every experiment condition were measured three times to eliminate errors.

Chemical oxygen demand (COD) was determined according to the Standard Methods by UV–vis spectrometer (Shimazu UV-1800). The percentage removal efficiency of COD is calculated from this equation:

$$\text{COD removal efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad (1)$$

In Eq. (1), C_0 and C_t are the initial and the times of t Chemical oxygen demand (g/L), respectively.

2.3. Electrochemical measurement

A CHI600C electrochemical workstation with three-electrode system was employed for electrochemical measurement. The Ti/SnO_2-SbO_2/PbO_2, Ti/Ti_4O_7, Ti/RuO_2-IrO_2 and Ti/RuO_2 electrodes were served as the work electrodes with a Pt wire electrode as counter electrode. The saturated calomel electrode was regarded as the reference electrode. The oxygen evolution potential (OEP) of the four different electrodes were tested for the linear polarization curves in 1.0 mol/L H_2SO_4. The linear polarization curves technique was tested at a scan rate of 50 $mV \cdot s^{-1}$.

2.4. Analytical methods

The different pH value of solution was recorded with a pH meter (PHS-3C, Shanghai). The concentration of intermediate compounds and BPA during the degradation, including organic acids and one-ring aromatic compounds, were measured with the high-performance liquid chromatograph (HPLC). A mixture of 30% water and 70% methanol (v/v) were used as the mobile phase. A BEH C_{18} column (5 μm*250 nm*4.6 mm) with the temperature of 25 ℃ was applied to separate the organic acids and aromatic compounds. The mobile phase flow rate was set as 0.8 ml/min and the wave length was performed at 280 nm.

3. RESULTS AND DISCUSSION

3.1. Effect of different current density

The ability of BPA degradation is affected by current density. Especially •OH radical generated ability from water electrolysis rely on the provider of current density. So different densities (5, 10, 20 and 40 mA/cm^2) was set to discuss the performance of current density on the remove rates of BPA. It can be found that the remove ratio of BPA increased with the increase of the provided current density. It was discovered that the conspicuous difference performance of BPA removed among the four different electrodes. As shown in Fig. 1, the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 electrodes displayed good electrochemical performance with a current density of 5 mA/cm^2 and it only took 120 min to complete BPA degradation. While increased the current density to 10 mA/cm^2, the rate of BPA degradation was double of the Ti/SnO_2-SbO_2/PbO_2 and Ti/Ti_4O_7 electrodes and it took less than 90 min to complete BPA degradation. But the Ti/RuO_2-IrO_2 and Ti/RuO_2 anodes were destructed only slightly under the same electrochemical experimental condition. The Ti/RuO_2 and Ti/RuO_2-IrO_2 exhibited better performance when increasing the current density from 5 mA/cm^2 to 40 mA/cm^2, but the BPA remove rates were still lower than that of the Ti/SnO_2-SbO_2/PbO_2 and Ti/Ti_4O_7 anodes. With the current density gradually increasing to 40 mA/cm^2, the Ti/RuO_2 anode had a less increasing trend of BPA remove rate than other three anodes. However, increasing the current density to 20 mA/cm^2, it was almost double charge consumption of BPA degradation than that of 5 mA/cm^2.

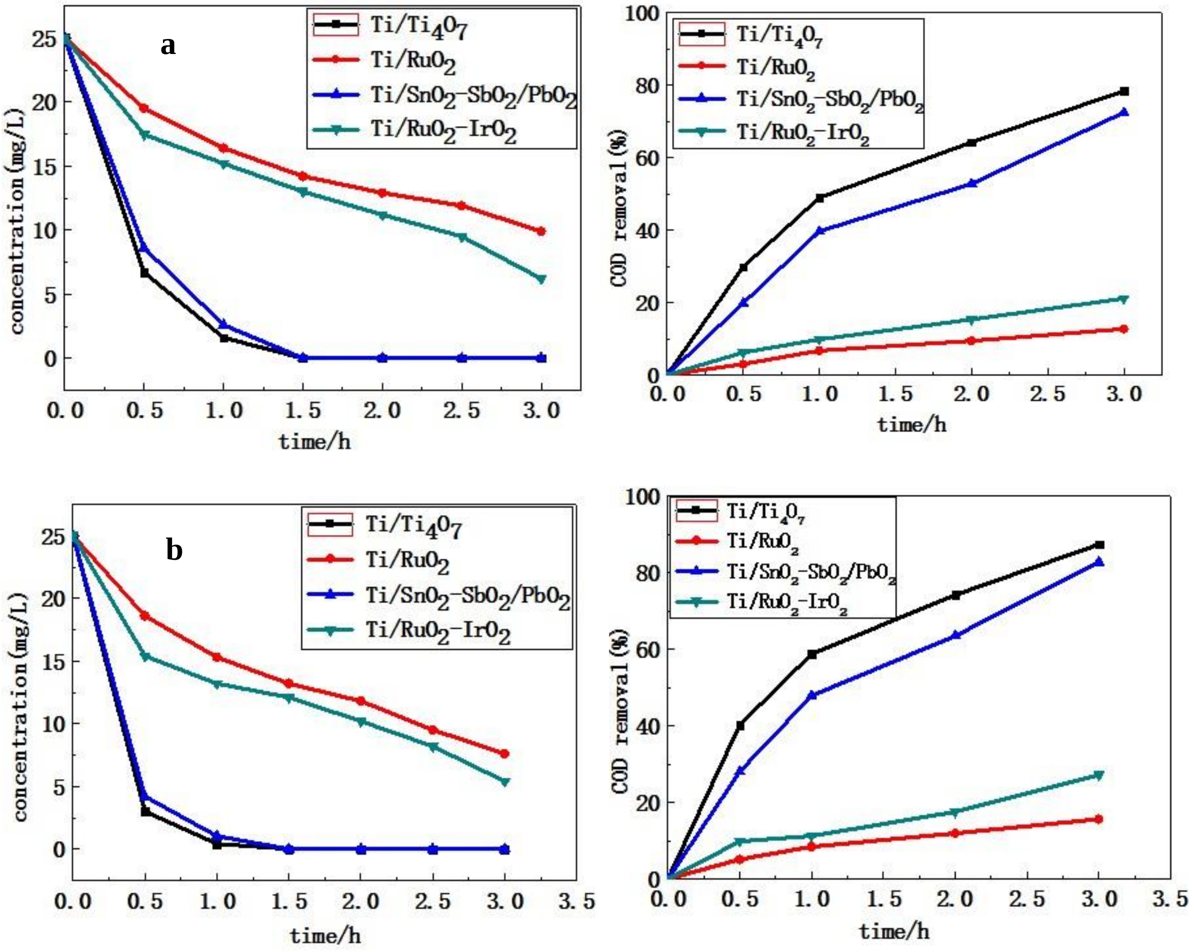

Figure 1. Electrochemical degradation and COD removal of 25 mg/L BPA as a function of electrolysis time at different current density, a: 5 mA/cm^2; b: 10 mA/cm^2.

Obviously, there were great differences in COD removal among the four types of anodes. The BPA solution of 25 mg/L was prepared with the initial COD of 112 mg/L. With a current density of 20 mA/cm^2, almost 92.4% of COD could be removed for the Ti/Ti_4O_7 anode. With the current density of 40 mA/cm^2, the higher COD removal rate of 95.8% could be obtained. For the Ti/SnO_2-SbO_2/PbO_2 anode at the current density of 20 mA/cm^2, the COD remove rate was 90.7%. The result of the COD remove rate was in following order: Ti/RuO_2<Ti/RuO_2-IrO_2<Ti/SnO_2- SbO_2/PbO_2<Ti/Ti_4O_7. The Ti/RuO_2-IrO_2 and Ti/RuO_2 anodes displayed weak COD remove capacity with the same current density among the four anodes. The data of BPA concentration and COD remove rates of four types anodes with differents current density were listed in Table 1. With the 40 mA/cm^2 current density, the COD remove rates for the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anodes were increased to 95.8% and 92.1%, respectively. With the 40 mA/cm^2 current density, the COD remove rates for the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes were increased to 23.4% and 35.7%, the COD remove rates of the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anode were increased to 95.8% and 92.1%, separately. The above results show that there were no significant growth of BPA degradation and COD removal with increasing current density, suggesting than low current density is sufficient for the electrochemical process. In addition, low voltage is good for the stability and durability of SnO_2-SbO_2, Ti_4O_7 and RuO_2-IrO_2 coating layer.

Table 1. The efficiency of the BPA degradation (electrolysis time: 3h)

Electrodes	BPA concentration (mg/L)				COD remove rate (%)			
	5 mA/cm^2	10 mA/cm^2	20 mA/cm^2	40 mA/cm^2	5 mA/cm^2	10 mA/cm^2	20 mA/cm^2	40 mA/cm^2
Ti/Ti_4O_7	0	0	0	0	78.3	87.3	92.4	95.8
Ti/SnO_2-SbO_2/PbO_2	0	0	0	0	72.4	82.7	90.7	92.1
Ti/RuO_2-IrO_2	6.2	4.9	4.0	3.4	21.1	27.1	31.9	35.7
Ti/RuO_2	9.9	7.6	6.4	5.9	12.7	15.6	19.8	23.4

3.2. Effect of different initial pH values

The different initial pH of the solution can change the surface characteristic feature of anode, the electrolytic state of organic product, as well as the transformation ratio of •OH radical and other kinds of reactive oxygen apply for the organic pollutants degradation [33]. The pH value of solution was another importance factor influencing the BPA degradation. Different initial pH values and the pH change were researched during the degradation procedure. Fig. 2 showed the efficiency of different initial pH value for the BPA degradation. At the pH of 3.40, the BPA degradation rate was lower than that at an initial pH value of 5.11 in the electrolysis time of 30 min. With the initial pH of 3.40 for 180 min, the BPA remove rates of both the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anodes were 96.4% and 92.4%, while the BPA remove rates of the Ti/RuO_2 and Ti/RuO_2-IrO_2 anode were much lower. It was found that there was a rapid growth in BPA degradation in 30 minutes when increasing the initial pH value to 8.20. Compared with acid condition, the weakly alkaline condition was more advantageous for the BPA remove, which could generate more •OH radical from water electrolysis and thus leading to a higher efficiency of BPA degradation. With the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anodes, the BPA were almost completely degraded in 60 min. The Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes showed best performances with pH value of 8.20, which obtained the BPA remove rates of 80% and 88.8%, separately. However, it was interesting to notice that the degradation rate of BPA decreased again under strong alkaline condition (pH=12.0). It was leaded to the ionization of BPA and the production of bisphenolate anion since those intermediate products pKa value were in the range of 9.60-10.20 [33]. During the degradation process, electrolysis produced •OH to break the structure of BPA resulting in the decline of pH value. The strong alkaline condition (pH=12.00) restrained the generation of bisphenolate anion and resulted in the change of pH, which would let to the decrease of BPA degradation.

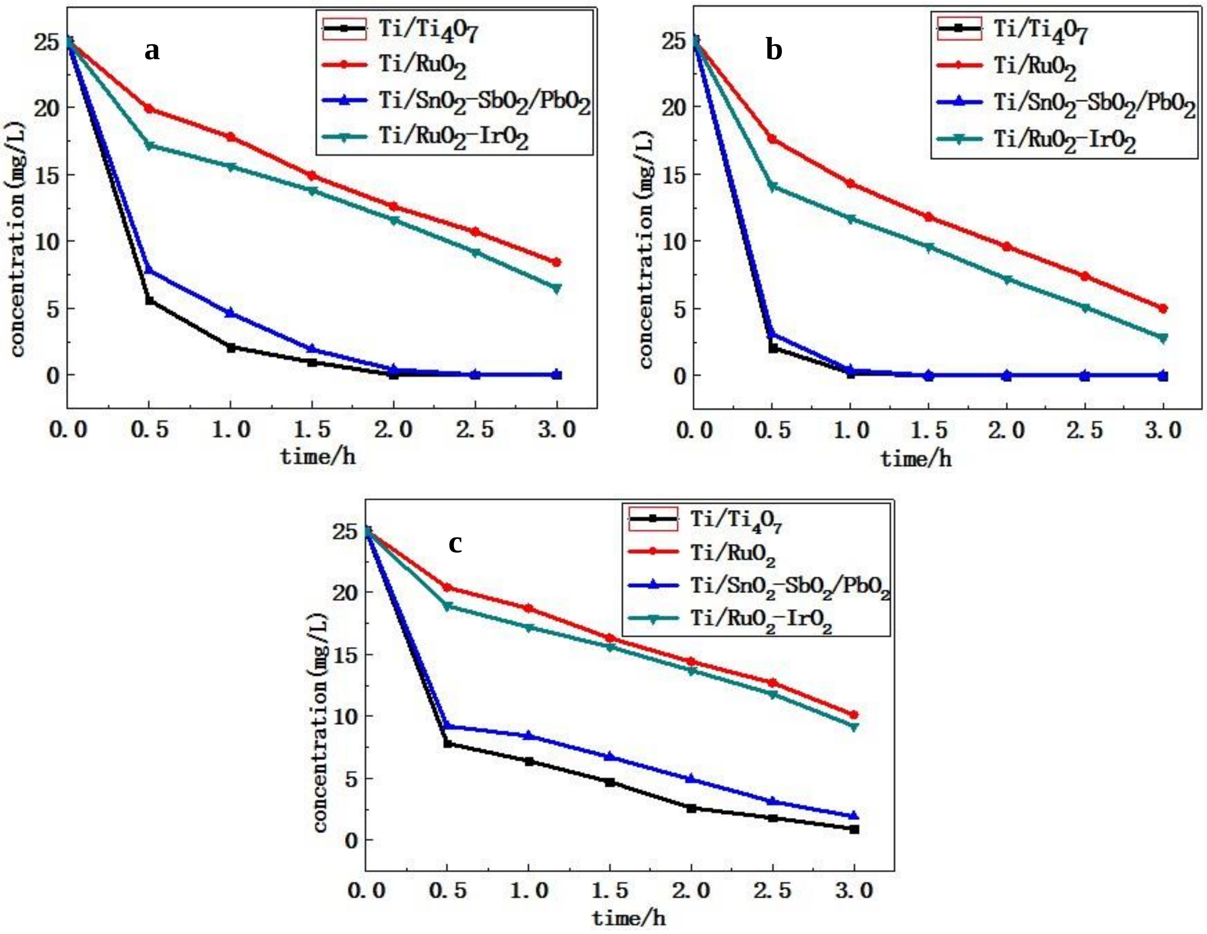

Figure 2. Electrochemical degradation of 25 mg/L BPA as a function of electrolysis time at current density of 10 mA/cm^2, different initial pH: a 3.40; b 8.20; c 12.00

3.3. Effect of plate distance

The degradation ratio of BPA decreased dramatically by expanding the plate distance which we can find in Fig. 3. With the current density of 10 mA/cm^2 for 90 min, the BPA degradation ratios of the Ti/Ti_4O_7 anode were 100%, 100%, 88.8% and 80.4% at the distance of 0.5, 1.0, 2.0 and 3.0 cm, separately. For the Ti/SnO_2-SbO_2/PbO_2 electrode, the degradation ratios of BPA were 100%, 100%, 74% and 64.4% at the distance of 0.5, 1.0, 2.0 and 3.0 cm, respectively. However, the BPA degradation ratio with the Ti/RuO_2 and Ti/RuO_2-IrO_2 electrodes decreased significantly with expanding plate distance. For the Ti/RuO_2 anode, the degradation ratios of BPA were 52.8%, 49.2%, 39.6% and 34.8% at the distance of 0.5, 1.0, 2.0 and 3.0 cm, separately.

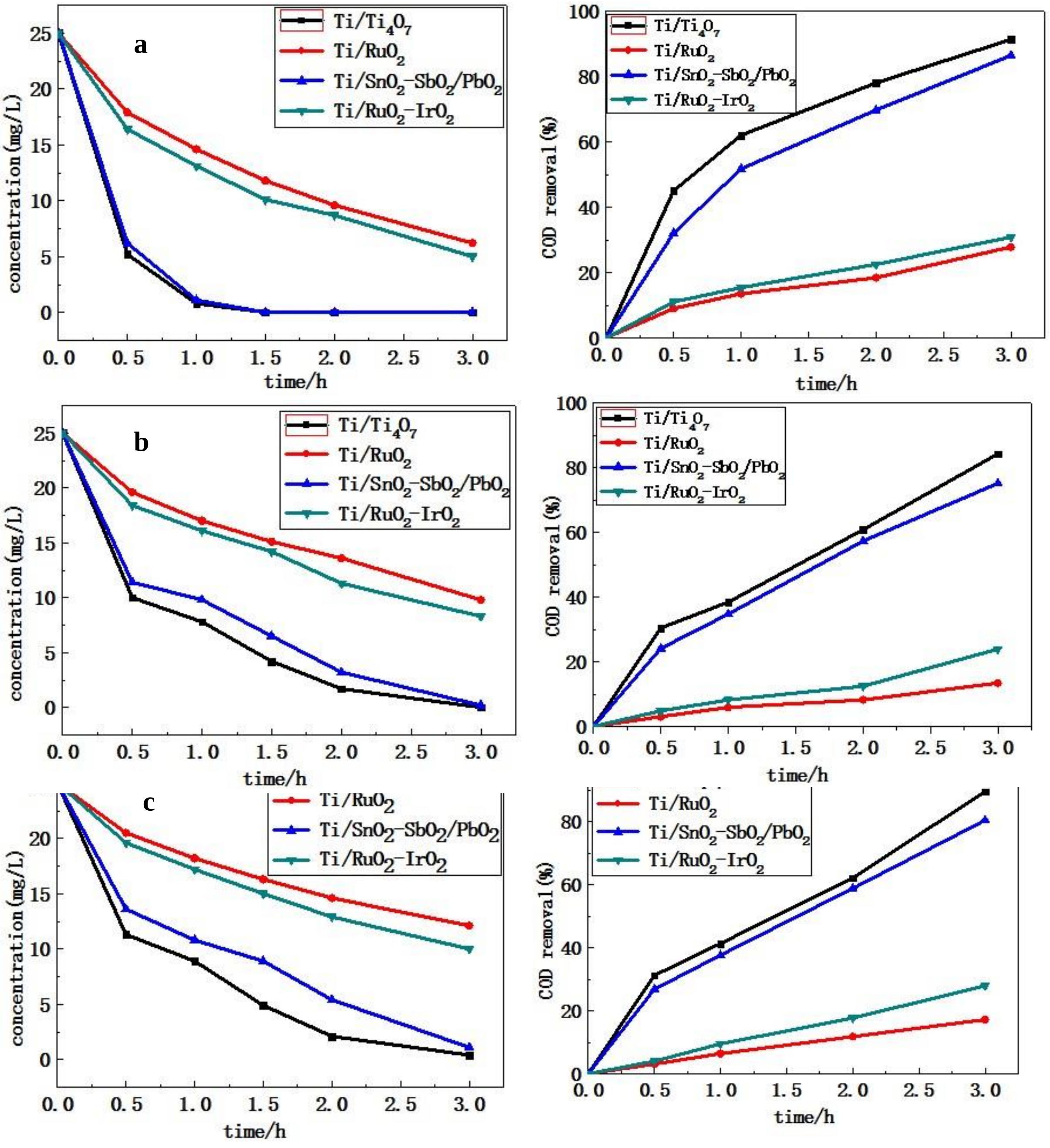

Figure 3. Electrochemical degradation and COD removal of 25 mg/L BPA as a function of electrolysis time at current density of 10 mA/cm^2, a: 0.5 cm; b: 2.0 cm; c: 3.0 cm.

For the Ti/RuO_2-IrO_2 anode, the degradation ratios of BPA were 59.6%, 44.8%, 43.2% and 38.4% at the distance of 0.5, 1.0, 2.0 and 3.0 cm, respectively. The decrease in BPA degradation rate might result from the competitive consumption of •OH among the intermediate compounds [34].

Interestingly, the COD removal of the electrolytic solution decreased with increasing appropriate plate distance. For the Ti/Ti_4O_7 electrode, the COD remove ratios were 91.3%, 87.3% and 84.2% at the distance of 0.5, 1.0 and 2.0 cm, separately, while the COD remove ratio increased to 89.5% with the distance of 3.0 cm. Correspondingly, for the Ti/SnO_2-SbO_2/PbO_2, Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes, the COD remove ratios relatively increased to 84.10%, 17.20% and 27.90%, respectively. We can know through the energy bond theory, when the free electron energy level given by the electrode was lower than the energy level of the highest occupied molecular orbital of BPA, the electron transfer reaction can be activated. The consumption of the voltage across the anode increased with the increase of plate distance. Especially, the voltage of the Ti/SnO_2-SbO_2/PbO_2 and Ti/Ti_4O_7 anodes electrodes were higher than Ti/RuO_2 and Ti/RuO_2-IrO_2 electrodes, while the COD remove rate at the distance of 3.0 cm increased slightly. It was clear that the BPA degradation and the COD remove were greatly increased in 30 min. It was apparent that faster decompose of aromatic compounds resulted in a rapider and higher production of aliphatic acids which would be broke down by the •OH radical [35]. It could be inferred that the higher voltage can provide •OH radical in the solution which can attack the short chain aliphatic acids. Then the BPA degradation and COD remove rate would be decreased. Furthermore, increasing the voltage through expanding the plate distance could overcome the electrode potential at a certain current density.

3.4. The intermediate change

The change of pH during the BPA degradation was showed in Fig. 4. During the degradation process, electrolysis produced •OH radical can break the structure of BPA which resulted in pH change. It could be found that the pH value decreased during the degradation process, and the pH value declined rapidly in 30 min. The initial pH value of solution was 5.10. For the Ti/SnO_2-SbO_2/PbO_2 electrode, the pH value was dropped to 4.24 and then rose to 7.11 during the process of BPA degradation at the current density of 5mA/cm^2. A similar pH change was written down for the Ti/RuO_2-IrO_2 anode. For the Ti/Ti_4O_7 electrode, at current density 5 mA/cm^2 the pH value dropped much lower to 3.12 and then rose to 6.11. However, for the Ti/RuO_2 anode, there was nearly no change of pH value with the BPA degradation. Increased the current density to 10, 20 and 40 mA/cm^2, the pH value was changed similar to the current density of 5 mA/cm^2. With the current density increased, the pH value variation was not obvious for the Ti/RuO_2 electrode. The pH value was associated with the degradation of BPA and COD removal. As the degradation time increased intermediate products made the pH value increased. Especially, the pH value of the solution rose from 5.10 to 7.11 after 3 hours of electrolysis with Ti/SnO_2-SbO_2/PbO_2 anode. The drop in pH value of solution might be caused by the accumulation of organic acids from BPA destruction. Later the pH rose to the neutral which was because the acid and phenols mineralized into CO_2 and H_2O.

Color changes of the solution were noticed during the degradation progress. For the Ti/SnO_2-SbO_2/PbO_2 and Ti/Ti_4O_7 electrodes, the transparent and colorless solution became light yellow and opaque with the concentration of BPA removed to almost zero, while the COD content of the solution stayed high. Then the color began to disappear and the solution became transparent once more.

Meanwhile the pH value increased and the COD decreased dramatically. For the Ti/RuO_2-IrO_2 anode, there was a slight change in solution color, BPA concentration and COD during the degradation process. For the Ti/RuO_2 anode, there was little color change of the solution during the degradation process.

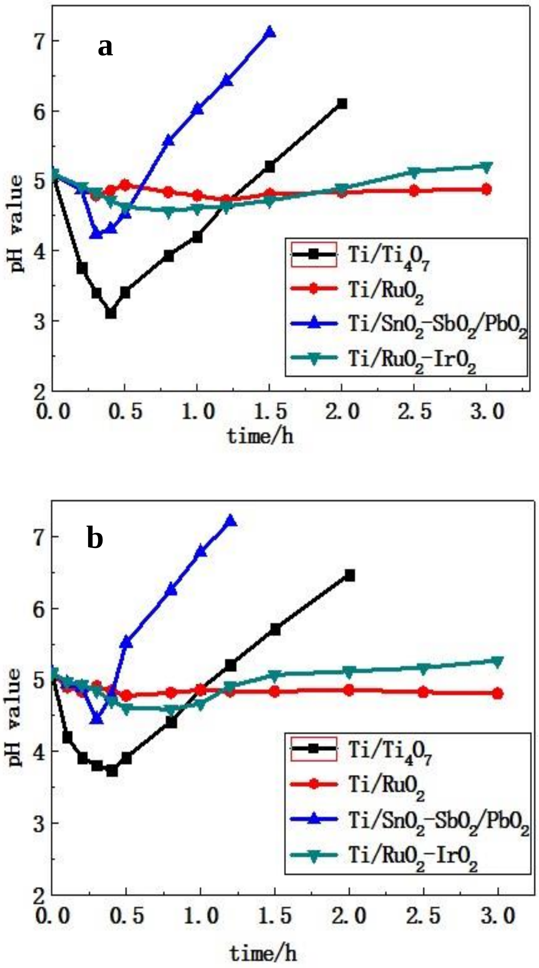

Figure 4. The pH of the solution changed during the electrochemical process at different current densities. a: 10 mA/cm^2; b: 30 mA/cm^2 current density

Table 2. The main organic intermediates of BPA and their retention time in HPLC analysis

Intermediate Products	retention time(min)	Intermediate Products	retention time(min)
BPA (A)	15.2	Hydroquinone (F)	6.3
4-isopropanolphenol (B)	14.0	Benzoquinone (G)	6.8
4-isopropenylphenol(C)	12.6	Phenol (D)	2.9
4-hydroxybenzealdehyde (E)	4.6	Tartaric acid	3.2

3.5. Pathways and Mechanisms of EC BPA degradation

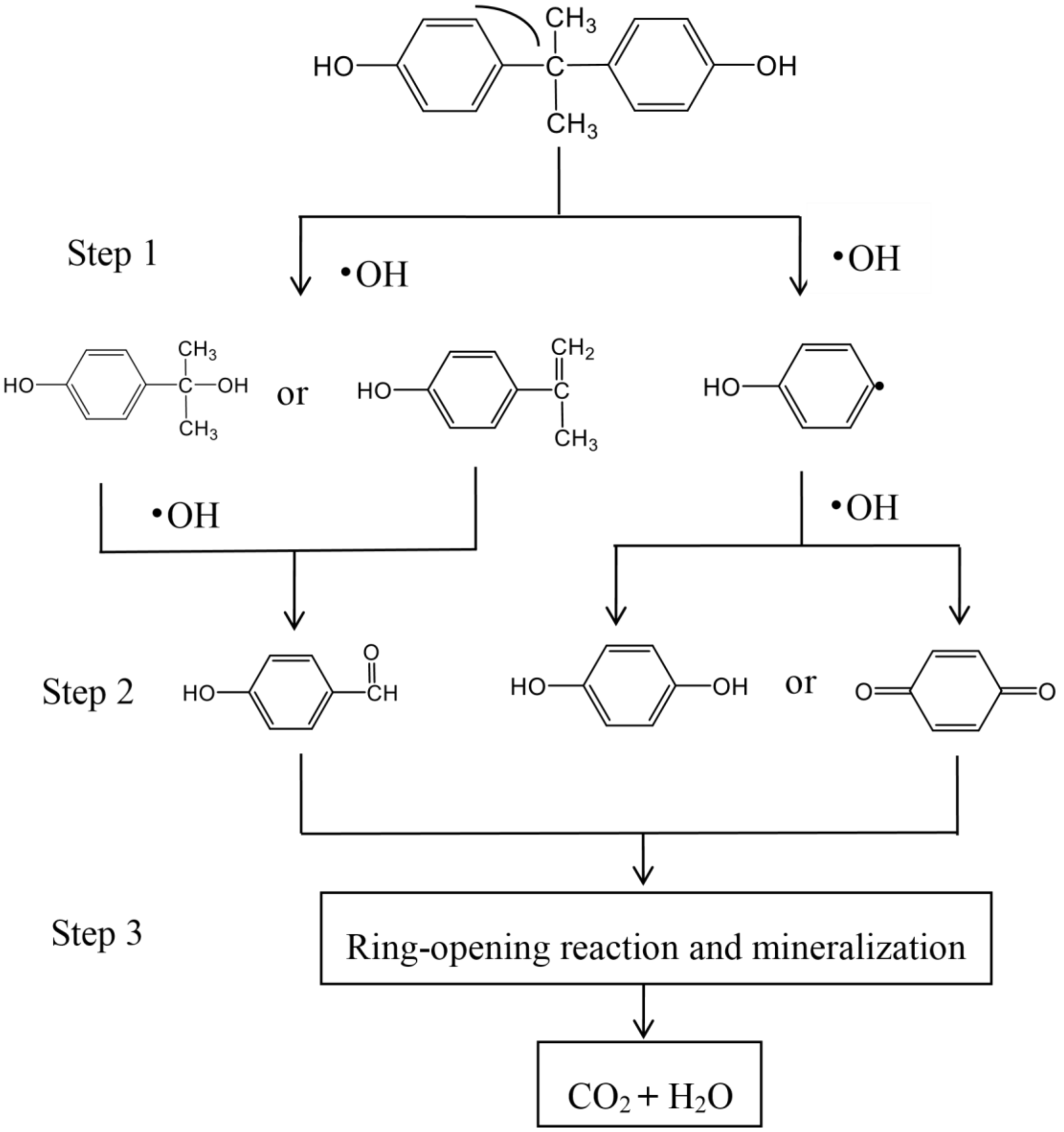

Figure 5. Reaction pathway of electrochemical degradation of BPA

The samples of BPA degradation during electrolysis process were separated by HPLC, and intermediates products were confirmed by MS. The mechanism of the electrochemical degradation of BPA process was researched and it could be divided into the following three steps. In the first step, BPA was decomposed to aromatic intermediates by direct oxidization at the electrode surface. Subsequently the intermediates were oxidized into short chain aliphatic acids by hydroxyl radicals. Finally, aliphatic acids were oxidized into carbon dioxide and water by hydroxyl radicals [36]. All of aliphatic acids and aromatic compounds were measured by HPLC, such as hydroxylated BPA derivatives, benzoquinone hydroquinone, isopropylphenol, fumaric acid, acetic acid, tartaric acid and maleic acid [37]. According to the HPLC and MS analysis of the intermediates product, a common degradation pathway could be deduced. In addition to the BPA peak area, six major products of attention time were lower than the BPA. As shown in Table 2, the BPA peak appeared at 15.2 min and the peaks of other intermediate products appeared at 14.0, 12.6, 2.9, 4.6, 6.3 and 6.8 min. Generally, the electrochemical degradation of BPA was believed to be originated in the attack by •OH generated from water, resulting in the generation of hydroxylated BPA derivatives [38].

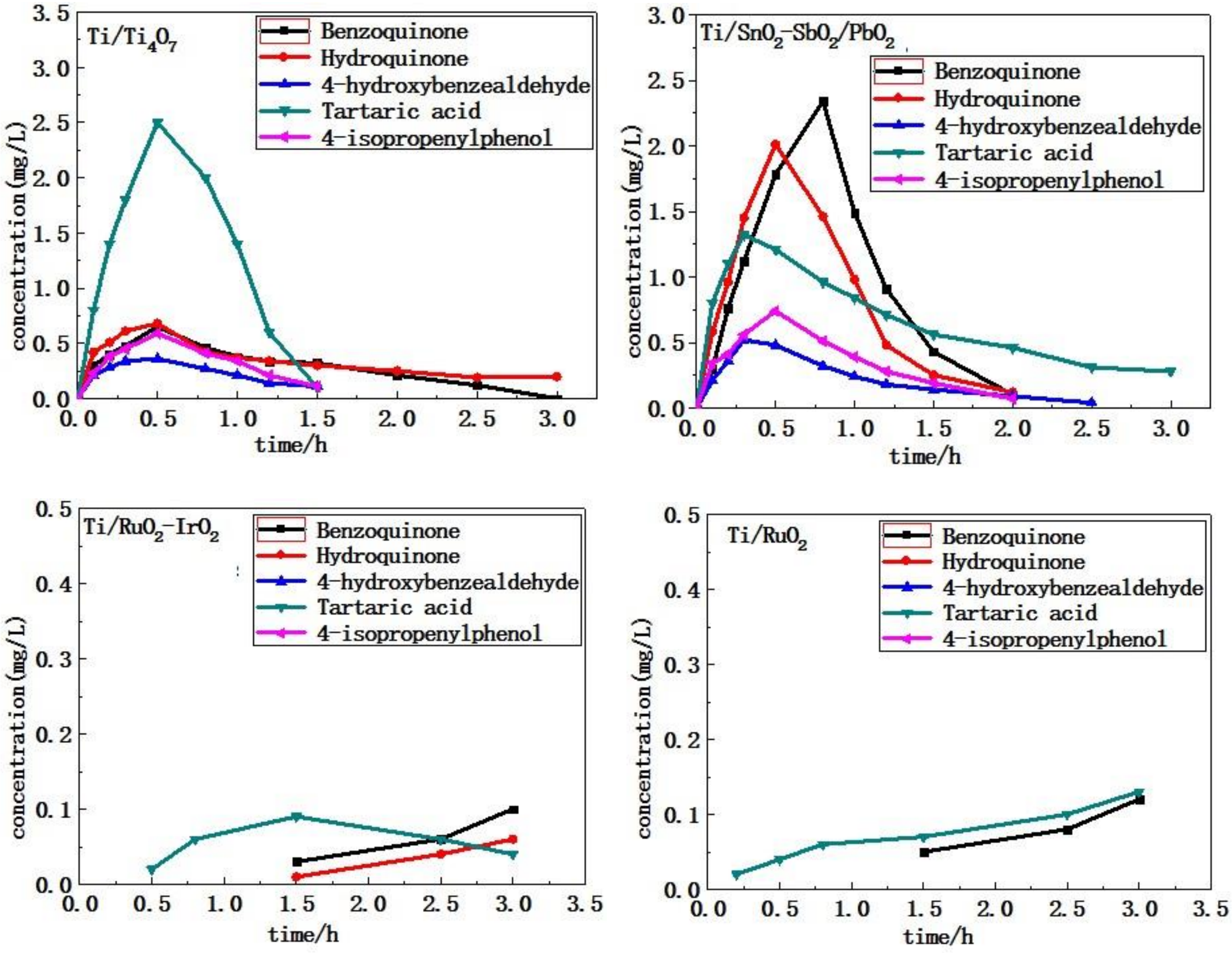

Figure 6. Concentrations of the intermediate compounds during electrochemical degradation of BPA at a current density of 10 mA/cm^2 for different anodes.

Those hydroxylated BPA derivatives were unstable and then rapidly became into 4-isopropanolphenol (B) and 4-isopropenylphenol(C) through the isopropylidene bridge division. Another structure of the cleavage compound was phenol (D) which had a molecular weight of 94. Than the accumulation of hydroxylated phenol derivatives resulted in the compounds of 4-hydroxybenzealdehyde (E), hydroquinone (F) and benzoquinone (G). Those organic molecules can be adsorbed on or in the anode surface which easily combined with the •OH radicals to cause the oxidation reaction. During the electrochemical degradation BPA process, those hydroxylated derivatives disappeared gradually, and the solution became colorless with the increase of the COD remove. For the Ti/SnO_2-SbO_2/PbO_2 electrode, the concentration of hydroquinone and benzoquinone were very high which caused the solution to be turbid and slight yellow. However, the solutions return clear and colorless as the COD remove rate reached 90%. In comparison, the concentration of the hdroquinone and benzoquinone were quiet low during the electrochemical progress for the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes. These one-ring aromatic compounds could be oxidized which were further transformed into short chain aliphatic acids (fumaric, maleic, acetic, and tartaric acid) by •OH [39]. The last step of the aromatic products underwent ring-opening reaction. Those productions of aliphatic acids made the solution pH value decrease which was exhibited in Fig. 4. All those intermediate products were eventually mineralized into CO_2 and H_2O. For the Ti/SnO_2-SbO_2/PbO_2 anode, it was more inclined to accumulate aromatic compounds and aliphatic acids on the surface which could be seen from Fig. 6. b. In comparison, for the Ti/Ti_4O_7 anode, both one-ring aromatic products and aliphatic acids were degraded rapidly, as shown in Fig. 6. a. However, the concentration of aromatic compounds and aliphatic acids were low for the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes (Fig. 6. c-d). The two types of electrodes might be less effective in absorption of small aromatic compounds and aliphatic acids.

3.6. Capability of BPA degradation with different anodes

The performances of BPA degradation have huge different among four different electrodes of Ti/Ti_4O_7, Ti/RuO_2-IrO_2, Ti/SnO_2-SbO_2/PbO_2 and Ti/RuO_2. BPA was totally completely degraded in 60 min by selected the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anodes. The COD remove rate of the Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 anodes can achieve to 95.8% and 92.1% in 180 min, separately. The TiO_2 SCs with 001 facets exposed anode also showed a nearly 100% removal efficiency in 180 min electrocatalysis, but after 10h of electrolytic reaction, the discoloration rate and COD removal rate can be reached 93% and 85%, respectively, [18]. The best performance of BPA degradation by the Ti/BDD and Ti/Sb-SnO_2 anodes with amounts of charge consumption. [37] While the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes, the degradation ratios of BPA were 52.8% and 59.6%, respectively. For the organic degradation, anodic oxygen evolution virtually causes a power loss, which decreases the reaction current efficiency for organic oxidation. As we know, an anode material presenting a high oxygen evolution potential can generate •OH effectively, which have a high oxidation ability [40]. A satisfying anode material with a high oxygen evolution potential which can reduces the needless power loss to generate •OH radicals. In this work, the oxygen evolution potentials of four different electrodes were tested through linear polarization curves. Through the linear polarization curves curves (Fig. 7), the Ti/Ti_4O_7 anode exhibited the highest oxygen evolution potential of 2.4 V and the Ti/SnO_2-SbO_2/PbO_2 anode had that of 1.6 V. It was noted that the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes had similar oxygen evolution potentials 1.1 V and 1.2 V, respectively. Inadditon, the Ti/BDD and Ti/Sb-SnO_2 anodes had similar oxygen evolution potentials (1.8 V and 1.7 V). [37] The TiO_2 SCs electrode showed the oxygen evolution potentials of 1.5 V which were much higer than the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes. A high oxygen evolution potential would supply a greater electron capture capability, which would greatly promote the cleavage of the bridge. At the different current densities from 5 to 40 mA/cm^2, the voltages of the four anodes were in the following order: Ti/Ti_4O_7 > Ti/SnO_2-SbO_2/PbO_2 > Ti/RuO_2-IrO_2 > Ti/RuO_2. A higher electron potential implied a greater electron trapping activity to generate •OH radicals, which was more likely to be transferred into the anodes surface [41]. While the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes of the working voltage was too low for BPA open loop decomposition in first step. The •OH radicals produced by water electrolysis was importance for the step 1 and step 2. In this study, the Ti/Ti_4O_7 anode generated plenty of •OH radicals which immediately applied to electrolysis process. All of BPA, one-ring aromatic products and aliphatic acids were eliminated and degraded rapidly. Thus, the Ti/Ti_4O_7 anode showed a highest efficient to oxidize aliphatic acid. The Ti/RuO_2-IrO_2 anode had a close potential to Ti/RuO_2 anode. The Ti/RuO_2 anode displayed lowest efficiency for the BPA degradation and COD remove rate because it potential was too low to produce enough •OH. In addition, the Ti_4O_7 coating layer is stable during the electrolysis process, especially at a high current density. The Ti/Ti_4O_7 anode may have a favourable chemical affinity which can readily combine with organic compounds.

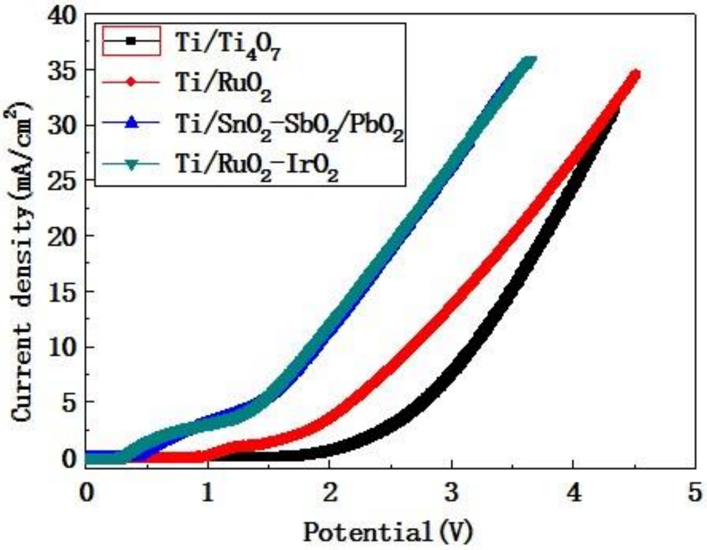

Figure 7. Electrochemical performance of degradation at the four different anodes by linear polarization curves

4. CONCLUSIONS

- The BPA Was degraded by anodic oxidation using four anodes: Ti/SnO_2-SbO_2/PbO_2, Ti/Ti_4O_7, Ti/RuO_2-IrO_2 and Ti/RuO_2. The best performance of BPA degradation and COD removal was gained with anodes of Ti/Ti_4O_7 and Ti/SnO_2-SbO_2/PbO_2 at the current density of 10 mA/cm^2. The highest COD removal rate of 95.8% was gained with anodes of Ti/Ti_4O_7 at the current density of 40 mA/cm^2. The degradation rate of BPA and COD removal increased though expanding current density, decreasing plate distance and increasing initial pH. The Ti/RuO_2-IrO_2 had a lower efficiency of BPA degradation and COD removal than Ti/SnO_2-SbO_2/PbO_2. The Ti/RuO_2 anode showed the lowest efficiency in BPA degradation and COD removal among the four type anodes.
- The samples of BPA degradation during electrolysis process were separated by HPLC, and intermediates products were confirmed by MS. The mechanism of the electrochemical degradation of BPA proceeded by the following three steps. The first step hydroxylated BPA derivatives were produced because of the attack by the •OH radicals generated from water electrolysis. These one-ring aromatic compounds could be oxidized and transformed into short chain aliphatic acids. Finally, those

intermediate products were eventually mineralized into CO_2 and H_2O, which caused the increase of the pH and colorless of electrolyzed solution.

•The oxygen evolution potentials of four electrodes were tested though linear polarization curves. The Ti/Ti_4O_7 anode had the highest oxygen evolution potential of 2.4 V, for the Ti/SnO_2-SbO_2/PbO_2 anode it was 1.6 V, the Ti/RuO_2 and Ti/RuO_2-IrO_2 anodes had similar oxygen evolution potentials of 1.1 V and 1.2 V. A good electrode presenting a high oxygen evolution potential which could effectively generated •OH from the solution. By comparing, the Ti/Ti_4O_7 anode had a high oxygen evolution potentials and good performance of organic degradation; it is a strong potential material for effective electrochemical degradation of BPA and other similar structure of organic pollutants. The Ti/Ti_4O_7 anode has great promising for the application of industrial wastewater treatment in the future.

CONFLICTS OF INTEREST
There are no conflicts to declare.

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