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Electrochemical Removal of Ammonia in Coking Wastewater Using $Ti/SnO_2+Sb/PbO_2$ Anode

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$Ti/SnO_2+Sb/PbO_2$ anode was prepared by combination technology of thermal decomposition and electrodeposition. The properties of the interlayer and activated layer of electrode were studied, and the anode electrochemical behavior was examined as well. The ammonia in coking wastewater was treated by electrochemical oxidation method using $Ti/SnO_2+Sb/PbO_2$ as anode. The effects of operating parameters including current density, anode material, pH and the concentration of chloride were inspected by orthogonal array experimental design. The results showed that anode material, current density, and chloride concentration have significant influences on the ammonia removal, and 250mg/L ammonia was removed totally within 60 minutes on $Ti/SnO_2-Sb/PbO_2$ anode at $0.05A/cm^2$ current density. The $Ti/SnO_2-Sb/PbO_2$ is a promising anode material for electrochemical coking wastewater treatment.

Keywords: Coking wastewater; Ammonia; $Ti/SnO_2+Sb/PbO_2$ anode

1. INTRODUCTION

NH_3 – nitrogen compounds in wastewater are an increasing problem, essentially related to intensive agriculture and industrial activity. They can promote eutrophication, which is fatal to aquatic life and a hindrance to the disinfection of water supplies, as well as an offensive smell and carcinogenesis [1]. The wastewater generated from the coal coking and coal gas purification presents a double fold difficulty for its treatment or purification [2]. Besides the very high ammonia contents, the biotoxic anions like cyanides render the frequently used biological treatments very inefficient [3]. The same difficulty applies for other treatments like steam/air stripping [4], catalytic [5], ozone oxidation [6], ion-exchange [7] and reverse osmosis [8].

Since discovered by Beer [9], the so-called dimensionally stable anode (DSA) has been successfully employed to destroy a variety of pollutants, nitrite [10], phenols [11], dyes [12] and so on. Ammonia has the possibility to be decomposed to nitrogen gas by an electrochemical method. Previous studies have demonstrated that metal oxide anodes (Ti/PbO_2, Ti/SnO_2) can be used successfully for the oxidation of pollutants, due to their high overvoltage for oxygen evolution and low cost [13–14]. Tin and antimony-oxide based electrode (Ti/SnO_2-Sb) is a promising anode for the electrochemical treatment of wastewater, however, the commercial application of Ti/SnO_2-Sb_2O_5 is hampered by its short lifetime [15]. PbO_2 calls the attention as an electrode material due to its easy and rapid preparation, besides being of low cost and stable in high-applied potentials in different pH medias. Although the stability of Ti/PbO_2 electrodes, as well as their electrocatalytic activity, can be enhanced by incorporating / doping other metal ions (e.g., Bi, Ce and Co) into the PbO_2 to form composite oxide materials by co-electrodeposition [16-18], interlayer added between PbO_2 activated layer and titanium substrate may enhance the stability and prolong the lifetime of these electrodes. It has been reported that antimony doped SnO_2 behaves as a metal-like material [19] and has similar crystal structure with PbO_2 and TiO_2. So a solid solution could be formed among these oxides. This solid solution can efficiently hamper the metallic support passivation by prevention the diffusion of fresh oxygen to the substrate. For these reasons, Ti/SnO_2+Sb/PbO_2 is a promising anodic material for industrial wastewater treatment. However, there were few reports about the electrolytic decomposition of ammonia in coking wastewater at Ti/SnO_2+Sb/PbO_2 electrode.

In the present study, the Ti/SnO_2+Sb/PbO_2 anode was firstly prepared, and the properties of Ti/SnO_2+Sb/PbO_2 anode were examined, including its morphology, crystal structure, composition valent states and stability. Then, coking plant wastewater was treated by Ti/SnO_2+Sb/PbO_2 electrode in order to attain the best degradation effect. An orthogonal array experiment was used to study the impact of anode materials, current density, chloride concentration and pH value. The electrochemical energy consumption was also estimated.

2. EXPERIMENTAL

2.1. Chemicals

All chemical materials employed are of analytical purity grade. Distilled water purified by a Milli-Q system (Millipore) was used to prepare all the solutions. Throughout the experiment, the wastewater was taken from the same batch collected from the same coking plant.

2.2. Electrode Preparation

The Ti plates (5 × 1 × 0.1 cm) were used as substrates. Prior to using as substrates, they were polished with 320-grit sandpaper, degreased in 40 wt% NaOH solution at 80℃ for 2 h, etched in a boiling 10 % oxalic acid solution during 1 h, after that, they were rinsed with distilled water and dried naturally.

The interlayer layers of electrodes were prepared following a standard thermal decomposition method and the procedures were as follows: a solution containing 10% $SnCl_4$ and 1% $SbCl_3$ was dissolved in a mixture of n-butanol + HCl. The precursor solution was distributed onto the pretreated Ti plates by brushing. The solvent was dried in air, and the electrode was introduced in an oven at 450℃ for 10 min for the decomposition of the salt and the formation of the metal oxides. This process was repeated for 15-20 times. A final annealing of the electrode was performed at 550℃ for 1 h.

The PbO_2 activated layer was prepared by electrochemical deposition method in 0.1 M HNO_3 containing 1 M $Pb(NO_3)_2$ and 0.1 M surfactant (sodium dodecyl sulfate, SDS) at 60℃ for 1 h. The voltage was 1.5–2.5 V and the current was 8 mA/cm^2. After deposition, the electrodes were removed from the depositing solutions and rinsed with distilled water. All experiments were performed at an electrolytic cell with a copper plate as cathode.

2.3. Characterization of the electrodes

The XRD patterns were obtained using a Rigaku D/max-2500 diffractometer using the Cu Kα radiation. The Scanning electron microscope (SEM) images were acquired using an Amray Model 1850 field emission SEM operated at a 20 keV acceleration voltage. An X-Ray ESCALab250 photoelectron spectrograph (XPS) was also used.

The anode electrochemical behavior was performed using a VMP3 model Potentiostat (Bio-Logic Science Instruments, France) controlled with EC-Lab software. A standard three-electrode cell was used, the electrode under study was employed as the working electrode (WE), a Pt sheet as counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE). Tafel plot was measured in 0.5 M H_2SO_4 solutions at 20 ℃.

2.4. Electrode Stability

The accelerated life test to determine the anodes stability was carried out in a galvanostatic conditions at 2 A/cm^2, the working electrode was the novel anode, Cu as a counter electrode, 0.5 M H_2SO_4 was used as electrolyte. The service life was taken as the anodization time for the potential overcomes 10 V from its initial value.

2.5. Ammonia Electrochemical Oxidation

The electrochemical oxidation of coking wastewater was carried out in an electrolytic cell of 100 ml volume. The Ti/SnO_2-Sb/PbO_2 electrode (5cm × 1cm × 0.1 cm) was used as an anode and a porous graphite plate (6cm × 11cm × 0.2cm) was employed as a cathode. The anode and cathode were positioned vertically and parallel to each other. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. A regulated DC power supply was used while the current and voltage were adjustable between 0–2.5 A and 0–35 V, respectively.

2.6. Methods For Measuring

The pH was measured with a PHS-3C pH-meter, the concentration of the ammonia in the wastewater was analyzed spectrophotometrically on a Cary50 UV–vis spectrophotometer (Varian Instruments, America). The concentration of chlorides, nitrates, nitrites, and hypochlorite was detected by ion chromatograph (Techcomp 1000, China).

The characteristic of raw wastewater is given by Table 1.

Table 1. Characteristics of raw coking wastewater

Parameter	pH	Conductivity (mS/cm)	NH4+ (mg/L)	COD (mg/L)	TOC (mg/L)	Cl- (mg/L)
Raw wastewater	8	0.71	258.45	2000	196.9	1300

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

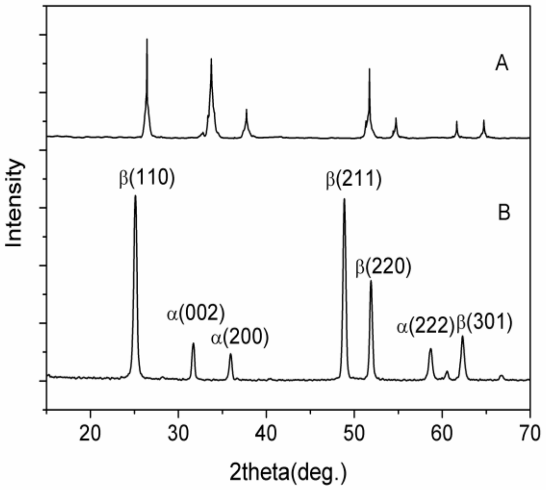

Figure 1. XRD pattern of Ti/SnO_2+Sb/PbO_2 electrode:(A) SnO_2+Sb interlayer. (B) PbO_2 activated layer.

Fig. 1A shows the X-ray diffraction patterns of interlayer of a Ti/SnO_2+Sb/PbO_2 electrode freshly prepared. The peak positions agree well with the reflections of SnO_2 cassiterite indicating a rutile-type structure. No additional peaks corresponding to different phases such as antimony oxides appear. Consequently, a solid solution is formed between the antimony oxides and tin dioxide [20].

The X-ray diffraction pattern of PbO_2 activated layer is shown in Fig. 1B. It reveals PbO_2 films consisted of a mixture of α-PbO_2 and β-PbO_2 crystallographic phases with a tetragonal structure [21].

The TiO_2, SnO_2 and PbO_2 are the tetragonal rutile structure, their lattice constants are similar to each other, hence, they can form a solid solution to increase the electrode service life.

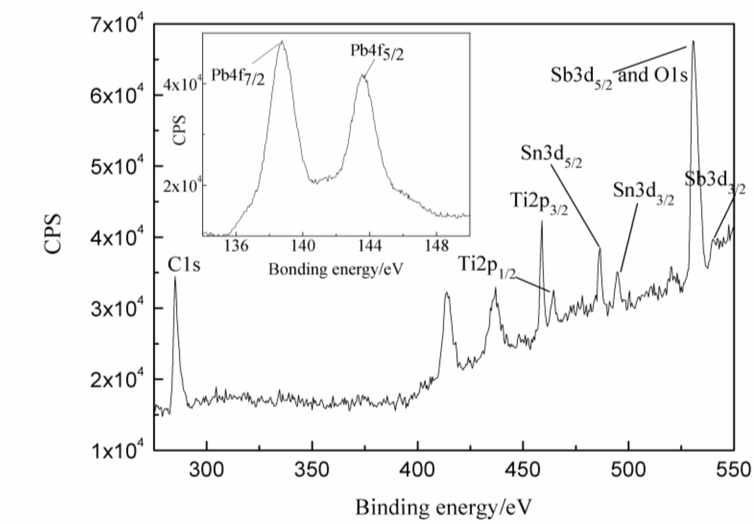

Figure 2. General XPS spectra of Ti/SnO_2+Sb/PbO_2 electrode

Fig. 2 shows the complete XPS spectrum of a Ti/SnO_2+Sb/PbO_2 electrode in which the peaks corresponding to C, Sn, Sb, O, Pb and Ti can be observed. The oxidation state of the elements has also been determined by XPS analysis. The binding energies of the transition Ti $2p_{3/2}$, Sn $3d_{5/2}$ Pb $4f_{7/2}$ is 458.7 eV, 487 eV and 139 eV respectively, it indicated that the TiO_2, SnO_2 and PbO_2 are formed during the preparation of Ti/SnO_2-Sb/PbO_2 electrode [22].

3.2. Surface Morphology

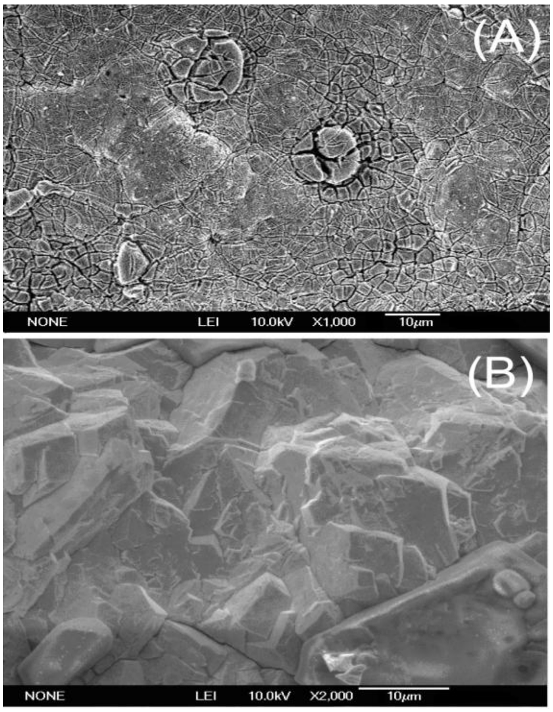

Figure 3. Morphology of the Ti/SnO_2+Sb/PbO_2 electrode: (A) SnO_2+Sb interlayer. (B) PbO_2 activated layer.

Fig. 3A shows that the crystal grains in the SnO_2+Sb surface inter layer are uniform and combine tightly each other, such grains can inhibit the diffusion of nascent oxygen and reduce the formation of TiO_2 insulating layer. So it is useful to lengthen the service life of the electrode. Fig. 3B shows that the surface of PbO_2 activated layer has a dense and pyramid morphology, of great degree of roughness. The rough surface of the PbO_2 activated layer enlarges the efficient area, and improves the absorption of the reactants. According to the morphology, we can see that the Ti/SnO_2+Sb/PbO_2 anode has a good electro-catalytic activity and corrosion resistance ability.

3.3. Electrochemical Behavior

Table 2. Anodes kinetic parameters and stability

Anode	a/V	b/V	i0 /A cm2	Service life/h	Oxygen evolution potential /V
Ti/SnO2-Sb	0.532	0.489	8.17×10^{-2}	20	2.15
Ti/PbO2	0.425	0.331	5.20×10^{-2}	35	1.78
Ti/SnO2-Sb/PbO2	0.290	0.208	3.99×10^{-2}	86	1.86

The anode kinetic parameters based on Tafel plot and anode stability are summarized in Table 2. The Tafel plot is obtained from the current potential curves (polarization curves) in 0.5 M H_2SO_4 solution. Kinetic parameters: a, b i_0 are deduced from the Tafel plot. The anode stability is based on the accelerated life test which has mentioned above.

As expected, the Ti/SnO_2-Sb is a promising anode for the electrochemical treatment of wastewater due to its higher oxygen evolution potential and lower a value. However, the application of Ti/SnO_2-Sb electrode is hindered by its short service life in anodic polarization condition. Though the Ti/PbO_2 service life is longer than Ti/SnO_2-Sb, its commercial application is also hampered by its short lifetime.

The introduction of SnO_2+Sb interlayer can improve the service life efficiently, we also observed the Ti/SnO_2+Sb/PbO_2 electrode coating has not detached until to the end of service life. The probably reason is that a solid solution is formed between activated layer and interlayer during the electrode preparation, this solid solution leads to excellent bonding quality. Another reason is the dense microstructure of the activated layer, as shown in the SEM images, (see Fig. 3B), the PbO_2 activated layer consisted of a mixture of α and β-PbO_2 crystallographic phases, it is also known that the α-PbO_2 has a compact structure [23].

The dense structure not only retards the penetration of the electrolyte through the cracks or pores, but also stops the generation of high pressure inside the coating due to internal O_2 evolution [24]. Besides the long service life of Ti/SnO_2+Sb/PbO_2 electrode, the higher oxygen evolution potential and lower a value are helpful to restrain the reaction of oxygen evolution and operation voltage during the electrochemical oxidation of wastewater, therefore, the current efficiency is improved and the energy consummation is lowered.

3.4. Electrochemical Removal Of Ammonia

$L_9(3^4)$ orthogonal array was chosen to study the effect of four factors including anode material, current density, chloride concentration and pH value in the analogue wastewater, see Table 3. The experimental results and difference analysis are showed in Table 4.

Table 3. Control factors and the studying levels of the orthogonal array experimental design

	Control factors	1	2	3
A	Anode material	Ti/SnO2-Sb	Ti/SnO2+Sb/PbO2	Graphite
B	current density(A/cm2)	0.05	0.10	0.15
C	pH value	5	8	10
D	Chloride concentration(g/L)	3	6	9

Table 4. The experimental results and difference analysis

Experiment	1	2	3	4	5	6	7	8	9	K1	K2	K3	R
A	A1	A1	A1	A2	A2	A2	A3	A3	A3	0.678	0.827	0.379	0.448
B	B1	B2	B3	B1	B2	B3	B1	B2	B3	0.471	0.614	0.800	0.329
C	C1	C2	C3	C2	C3	C1	C3	C1	C2	0.616	0.600	0.669	0.069
D	D1	D2	D3	D3	D1	D2	D2	D3	D1	0.505	0.642	0.737	0.232
Removal efficiency/ %	38.6	64.9	100	75	73	100	27.6	46.2	40				

From Table 4, we can see that the anode material, current density, chloride concentration have significant effects on the ammonia removing, while the pH value effect is insignificant, and the effect of anode material is more important than the other factors. Among the four anode materials, the k value of $Ti/SnO_2+Sb/PbO_2$ is the highest. This result can be explained by the high electrocatalytic activity, higher oxygen evolution over-potential and longer service life of $Ti/SnO_2+Sb/PbO_2$ anode. So the $Ti/SnO_2+Sb/PbO_2$ can degrade ammonia completely in the shortest time (40min) at pH 5, with 6 g/L chloride in addition and 0.15 A/cm^2 current density condition.

The current efficiency can be calculated by the equations expressed below:

$$\eta = (Q/Q_r) \times 100\% \quad (1)$$

$$Q = (m/M) \times zF \quad (2)$$

$$Q_r = it \quad (3)$$

Where

m is the mass of the product (N_2, g);
M is the molecular weight of N_2 (28 g/mol);
z is the number of electrons-transfer;
F is the Faraday's constant 96500 (C/mol);
i is the current density (A);
t is the operating time;
Q is the theoretic electrochemical energy consumption(C);
Q_r is the real electrochemical energy consumption (C);
η is the current efficiency.

3.4.1. The Effect of Current Density

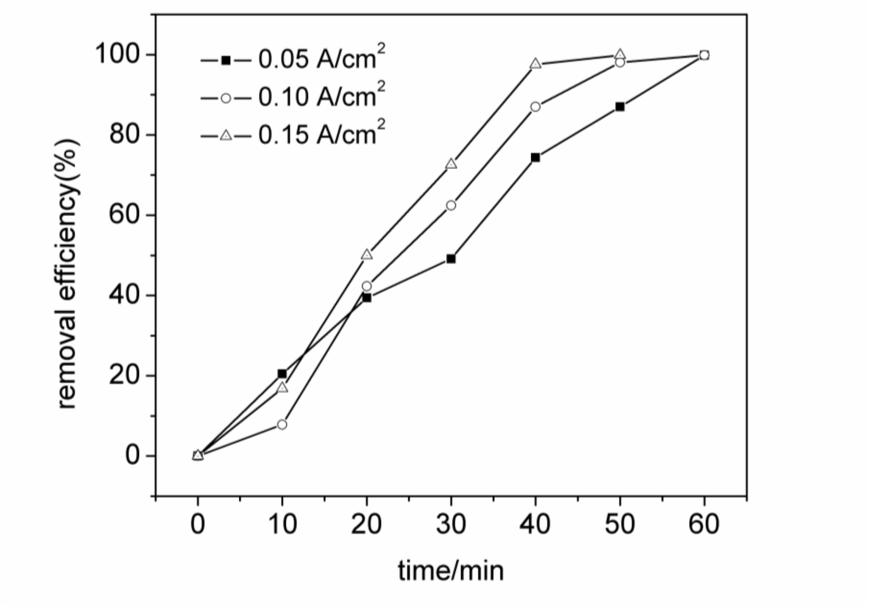

Figure 4. The relationship between the current density and ammonia removal efficiency

Fig. 4 shows the relationship between the current density and ammonia removal efficiency in the electrochemical oxidation treatment of raw coking wastewater progress. When the current density increased from 0.05 to 0.15 A/cm^2, ammonia removal efficiency increased. The current efficiency was 90.0%>54.7%>40.5% when the current density were 0.05, 0.10, 0.15 A/cm^2 respectively. It indicates that increasing current density to improve ammonia removal efficiency is not economical.

3.4.2. The Effect of Chloride Concentration

The effect of chloride concentration is shown in Fig. 5. We can see that increasing chloride concentration brings the improvement of the removal efficiency. A higher chloride concentration leads to a ClO^- production increase and the ammonia oxidation [25]. The current efficiency was 80.9%, 60.7%, 72.9%, 83.5% respectively with the addition of 0, 3, 6, 9 g/L of chloride. So increasing the chloride concentration is not very useful, because there are a lot of chloride existed in the coking wastewater, increasing chloride concentration only slightly improves the current efficiency. This result is confirmed by others [26].

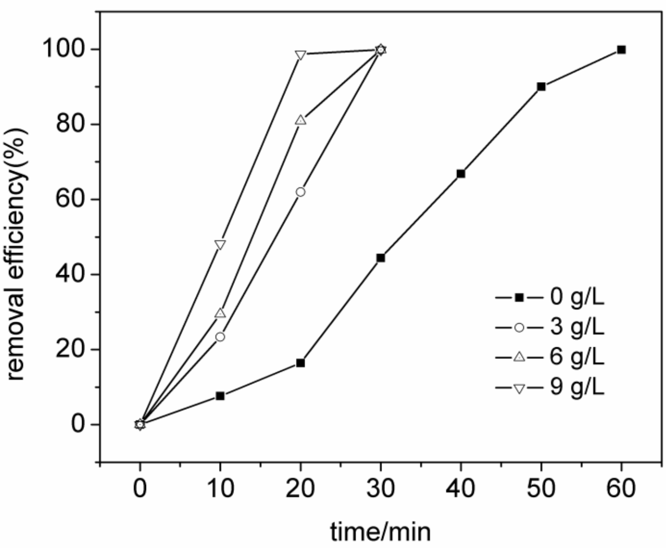

Figure 5. The relationship between the chloride concentration and ammonia removal efficiency

3.4.3. The Ph Value And Degradation Mechanism

According to the orthogonal array experimental results, though the effect of initial pH value is unessential, the change of pH value in the progress of electrochemical treatment is worth of paying attention to.

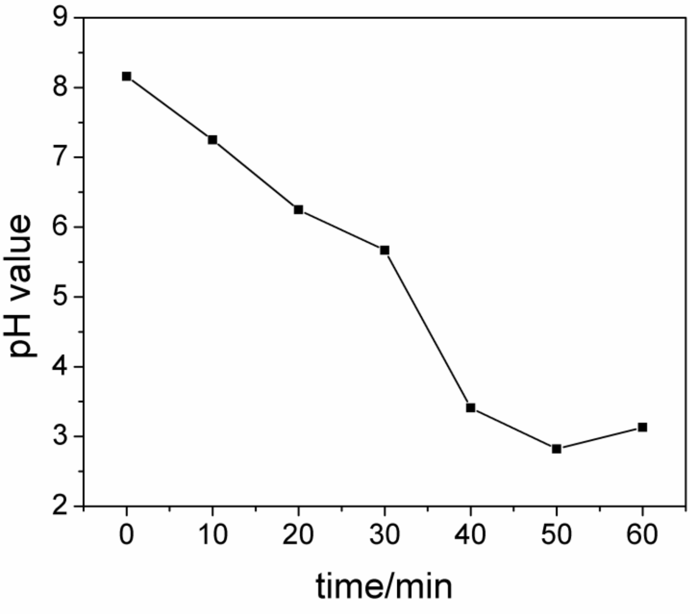

Figure 6. The change of pH value with treatment time

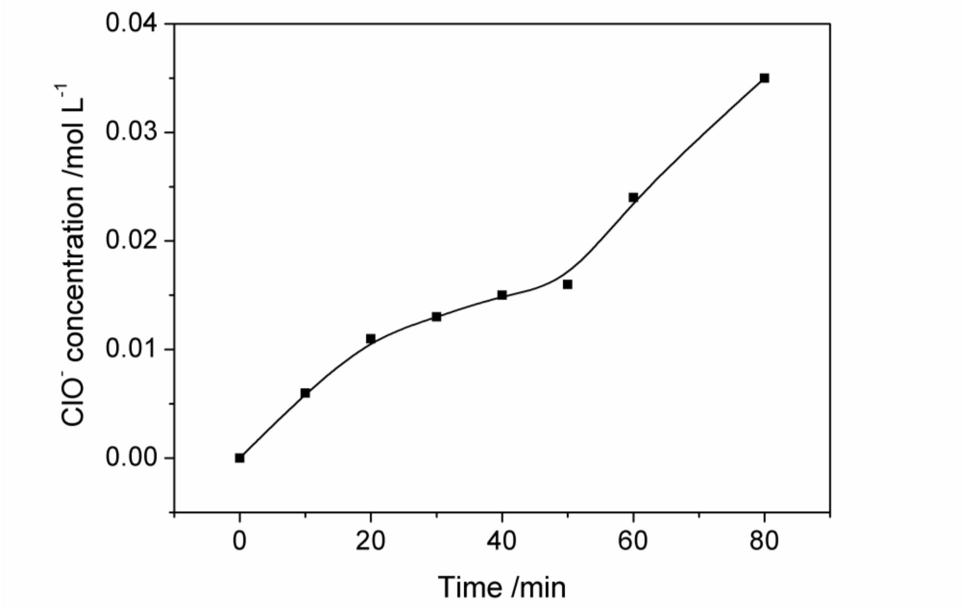

Figure 7. ClO^- concentration at different treatment time by ion chromatograph

Fig. 6 represents the change of pH value with time, from Fig. 6, we can see that the pH value decreases with passage of time; Fig. 7 represents the concentration of ClO^- at different time by ion chromatograph. From Fig.7 we can see no ClO^- was detected at the initial time in the raw wastewater. But the ClO^- concentration increased with the passage of time. So we deduced that the H^+ and ClO^- ion produced in the following progress:

$$Cl^- \rightarrow Cl_{(ad)} + e^- \quad (4)$$

$$2Cl_{(ad)} \rightarrow Cl_2 \quad (5)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (6)$$

$$HClO \rightarrow H^+ + ClO^- \quad (7)$$

Some investigations have been focused on direct anodic oxidation of ammonia in the electrochemical treatment progress like Eqs. (8) [27].

$$NH_3 + 3OH^- \rightarrow 1/2N_2 + 3H_2O + 3e^- \quad (8)$$

But when we treated $(NH_4)_2SO_4$ solution without Cl^- at Ti/SnO_2+Sb/PbO_2 anode, we found the removal efficiency is only 6% after 6 hours. Hence, indirect anodic oxidation is the main electrochemical treatment progress.

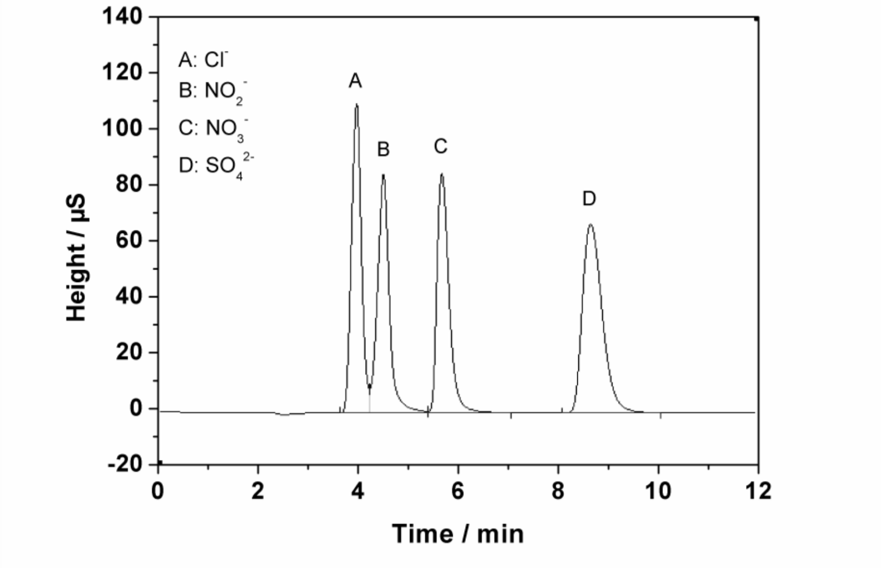

Figure 8. The standard ion chromatograph

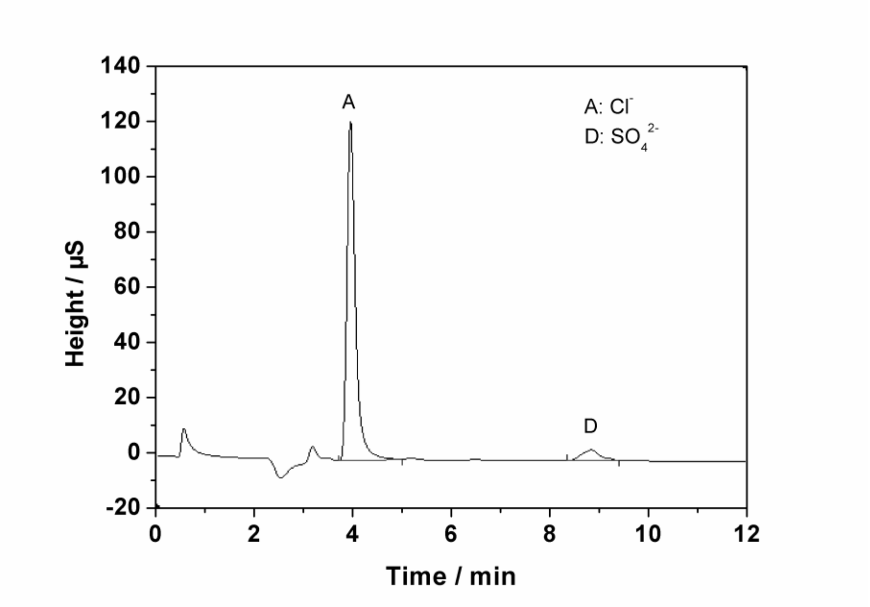

Figure 9. The ion chromatograph at the end of treatment

Fig. 8 is the standard ion chromatograph and Fig. 9 is the ion chromatograph determined at the end of wastewater treatment. Compared Fig. 9 with Fig. 8, no NO_3^-, NO_2^- and other NO_x substances were detected at the end. So the ammonia nitrogen was changed to nitrogen totally and the overall reaction is analogous to the break-point chlorination [28]:

$$2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \quad (9)$$

3.4.4. Energy Consumption

When the current density is 0.05 A/cm^2 and no chloride was addition (η=0.8099), after 250 mg/L ammonia was eliminated completely, the energy consumption calculated by Eqs. (10) and Eqs.

(11) is 43.23 kWh/kg NH_3-N. That means treating 1 ton coking wastewater containing 250 mg/L ammonia consumes only 10.8 kWh electric energy.

$$k = \frac{zF}{M} = \frac{6 \times 26.8}{28} = 5.74 kAh / kgNH_4^+ - N \ (10)$$

$$Q = \frac{kV}{\eta} = \frac{5.74 \times 6.1}{0.8099} = 43.23 kWh / kgNH_4^+ - N \qquad (11)$$

Where

k is the theoretic electrochemical energy consumption (kWh/kgNH_3-N);

V is the operation voltage.

4. CONCLUSION

Based on the results of SEM, XRD and XPS, the electrode surface possess a great degree of roughness and the interlayer SnO_2+Sb can generate solid solution well. Electrochemical oxidation of ammonia is an indirect reaction, there was no NO_x substance was detected. The best operating condition is that using Ti/SnO_2+Sb/PbO_2 anode, the current density is 0.05 A/cm^2 and no chloride in addition. And treating 1 ton coking wastewater containing 250 mg/L ammonia consumes only 10.8 kWh energy. Ti/SnO_2+Sb/PbO_2 anode with higher oxygen evolution over-potential and longer service life is the present most promising anode material for electrochemical coking wastewater treatment.

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