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Article

Electrochemical oxidation of aniline by a novel Ti/TiO_xH_y/Sb-SnO₂ electrode

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ABSTRACT

Electrochemical oxidation of aniline in aqueous solution was investigated over a novel Ti/TiO_xH_y/Sb-SnO₂ electrode prepared by the electrodeposition method. Scanning electron microscopy, X-ray diffraction, and electrochemical measurements were used to characterize its morphology, crystal structure, and electrochemical properties. Removal of aniline by the Ti/TiO_xH_y/Sb-SnO₂ electrode was investigated by ultraviolet-Visible spectroscopy and chemical oxygen demand (COD) analysis under different conditions, including current densities, initial concentrations of aniline, pH values, concentrations of chloride ions, and types of reactor. It was found that a higher current density, a lower initial concentration of aniline, an acidic solution, the presence of chloride ions (0.2 wt% NaCl), and a three-dimensional (3D) reactor promoted the removal efficiency of aniline. Electrochemical degradation of aniline followed pseudo-first-order kinetics. The aniline (200 mL of 100 mg·L⁻¹) and COD removal efficiencies reached 100% and 73.5%, respectively, at a current density of 20 mA·cm⁻², pH of 7.0, and supporting electrolyte of 0.5 wt% Na₂SO₄ after 2 h electrolysis in a 3D reactor. These results show that aniline can be significantly removed on the Ti/TiO_xH_y/Sb-SnO₂ electrode, which provides an efficient way for elimination of aniline from aqueous solution.

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1. Introduction

Aniline is an important raw material that is commonly used as a precursor of dyes, medicines, paper, explosives, coal, and rubber [1,2]. With the development of the chemical industry in recent years, the demand for aniline has increased. Large-scale production and use of aniline means that it exists in many effluents from the chemical industry. However, aniline is a highly toxic material that can cause cancer and mutations. Moreover, aniline can be easily adsorbed in sediments and becomes a permanent pollutant in aquatic environments. The increase of

the aniline concentration in natural water sources can have serious consequences to ecological systems and human health [3,4]. Therefore, wastewater effluents containing aniline should be cautiously disposed of by an efficient and cost effective method prior to release into natural watercourses.

Many techniques have been used to treat aniline-containing wastewaters, including biodegradation [4], supercritical oxidation [5], photocatalytic oxidation [6], ozonation [7], separation using membranes [8], electrochemical oxidation (EO) [9–11], and so forth. Among the various techniques, EO is a promising method for treatment of aniline-containing wastewaters,

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mainly because of its high efficiency, simplicity, relatively mild conditions, and environmental friendliness [12–15]. However, the excessive energy consumption and high cost in the electrolysis process is a great limitation for its application to electrochemical degradation of aniline. It is well-known that the anode is important in EO reactions [16,17]. Therefore, development of an effective and inexpensive anode is urgently required. Optimization of the aniline degradation conditions is also required.

Various electrodes have been investigated to treat aniline-containing wastewater. Ferreira et al. [3] investigated the performance of aniline EO using the BDD electrode. The results showed that an acidic environment and high voltage were beneficial for EO of aniline. Li et al. [18] reported EO of aniline using the $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-PtO}$ anode. These studies show that electrocatalytic oxidation is an effective process for degradation of aniline. Other electrode materials are also used for electrochemical degradation of aniline, including PbO_2 [1], mono and bimetallic carbon nanotubes [2], carbon fiber [19], graphite rod [20], and so forth. Compared with other electrode materials, Ti/Sb-SnO_2 has many advantages, including easy preparation, high oxygen evolution potential (OEP), cost efficiency, and strong electrocatalytic oxidation ability, and it is widely used in EO processes [21–25]. However, the stability of Ti/SnO_2 is relatively poor compared with Ti/PbO_2 and Ti/RuO_2 , which could shorten the service life of the electrode [23,26].

In this study, a stable $\text{Ti/TiO}_x\text{H}_y\text{/Sb-SnO}_2$ anode was fabricated and applied to remove aniline from aqueous solution. To obtain the optimized operation conditions for removal of aniline from wastewater, the operating parameters, such as the current density, initial concentration of aniline, pH value, concentration of chloride ions, and type of reactor, were determined. The removal efficiency of aniline, chemical oxygen demand (COD), instantaneous current efficiency (ICE), and energy consumption (E_p) were investigated during the EO process. The purpose of this work is to provide an efficient low-energy electrochemical method for degradation of aniline in aqueous solution.

2. Experimental

2.1. Materials and reagents

High-purity (>99.6%) titanium plates (BaoTi Ltd., China) were used as the substrate in this study. All of the chemical reagents were of analytical grade and used as received without further purification. They were all purchased from Sinopharm Chemical Reagent Xi'an Co., Ltd. Deionized water (18 $\text{M}\Omega\cdot\text{cm}$) was obtained by an EPED-40TF water purification laboratory system (Yipuyida Technology development Ltd., Nanjing, China).

2.2. Electrode preparation and characterization

The stable $\text{Ti/TiO}_x\text{H}_y\text{/Sb-SnO}_2$ electrode production process has been reported in detail elsewhere [27]. The service life of the electrode can reach 32 h in 0.5 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 solution at a

current density of 200 $\text{mA}\cdot\text{cm}^{-2}$ (25–35°C), which is approximately two times higher than that of the conventional Ti/Sb-SnO_2 electrode (10 h). The electrode was fabricated by introducing a TiO_xH_y interlayer in a simple way, which can not only effectively improve the stability of the electrode, but can also maintain the high performance of the electrode for a long time. The Ti substrate was modified by thermal oxidation followed by an electrochemical reduction process. The pretreated Ti plate (used as the cathode) was then inserted into an electrodeposition liquid containing Sn and Sb elements with a graphite anode as the counter electrode. After calcination and annealing, the $\text{Ti/TiO}_x\text{H}_y\text{/Sb-SnO}_2$ electrode was obtained.

The microstructure and morphology of the electrode were analyzed by scanning electron microscopy (SEM, JEOL, JSM-6390A). The crystal structure was identified by an X'pert PRO MRD diffractometer (XRD, PAN Analytical, The Netherlands) using a $\text{Cu K}\alpha$ source ($\lambda = 0.15416$ nm) with a scanning angle (2θ) ranging from 10° to 80°.

2.3. Cyclic voltammetry experiments

Cyclic voltammetry (CV) experiments of the electrode were performed with an electrochemical workstation (CHI 660D, Chenhua, Shanghai, China) using a standard three-electrode cell. The OEP of the electrode and the manner of oxidation of aniline were determined by CV (scan rate 0.05 $\text{V}\cdot\text{s}^{-1}$) in 0.5 wt% Na_2SO_4 solution or 0.5 wt% Na_2SO_4 solution with 100 $\text{mg}\cdot\text{L}^{-1}$ aniline. The $\text{Ti/TiO}_x\text{H}_y\text{/Sb-SnO}_2$ electrode served as the working electrode (2 cm^2). Two platinum-foil plates (3 $\text{cm} \times 3$ cm) and Ag/AgCl (sat KCl) were used as the counter electrode and reference electrode, respectively.

2.4. Electrochemical oxidation of aniline

As shown in Fig. 1, EO of aniline was carried out in a two-dimensional (2D) or three-dimensional (3D) reactor. In the 3D reactor, the space between the electrodes was filled with iron-carbon particles (grain size 0.5–1.0 cm, dose 300 g), which were immersed in wastewater several times before the exper-

Fig. 1. Scheme of 2D and 3D electrode system.

iment. The Ti/TiO_xH_y/Sb-SnO₂ electrode was used as the anode and graphite was used as the cathode. The distance between the anode and the cathode was set at 2.0 cm. To evaluate the influential parameters, an aniline solution (200 mL, 100 mg·L⁻¹) was used for the electrochemical experiments concerning the effects of the current density (5–40 mA·cm⁻²), initial aniline concentration (10–500 mg·L⁻¹), initial pH value (3–11), sodium chloride concentration (0–0.5 wt%), and type of reactor (2D and 3D reactors). The solution pH was adjusted by 5% (V/V) H₂SO₄ and 5% (w/w) NaOH. Samples were collected from the reactor at certain time intervals at room temperature (25 ± 1 °C). The concentration of aniline was measured by ultraviolet-visible absorption spectroscopy (230 nm) (Agilent 8453). In addition, the COD (ET 125 SC, CSB/COD reactor), ICE, and *E_p* were combined to characterize the degradation performance. The ICE and *E_p* were calculated with the following equations:

$$\text{ICE} = \frac{(\text{COD}_{t_1} - \text{COD}_{t_2})}{8I(t_1 - t_2)} FV \quad (1)$$

$$E_p = \frac{UI_t}{(\text{COD}_{t_1} - \text{COD}_{t_2})V} \quad (2)$$

where COD_{*t*1} and COD_{*t*2} are the COD at times *t*₁ and *t*₂, respectively, *I* is the current (A), *F* is the Faraday constant (96487 C·mol⁻¹), *V* is the volume of the electrolyte (L), and *U* is the cell voltage (V).

3. Results and discussion

3.1. Characterization of the Ti/TiO_xH_y/Sb-SnO₂ electrode

Fig. 2 shows SEM image and XRD pattern of the Ti/TiO_xH_y/Sb-SnO₂ electrode. The amount of the Sb-SnO₂ coating is about 5.37 mg·cm⁻². From Fig. 2(a), the surface layer of the Ti/TiO_xH_y/Sb-SnO₂ electrode is compact and even. There are no cracks on the surface coating layer. Many researchers believe that electrodes with a uniform and less “cracked-mud” structure favor extension of the electrode life and improvement of the stability [26,28,29]. Fig. 2(b) shows XRD patterns of the Ti/TiO_xH_y/Sb-SnO₂ coating layer. There are crystallized SnO₂ peaks (ICDD 00-001-0657, SnO₂ rutile) of the Sb-SnO₂ coating

layer and no diffraction peaks of Sb. These results can be explained by the Sb phase being well dispersed on the coating and forming a solid solution [30]. In addition, no diffraction peaks of Ti are present, indicating good coverage of the Ti substrate, which prevents infiltration of the electrolyte and maintains the stability of the electrode.

3.2. CV experiments

The electrochemical properties of aniline at the Ti/TiO_xH_y/Sb-SnO₂ electrode were investigated by CV, and the results are shown in Fig. 3. Fig. 3(a) shows the cyclic voltammograms of the Ti/TiO_xH_y/Sb-SnO₂ electrode in aqueous 0.5 wt% Na₂SO₄ solution and 0.5 wt% Na₂SO₄ solution with 100 mg·L⁻¹ aniline. The Ti/TiO_xH_y/Sb-SnO₂ electrode has a high OEP (2.0 V vs. Ag/AgCl). Anode materials with high OEPs are desirable for direct anodic oxidation for organic removal because of inhibition of unwanted power loss on oxygen generation [23,31]. Therefore, this result indicates that the novel electrode might have strong catalytic oxidation ability for organics. When 100 mg·L⁻¹ aniline was added to the supporting electrolyte, the maximum current density decreased from 46.4 to 37.2 mA·cm⁻². This indicates that some intermediate product adsorbed on the electrode surface, inhibiting the electron transfer rate and lowering the maximum current density, confirming that direct EO of aniline occurred [2]. Fig. 3(b) shows the cyclic voltammograms for the Ti/TiO_xH_y/Sb-SnO₂ electrode between 0 and 2.5 V at different sweep rates. The voltammetric charge (area under the response curve) increases with increasing scan rate from 10 to 200 mV·s⁻¹ in all of the cyclic voltammograms. The voltammetric charge is related to the real surface area and the specific electroactivity of sites for charge transfer, which determines the electroactivity of the electrode [32]. The total voltammetric charge *q*^{*}_T, which is related to electrochemically active surface area of the oxide, was obtained by plotting the reciprocal of *q*^{*} against the square root of the potential scan rate (*v*) using the following Eq. (3).

$$(q^*)^{-1} = (q_T^*)^{-1} + kv^{1/2} \quad (3)$$

The total voltammetric charge can be divided into two parts *q*^{*}_o and *q*^{*}_i. *q*^{*}_o represents the outer charge, which is related to

Fig. 2. SEM image and XRD pattern of Ti/TiO_xH_y/Sb-SnO₂ electrode.

Fig. 3. Cyclic voltammograms for Ti/TiO_xH_y/Sb-SnO₂ electrode (a) in aqueous 0.5 wt% Na₂SO₄ solution or 0.5 wt% Na₂SO₄ solution with 100 mg·L⁻¹ aniline and (b) with sweep rates from 10 to 200 mV·s⁻¹ in 0.5 wt% Na₂SO₄ solution; (c) Reciprocal voltammetric charge (q^*)⁻¹ versus the square root of the voltammetric scan rate $v^{1/2}$; (d) Voltammetric charge q^* versus the reciprocal square root of the voltammetric scan rate $v^{1/2}$.

the outer surface of the oxide coating directly exposed to the electrolyte. q_o^* can be obtained with the following Eq. (4).

$$q^* = q_o^* + k' v^{-1/2} \quad (4)$$

q_i^* represents the inner charge, which is related the inner surface of the coating, including loose grain boundaries, pores, and microcracks. q_i^* can be obtained with the following Eq. (5).

$$q_T^* = q_o^* + q_i^* \quad (5)$$

Fig. 3(c) and 3(d) show these plots for the Ti/TiO_xH_y/Sb-SnO₂ electrode in 0.5 wt% Na₂SO₄ solution, and good linear fitting is observed. From Fig. 2(c) and 2(d), the q_T^* , q_o^* and q_i^* are 2.795 C·cm⁻², 0.662 C·cm⁻², and 2.133 C·cm⁻², respectively. The electrochemical porosity can be obtained by the ratio of q_i^* and q_T^* :

$$\varepsilon = q_i^*/q_T^* \times 100\% \quad (6)$$

using Eq. (6), the electrochemical porosity of the novel electrode is 76.31%, which is higher than the electrochemical porosities of Ti/Cu-NRs/SnO₂-Sb (71.15%) [23], 3D-Ti/PbO₂ (54%) [33], and Ti/Sb-SnO₂-TiN (61.54%) [34]. A electrode with a high electrochemical porosity can provide more active sites for EO, indicating that the Ti/TiO_xH_y/Sb-SnO₂ electrode will have a good catalytic effect on aniline wastewater.

3.3. Electrochemical oxidation of aniline

3.3.1. Effect of the current density

The applied current density is an important factor and has a significant influence on the EO process. To assess the effect of this factor, applied current densities ranging from 5 to 40

mA·cm⁻² were applied to degradation of aniline. Fig. 4 shows the effect of the current density on aniline and COD removal. As shown in Fig. 4(a) and 4(b), there is a significant increase in the aniline removal rate with increasing current density from 5 to 40 mA·cm⁻². The aniline and COD removal efficiencies increase from 38.4% to 93.5% and 35.9% to 82.9% after 2 h electrolysis, respectively. In general, a high applied current density can promote electron transfer and HO· generation on the electrode surface. Therefore, a higher current density can improve the degradation rate of aniline. However, the degradation rate of aniline only slightly increases when the current density is above 20 mA·cm⁻². This can be explained by the theory of limiting current density [35]. A k_m value of 6.4×10^{-5} m·s⁻¹ was obtained using the Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox couple at a flow rate of 5 L·min⁻¹ [36,37].

$$j_{lim}^0 = 4Fk_m C_0(\text{COD}) \quad (7)$$

j_{lim}^0 is the limiting current density for organic mineralization (A·m⁻²), F is the Faraday constant (96487 C·mol⁻¹), k_m is the mass transport coefficient (m·s⁻¹) and $C_0(\text{COD})$ is the initial chemical oxygen demand (100 mg·L⁻¹ aniline is approximately equal to 8.64 mol·m⁻³ O₂).

Using Eq. (7), the j_{lim}^0 for the reaction is 21.3 mA·cm⁻². Palma-Gdyes et al. [38] found that when the current density was lower than the limiting current density, side reactions rarely occurred. In contrast, when the applied current density is higher than the limiting current density, lots of energy is consumed by side reactions, for example,

Fig. 4. Effect of current density on (a) aniline and (b) COD removal, (c) instantaneous current efficiency and (d) energy consumption. Reaction conditions: initial pH value 7.0, supporting electrolyte 0.5wt% Na_2SO_4 solution, 2D reactor.

the oxygen evolution reaction, heat loss, and so forth. Considering the energy consumption and current efficiency, 20 $\text{mA}\cdot\text{cm}^{-2}$ is considered to be the most appropriate current density, and we chose this value to investigate the effects of other factors on electrochemical degradation of aniline in aqueous solution.

As shown in Fig. 4(c) and 4(d), with increasing current density, the ICE gradually decreases, and E_p gradually increases. This can be explained by the higher current density promoting the oxygen evolution reaction, which would compete with EO of aniline. Furthermore, with higher current density, more heat would be lost. Therefore, the current density has a significant effect on the ICE and E_p . The ICE values under different current densities are all not 100%, indicating that the system is mass-transfer controlled.

The degradation reaction follows pseudo-first-order kinetics at all of the applied current densities. As shown in Table 1, at 40 $\text{mA}\cdot\text{cm}^{-2}$, the $t_{1/2}$ value for degradation of aniline remarkably decreases from 3.19 h at 5 $\text{mA}\cdot\text{cm}^{-2}$ to 0.68 h, while the k value increases from 0.21 h^{-1} at 5 $\text{mA}\cdot\text{cm}^{-2}$ to 1.73 h^{-1} .

3.3.2. Effect of the initial aniline concentration

Fig. 5 shows the effect of the initial aniline concentration in the range 10 to 500 $\text{mg}\cdot\text{L}^{-1}$. The aniline and COD removal ratios of the initial concentration (10–500 $\text{mg}\cdot\text{L}^{-1}$) increase from 72.6% to 83.9% and 51.5% to 79.9% after 2 h electrolysis, respectively. This indicates that the $\text{Ti}/\text{TiO}_x\text{H}_y/\text{Sb}-\text{SnO}_2$ electrode

shows excellent performance for aniline degradation at various concentration levels.

The ICE and E_p values for different initial aniline concentrations are shown in Fig. 5(c) and 5(d). With increasing initial aniline concentration, ICE increases and E_p decreases. This is because for the same current density, production of $\text{HO}\cdot$ is constant. For a relatively low aniline concentration, excess $\text{HO}\cdot$ would be converted to oxygen and a large amount of electric energy would be converted into heat energy. Therefore, most of the $\text{HO}\cdot$ and electric energy is wasted, leading to a relatively low ICE and a relatively high E_p .

As shown in Table 1, for aniline electrolysis with initial concentrations of 10, 50, 100, 200, and 500 $\text{mg}\cdot\text{L}^{-1}$, the $t_{1/2}$ values are 0.41, 0.72, 0.84, 0.91, and 0.94 h, and the k values are 0.83, 0.81, 0.63, 0.61, and 0.46 h^{-1} , respectively. It is clear that the degradation rate is lower for higher initial aniline concentration. This can be explained by diffusion control [39]. More intermediates would be generated by the electrolysis process at a higher aniline concentration, which may accumulate on the anode surface or compete with aniline for the same area of the anode [3,40]. Comparatively, for lower initial aniline concentration, more aniline is expected to be completely degraded at the electrode surface. However, a higher amount of aniline is removed per unit time at a higher aniline concentration. This is because of diffusion, where more aniline molecules would approach the surface of the anode at a high aniline concentration than at a low aniline concentration. Therefore, the constant $\text{HO}\cdot$

Table 1Electrochemical oxidation of aniline over Ti/TiO₂H₂/Sb-SnO₂ electrode under different experimental factors.

Item	Value	Rate constant (k , h^{-1}) ^a	Half-life ($t_{1/2}$, h)	R^2	ICE (%) ^b	E_p (kWh/gCOD) ^c
Current density ($\text{mA}\cdot\text{cm}^{-2}$)	5	0.21	3.19	0.989	27.9	0.117
	10	0.33	1.76	0.992	19.6	0.186
	20	0.63	0.84	0.992	14.6	0.295
	30	0.85	0.76	0.991	9.7	0.323
	40	1.73	0.68	0.995	7.2	0.336
Initial concentration ($\text{mg}\cdot\text{L}^{-1}$)	10	0.83	0.41	0.987	3.8	0.483
	50	0.81	0.72	0.989	10.9	0.327
	100	0.63	0.84	0.992	14.6	0.295
	200	0.61	0.91	0.995	27.9	0.09
	500	0.46	0.97	0.986	29.4	0.07
Initial pH	3	1.35	0.41	0.989	16.3	0.244
	5	1.14	0.48	0.987	16.1	0.251
	7	0.63	0.84	0.992	14.6	0.295
	9	0.85	0.71	0.991	14.7	0.277
	11	0.94	0.67	0.991	15.1	0.264
NaCl concentration (wt%)	0	0.63	0.84	0.992	14.6	0.295
	0.05	0.71	0.83	0.989	16.8	0.233
	0.1	0.79	0.65	0.994	19.5	0.182
	0.2	1.09	0.48	0.996	30.2	0.149
	0.5	0.94	0.55	0.998	15.1	0.275
Reactor	2D	0.63	0.84	0.992	14.6	0.295
	3D	1.69	0.55	0.981	22.1	0.164
	I-C ^d	—	—	—	—	—

^a Pseudo-first-order rate constant of aniline electrochemical degradation.^{b,c} The values of ICE and E_p were both obtained at the time of 50% COD removal.^d I-C represents iron-carbon micro electrolysis experiment. **Fig. 5.** Effect of initial concentration on (a) aniline, (b) COD removal, (c) instantaneous current efficiency and (d) energy consumption. Initial pH value 7.0, current density $20 \text{ mA}\cdot\text{cm}^{-2}$, supporting electrolyte $0.5 \text{ wt}\% \text{ Na}_2\text{SO}_4$ solution, 2D reactor.

could rapidly react with the contaminants.

3.3.3. Effect of the initial pH value

The initial pH is also an important factor that influences the removal of pollutants. Fig. 6 shows the effect of the initial solution pH on removal of aniline. From Fig. 6(a), the aniline re-

Fig. 6. Effect of pH on (a) aniline, (b) COD removal, (c) instantaneous current efficiency and (d) energy consumption. Current density 20 mA·cm⁻², supporting electrolyte 0.5 wt% Na₂SO₄ solution, 2D reactor.

removal rate is higher in acid or alkaline conditions than in neutral conditions. The maximum removal rate of aniline is at pH = 3 (94.5%), which is higher than that at pH = 7 (80.94%) and pH = 11 (88.6%) after 2 h electrolysis. The k value at an initial pH of 3 is 1.35 h⁻¹, which is about 2 times higher than that at pH = 7 (0.63 h⁻¹), and the $t_{1/2}$ value is lower at pH = 7 (0.84 h) than at pH = 3 (0.41 h). This suggests that the aniline oxidation process is more favorable in acidic solution. This is because the oxidation potential of the hydroxyl radical is higher in acidic conditions. Thus, low pH can inhibit the oxygen evolution reaction and improve the aniline degradation efficiency [41]. It is widely accepted that an increase in the solution pH is favorable for oxygen evolution and more HO• radical would be generated, which promotes degradation of aniline [42,43]. A reasonable explanation is that the promoting effect is greater in acidic conditions than in alkaline conditions. Therefore, the degradation rate of aniline is higher in acidic conditions than in alkaline and neutral conditions.

The initial pH value had little effect on the removal of COD (Fig. 6(b)). The maximum COD removal ratio in the initial pH range (3–11) is around 63% after 2 h electrolysis, which is lower than the removal ratio of aniline. This can be explained by aniline decomposing into many intermediate products in the oxidation process. However, the intermediate products are difficult to further decompose in aqueous solution. Therefore, the COD is not different.

As shown in Fig. 6(c) and 6(d), the pH also has little effect on

the ICE and E_p during the electrolysis process. Compared with alkaline and neutral environments, an acidic environment is slightly more favorable for obtaining a high ICE and a low E_p . This is because the values of ICE and E_p are closely related to the COD removal efficiency. Acidic conditions are more beneficial for inhibiting the oxygen evolution reaction. Therefore, the utilization efficiency of the HO• radical for attacking organic molecules is higher and the energy loss is less.

3.3.4. Effect of chloride ions

Chloride ions often exist in wastewater, so the effect of chloride ions on oxidation of aniline was also investigated (Fig. 7). Many researchers believed that Cl⁻ can react with HO• and produce hypochlorite ions and other reactive oxygen species [44,45]. These reactive oxygen species can effectively enhance the electrode ability for degradation of organics. From Fig. 7(a) and 7(b), both the aniline and COD removal ratios increase as the Cl⁻ concentration increases. Pereira et al. [46] reported that when Cl⁻ was added to the solution, the performance of the Ti-Pt/PbO₂ anode improved and the active chlorine species significantly contributed to degradation of organics (Eqs. (11)–(13)). However, when the NaCl dosage was 0.5 wt%, the aniline and COD removal ratios decreased. Yu et al. [47] found that oxidizing groups could be suppressed when the Cl⁻ concentration is very low. The excess Cl concentration may lead to side reactions (Eq. (10)) and a large amount of energy would be wasted. Therefore, 0.2 wt% was considered to be the optimal

Fig. 7. Effect of chloride ions on (a) aniline, (b) COD removal, (c) instantaneous current efficiency and (d) energy consumption. Current density 20 mA·cm⁻², supporting electrolyte 0.5 wt% Na₂SO₄ + *x* wt% NaCl solution, 2D reactor.

NaCl dosage, and the aniline and COD removal ratios reach 79.4% and 76.4% after 2 h electrolysis, respectively.

where R represents organics.

Fig. 7(c) and 7(d) shows the values of ICE and E_p with different dosages of NaCl. The ICE increases and E_p decreases as the NaCl dosage increases from 0 to 0.2 wt%. However, when the NaCl dosage reaches 0.5 wt%, the ICE decreases and the E_p increases. This is consistent with the results of Fig. 7(a) and 7(b), and this phenomenon can also be explained by above mentioned reasons.

As shown in Table 1, for NaCl dosages of 0, 0.05, 0.1, 0.2 and 0.5 wt%, the k values are 0.63, 0.71, 0.79, 1.09, and 0.94 h⁻¹, and the $t_{1/2}$ values are 0.84, 0.83, 0.65, 0.48, and 0.55 h, respectively. Therefore, chloride ions have a great influence on the degradation of aniline. However, some toxic byproducts would form during EO in the presence of chloride ions [42,48]. Therefore, addition of chloride ions should be carefully considered.

3.3.5. Effect of the reactor

The electrode reactor also plays an important role in EO. Fig. 8 shows a comparison of the performance of a traditional 2D and 3D reactors under the same operation conditions. To more

accurately compare the effect of the type of reactor, an iron-carbon microelectrolysis experiment was performed as a blank control group. The conditions were the same as those in the 3D reactor without an applied current. As shown in Fig. 8(a) and 8(b), the aniline and COD removal ratios in the 2D electrode system reach 80.94% and 61.9% after 2 h electrolysis, respectively. The corresponding aniline and COD removal ratios for the 3D electrode system and blank control group after 2 h electrolysis are about 100% and 31.8%, and 73.5% and 22.8%, respectively. The k and $t_{1/2}$ values for the 2D and 3D reactors are 0.63 h⁻¹ and 0.84 h, and 1.69 h⁻¹ and 0.55 h, respectively (Table 1). Therefore, the 3D electrode system is more effective than the 2D electrode system. Furthermore, as shown in Fig. 8(c) and 8(d), comparing the 2D with 3D reactors, higher ICE and lower E_p were obtained in the 3D electrode system.

This result can be explained by the synergistic effect of electrocatalysis and iron-carbon microelectrolysis. The iron-carbon particles in the 3D electrode system form numerous microelectrodes in the electric field and provide more reactive sites for pollutant adsorption or even catalytic reactions, which is beneficial for aniline EO [49,50]. Furthermore, because of the presence of iron-carbon particles, the transmission rate of charge or pollutant molecules could be faster in the 3D electrode system than in the 2D electrode system, promoting the electrocatalytic oxidation process. In addition, the widely used iron-carbon microelectrolysis technique (no external power is required)

Fig. 8. Effect of reactor on (a) aniline, (b) COD removal, (c) instantaneous current efficiency and (d) energy consumption. Initial pH value 7.0, current density $20 \text{ mA}\cdot\text{cm}^{-2}$, supporting electrolyte 0.5 wt% Na_2SO_4 .

could also promote degradation of aniline. Therefore, this 3D EO process shows better performance than the conventional 2D system.

3.4. Instantaneous current efficiency and energy consumption

To simply and accurately compare the ICE and E_p values for different parameters, the ICE and E_p values obtained at the time of 50% COD removal are shown in Table 1. From Table 1, it can be concluded that a lower current density, a higher initial concentration, acidic conditions, an appropriate chlorine dosage, and a 3D system favor a higher ICE and a lower E_p . At the time of 50% COD removal under the various conditions, the ICE and E_p values vary from 3.8% to 30.2% and 0.07 to 0.483 kWh/gCOD, respectively.

For an initial concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ aniline at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ in 0.5 wt% Na_2SO_4 solution (without Cl^-), the maximum ICE and minimum E_p reach 22.1% and 0.164 kWh/gCOD in the 3D system. Although low energy consumption (0.117 kWh/gCOD) was achieved at a low current density ($5 \text{ mA}\cdot\text{cm}^{-2}$), the degradation efficiency was low. In addition, the addition of Cl^- might increase the water toxicity and the acidic environment would shorten the service life of the electrode. Therefore, considering the economic cost and toxicity in the EO process, a relatively energy efficient process was conceived: dilute aniline wastewater is firstly concentrated and then electrochemically treated in a 3D system.

4. Conclusions

A stable $\text{Ti}/\text{TiO}_x\text{H}_y/\text{Sb-SnO}_2$ electrode was prepared by the electrodeposition method. SEM images and XRD patterns showed that the electrode coating was completely covered with no cracks. CV analysis indicated that the novel electrode had a high OEP (2.0 V vs Ag/AgCl) and high electrochemical porosity (76.31%), which are favorable for the catalytic performance of the electrode. EO of aniline using the $\text{Ti}/\text{TiO}_x\text{H}_y/\text{Sb-SnO}_2$ anode followed pseudo-first-order kinetics. A high current density, an acidic solution, and an appropriate NaCl dosage (0.2 wt%) had a positive effect on the removal of aniline. In addition, the $\text{Ti}/\text{TiO}_x\text{H}_y/\text{Sb-SnO}_2$ electrode showed better aniline oxidation ability in a 3D reactor than that in a 2D reactor.

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Graphical Abstract

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Electrochemical oxidation of aniline by a novel Ti/TiO_xH_y/Sb-SnO₂ electrode

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A stable Ti/TiO_xH_y/Sb-SnO₂ anode was fabricated and applied to eliminate aniline from aqueous solution under different operating parameters. The novel electrode exhibited an excellent electrocatalytic activity for aniline removal and the optimized operation conditions for removal of aniline were also determined.

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新型Ti/TiO_xH_y/Sb-SnO₂电极上苯胺电化学氧化反应

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摘要: 苯胺是一种重要的化工原料, 广泛应用于印染、制药、造纸、橡胶等领域. 随着化工行业的迅速发展, 苯胺的需求量越来越大. 然而, 苯胺毒性高, 大量使用势必造成水体中苯胺浓度的升高, 给人类健康及生态环境造成危害. 因此, 急需一种高效、洁净、经济的方法处理含苯胺废水.

电化学氧化法比较新颖, 相比传统废水处理方法, 它具有高效、简单、清洁等优点, 因此被应用于很多废水处理当中, 但过多的能耗限制了其进一步广泛应用. 阳极作为电化学氧化技术的核心部件, 直接影响到电化学氧化反应性能. 因此开发出一种高效、经济的阳极材料很有必要. 此外, 对苯胺降解条件的优化也同样重要.

关于苯胺电化学氧化, 已有的研究包括Pt电极、PbO₂电极和石墨电极等阳极材料. 比较而言, Ti/Sb-SnO₂电极具有制备工艺简单, 析氧过电位较高, 材料廉价和电催化性能较强等优点. 然而, 它的稳定性仍有待提高. 因此本文制备了一种高稳定性的Ti/TiO_xH_y/Sb-SnO₂电极, 并用于处理苯胺废水. 较为系统地研究了电流密度、苯胺初始浓度、pH、NaCl投加量及反应器类型对苯胺电催化氧化性能的影响, 同时采用扫描电镜(SEM)、X射线衍射(XRD)和电化学测试对该电极进行了表征, 并应用紫外-可见光谱、化学需氧量、电流效率及能耗对不同参数进行评定和优化.

SEM及XRD结果表明, Ti/TiO_xH_y/Sb-SnO₂电极涂层覆盖比较完全、紧实, 未出现裂缝的发生, 因而有利于提高电极稳定性. 循环伏安测试结果表明, 此电极具备较高的析氧过电位(2.0 V vs Ag/AgCl)及电化学孔隙度(76.31%), 因此有利于电极催化性能的提高. 苯胺电化学氧化实验结果发现, 该反应符合准一级动力学模型, 且高电流密度、酸性环境、适当NaCl投加量(0.2 wt%)更有利于苯胺的降解. 另外, Ti/TiO_xH_y/Sb-SnO₂电极在三维反应器中对苯胺的处理效果要远远好于在二维反应器中. 可以看出, Ti/TiO_xH_y/Sb-SnO₂电极具有较好的处理苯胺性能, 可为苯胺废水处理的应用提供了一定的理论指导.

关键词: 苯胺; Ti/TiO_xH_y/Sb-SnO₂电极; 电化学氧化; 氯离子; 三维反应器

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