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Electrochemical Oxidation of Tetracaine Hydrochloride using a Transition Metal Doped PbO_2 Electrode

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Pharmaceutical wastewater is a kind of biorefractory organic wastewater and could not be treated efficiently by the traditional biological wastewater process with the ever-increasing discharge standard. This work prepared Al/Zn doped PbO_2 anodes and used them to treat tetracaine hydrochloride by electrochemical oxidation process. The effects of operational factors, such as current density, initial concentration of tetracaine hydrochloride and the initial value of pH, were explored and discussed. The results showed that the electrochemical oxidation using Al/Zn doped PbO_2 electrode is an effective solution to treat this kind of wastewater. And the removal efficiency of tetracaine hydrochloride and COD were above 97.35% and 59.56% after 120 min at typical condition. The degradation mechanism was analyzed and the reaction mechanism was discussed by the free radical reaction mechanism of direct oxidation and indirect oxidation. This paper could provide basic data of electrochemical oxidation for the tetracaine hydrochloride and other pharmaceutical wastewater pollution control.

Keywords: Electrochemical oxidation, Tetracaine hydrochloride, Degradation mechanism; Al/Zn doped PbO_2 electrode

1. INTRODUCTION

Pharmaceutical wastewater is a kind of biorefractory organic wastewater and could not be treated efficiently by the traditional biological wastewater process with the ever-increasing discharge standard. The biorefractory organics in the wastewater would cause ecological risks to the environment without suitable treatment [1-2]. Therefore, pharmaceutical wastewater treatment technology without second pollution has been attracted the attention by both scientists and the government.

Electrochemical oxidation is a promising technology in organic wastewater pollution control by direct oxidation through electron transfer and indirect oxidation through the generation of highly reactive radicals, such as hydroxyl radicals, and so on [3-8]. The electrodes play the key role in

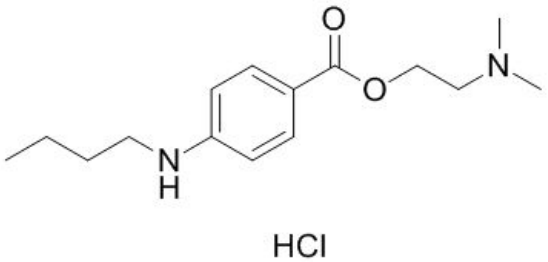
electrochemical oxidation and different kinds of anodes have been explored for the degradation of organic pollutants. Lead dioxide electrode has received rising attention for wastewater treatment and the results showed that it is a promising material due to the high oxygen evolution potential, strong corrosion resistance, good conductivity and low cost [9-12]. It was found that after doping several elements, the electrocatalytic oxidation efficiency and the stability of lead dioxide electrode could be improved, including Co [13, 14], Al [15], Ni [16], and so on. The catalytic activity effect would be enhanced if the electrode surface could appear as the nanometer crystal. So, if the nanometer crystal lead dioxide electrode doped with transition metal was prepared, it would be potential widely used for the application of electrochemical oxidation in organic wastewater treatment. However, the research on PbO_2 electrodes doped with transition metal is still limited.

In this study, Al and Zn were selected as the typical transition metals and used to prepare the transition metal doped PbO_2 electrode. Tetracaine hydrochloride was selected as the mode organic pollutant because it was a typical medicine and could be found in pharmaceutical wastewater all over the word. The Al/Zn doped PbO_2 electrode was prepared by electrodeposition and was used to degrade tetracaine hydrochloride. The operational factors on tetracaine hydrochloride and COD removal were studied, including the current density, initial tetracaine hydrochloride concentration and initial value of pH. Also, the characteristic of the doped electrodes and the degradation mechanism of tetracaine hydrochloride in electrochemical oxidation were discussed. This paper could provide basic data and technique reference for the tetracaine hydrochloride wastewater and other pharmaceutical wastewater pollution control.

2. EXPERIMENTAL

2.1 Materials and reagents

Tetracaine hydrochloride used in the study was purchased from Aladdin Chemicals (Shanghai, China) and it was analytical reagent. The chemical structure was shown in Schema 1.



Scheme 1.

2.2 Electrode preparation and characterization

Al/Zn doped PbO_2 was prepared by Sn-SbO_x thermal decomposition, α-PbO_2 intermediate electrodeposition and Al/Zn doped PbO_2 active layer electrodeposition [11]. The surface morphology was observed using a scanning electron microscope (Hitachi-S570, Hitachi, Japan). X-ray

diffractometer (XRD) patterns were obtained with an X-ray diffraction (PANalytical, Metherlands), using Cu Kα radiation at 40 KV and 40mA.

2.3 Electrochemical oxidation experiments

Electrochemical oxidation experiments were performed to explore the effects of operational factors, including current density (10 – 50 mA/cm^2), initial concentration (50 – 1000 mg/L) and the initial pH value (3.0 – 11.0). The doped electrode was used as the electrochemical oxidation system anode and the titanium plate with the same area was used as the cathode.

2.4 Analytical methods

The concentration of tetracaine hydrochloride was determined by high performance liquid chromatography (1200, Agilent Technologies, USA) with an ultraviolet detector and a C18 column (250 mm×4.6 m, 5 μm). The detection wavelength was 310 nm and the column temperature was 25 ºC. The mobile phase was methanol and water (1% three ethylamine) with the ration of 65:35 (v/v) at the flow rate of 1.0 mL/min. The injection volume was 5 μL. The chemical oxygen demand (COD) was analyzed using fast digestion spectrophotometer method (DRB200, Hach, USA). The intermediates of small molecular organic acids were analyzed with ion chromatograph (ICS-200, Dionex, USA).

The instantaneous current efficiency (ICE) was calculated using the following equation:

$$ICE=\frac{(COD_0\text{-}COD_t)}{8It}FV\times 100\% \quad (1)$$

Where COD_0 and COD_t (g/L) are the chemical oxygen demand at the initial time and the reaction time t, respectively. F is the Faraday constant (96487 C/mol), V is the volume of the solution (dm^3), I is the current (A) and t is the reaction time (s).

3. RESULT AND DISCUSSION

3.1 The effects of doped and undoped electrodes

The electrodes of Al/Zn doped electrodes were prepared and the effects of doped and undoped electrodes were analyzed. As were shown in Figure 1, the effects of undoped and Al/Zn doped PbO_2 were studied on condition of tetracaine hydrochloride 100 mg/L, pH 5.0, 0.1 mol/L Na_2SO_4 and current density 30mA/cm^2.

The tetracaine hydrochloride could be removed with 62.71% after 30min treatment, while the effect of undoped electrode is 46.52%. After 120 min treatment, the tetracaine hydrochloride could be almost total removed with Al/Zn doped PbO_2 electrode, and the effect of undoped electrode is 85.04%. The results showed that the structure of the pollutant could be almost total destroyed after 2 h treatment with Al/Zn doped electrode, which means that electrochemical oxidation with this Al/Zn doped electrode could be used in organic wastewater treatment with potential widely application.

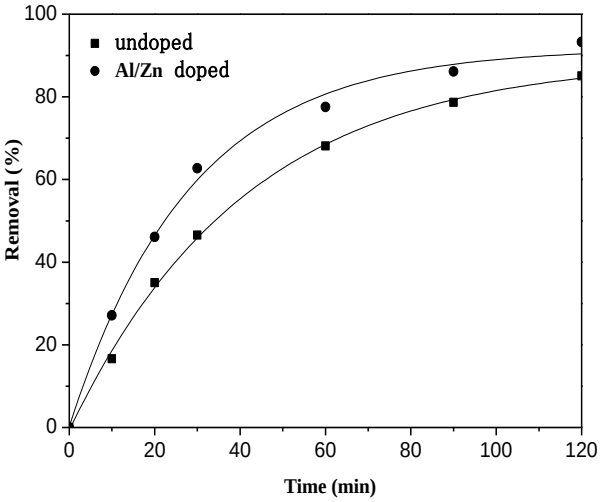


Figure 1. The effect of doped and undoped electrodes on condition of tetracaine hydrochloride 100 mg/L, pH 5.0, Na_2SO_4 0.1 mol/L and current density 30mA/cm^2.

3.2 Morphologies of doped and undoped electrodes

The morphology of electrode active layer is greatly influencing the effects of organics degradation. And the microstructures of PbO_2 layer was analyzed by SEM for both doped and undoped electrodes.

Figure 2 (a) and (b) showed the micrographs of the undoped and Al/Zn doped PbO_2 electrode surfaces. Both undoped and Al/Zn doped PbO_2 electrodes showed that the surface was compact with pyramidal crystals. Compared with these two images, it could be found that after doped, the electrode surface angle was greatly enhanced with an obviously present of nanoparticles. For the electrochemical catalytic efficiency, the electrodes surface with nanoparticles could express a higher reactivity than relatively big particles due to the smaller particles could promote the reaction efficiency of the electrode [9]. Compared with undoped electrode, the surface of Al/Zn doped electrode was rougher with more nanocrystal particles, which would enhance the catalytic performance of the electrodes [17-20].

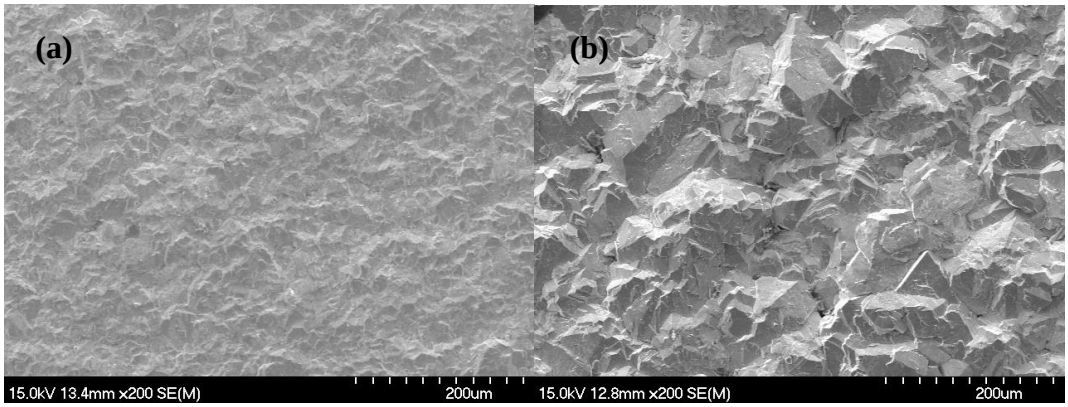


Figure 2. SEM of PbO_2 electrodes (a) undoped; (b) Al/Zn doped

3.3 Effect of current density

Current density is a key factor for the electrochemical oxidation of tetracaine hydrochloride with Al/Zn doped electrode. The degradation of tetracaine hydrochloride could be simplified as the direct oxidation and indirect oxidation. The direct oxidation is based on the electron transfer oxidation and the indirect oxidation is controlled by hydroxyl radicals formed on the electrode surface. For the PbO_2 electrode, the indirect oxidation is the main pathway by hydroxyl radicals on the anode surface for the degradation of organics [16, 21-24].

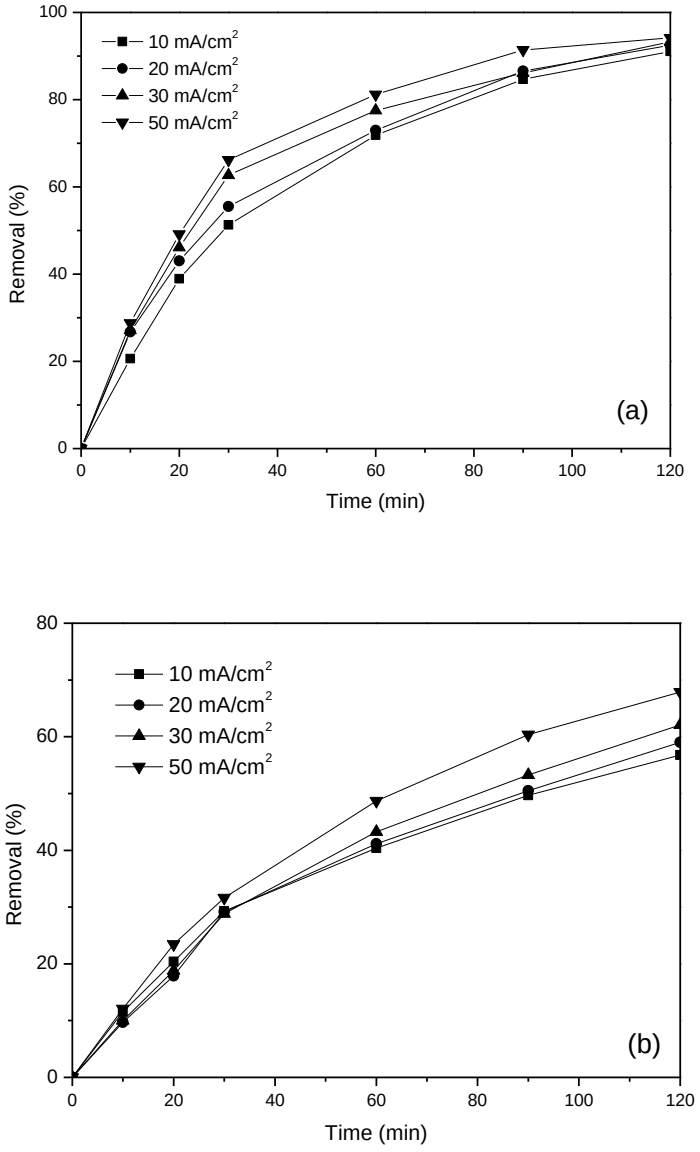


Figure 3. Effect of current density on tetracaine hydrochloride removal on condition of tetracaine hydrochloride 100 mg/L, pH 5.0 and Na_2SO_4 0.1 mol/L.: (a)Concentration, (b) COD

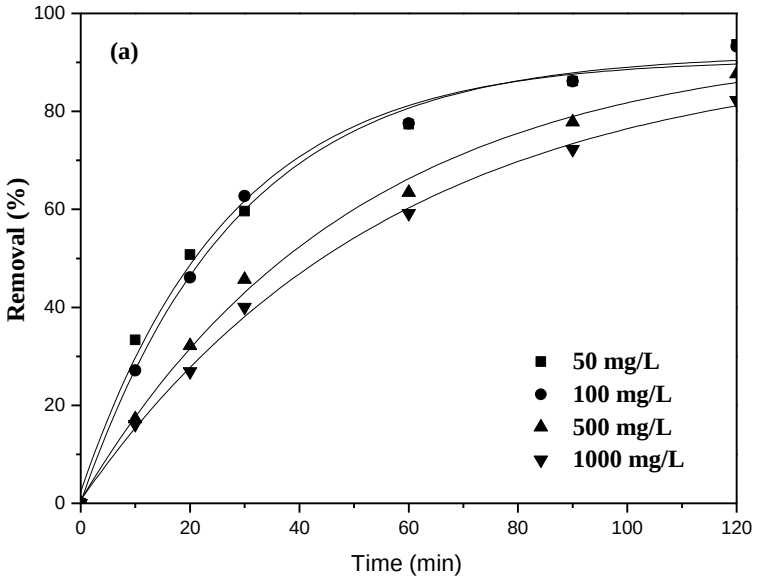
The effect of different current densities, ranging from 10 mA/cm^2 to 50 mA/cm^2, were selected to explored on the degradation of tetracaine hydrochloride and COD removal.

Figure 3 (a) and (b) showed the removal of tetracaine hydrochloride and COD under different current densities at time intervals. The results showed that the removal of tetracaine hydrochloride and COD were enhanced with the increase of the current density. And it also could be seen that the removal of tetracaine hydrochloride increased greatly with the rose when the current density was up to 50 mA/cm^2. On condition of $10mA/cm^2$, $20mA/cm^2$, $30mA/cm^2$ and $50mA/cm^2$, the tetracaine hydrochloride removal efficiency after 120 min treatment was 91.04%, 92.47%, 93.27% and 94.13%, respectively. While for the COD removal, the efficiency on the different current density was 56.76%, 59.03%, 62.07% and 67.85%, respectively. The results showed that the trend of COD removal was similar as that of tetracaine hydrochloride. The results showed that at a higher current density, the formation of kind of radicals, such as the hydroxyl radicals, would be enhanced. Thus, the removal efficiency would be greater for degradation of tetracaine hydrochloride and COD.

However, when the current density increase, the side reactions would also be more obvious. The ICE at different current density were calculated to show the energy consumption. The ICE results showed that the maximum ICE was 77.82% on condition of $10mA/cm^2$ after 10 min treatment. With the rose of current density, the ICE decreased obviously. When the current density reached $30mA/cm^2$, the ICE decreased not as obvious as that of $10mA/cm^2$ during the 120 min reaction.

3.4 Effect of initial concentration of tetracaine hydrochloride

Initial concentration of tetracaine hydrochloride is related to the final removal efficiency and cost for organic wastewater treatment. In this study, the effect of different concentrations of tetracaine hydrochloride, ranging from 50 mg/L to 1000 mg/L, was studied on condition of pH 5.0, Na_2SO_4 0.1 mol/L and current density 30 mA/cm^2. The results were shown in Figure 4 and it could be concluded that the removal of tetracaine hydrochloride concentration and COD were decreased with the tetracaine hydrochloride initial concentration increased.



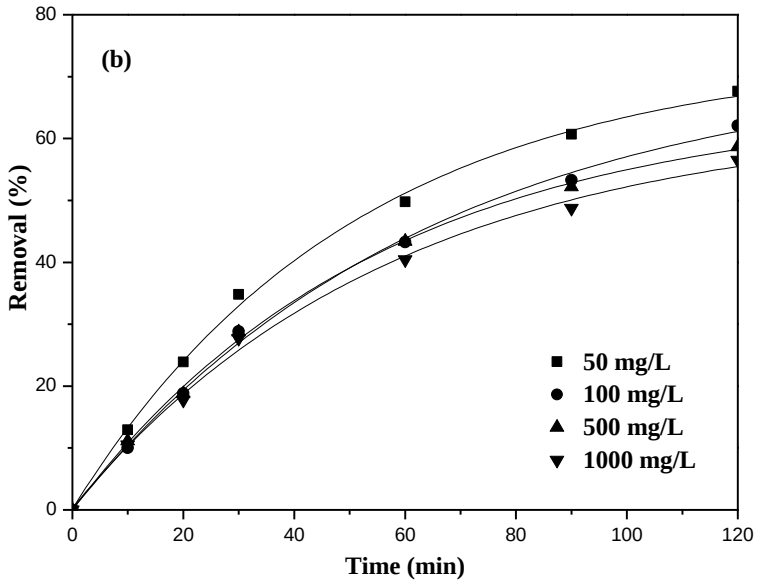


Figure 4. Effect of initial concentration on tetracaine hydrochloride removal on condition of current density 30 mA/cm^2, pH 5.0 and Na_2SO_4 0.1 mol/L.: (a) Concentration, (b) COD

The tetracaine hydrochloride concentration removal was more obvious than other initial concentration when the concentration was not more than 100 mg/L. After 120min treatment, the tetracaine hydrochloride concentration removal was 93.68%, 93.27%, 87.65% and 82.28% for 50mg/L, 100mg/L, 500mg/L and 1000mg/L, respectively. And after 60min treatment, the tetracaine hydrochloride concentration removal was 78.44%, 77.55%, 63.46% and 59.19% for 50mg/L, 100mg/L, 500mg/L and 1000mg/L, respectively. These results indicated that the Al/Zn doped electrode is promising for the degradation of tetracaine hydrochloride on different concentration levels.

As for COD removal, the effect after 120 min treatment was 67.66%, 62.07%, 58.65% and 56.51% for 50mg/L, 100mg/L, 500mg/L and 1000mg/L, respectively. Compared with that of concentration removal, the results showed that the reaction constants would change with the different initial concentration, and a better removal result could be achieved when the initial concentration is 50mg/L and 100mg/L.

There were a number of hydroxyl radicals and other radicals were produced during the reaction, the hydroxyl radicals and other radicals could react with tetracaine hydrochloride and thus the pollutant concentration would reduce, resulting the decline of the removal of tetracaine hydrochloride and COD. When the initial concentration of tetracaine hydrochloride was not high, the organics would be degraded quickly, together with the intermediates. That would lead to an obvious mineralization of organics and the pollutants could be removed effectively. However, when the initial concentration of tetracaine hydrochloride at a high level, some of the intermediates could not be totally degraded and thus lead to the accumulation of kinds of intermediates during the reaction. The intermediates could transfer to the electrode surface and influence the reaction diffusion process. Considering the consists of wastewater discharged by the industrial factories, the level of 100 mg/L of tetracaine hydrochloride was selected with subsequent experiments.

3.5 Effect of initial pH

The pH value is an important factor in electrochemical oxidation of organics. The organics also could be a certain dissociation at a certain pH value in the solution. So, the solution of initial pH would influence reaction and dissociation of tetracaine hydrochloride. In this paper, the effect of initial pH on the removal of tetracaine hydrochloride and COD was studied when the initial pH range was between 3 and 11 on condition of tetracaine hydrochloride 100 mg/L, Na_2SO_4 0.1 mol/L and current density 30 mA/cm^2. As were shown in Figure 5, the tetracaine hydrochloride removal after 30 min treatment was 40.62%, 35.51%, 37.91% and 55.65% on condition of pH is 3, 5, 7 and 11, respectively. And the removal of tetracaine hydrochloride were 70.61%, 62.49%, 66.39% and 76.93% after 60 min treatment on condition of pH is 3, 5, 7 and 11, respectively. After 120 min treatment, the tetracaine hydrochloride removal efficiency were all above 95%, which showed that at acid and alkaline condition, the reaction constants were relatively higher during the reaction and after 120 min treatment, almost all pollutants could be removed.

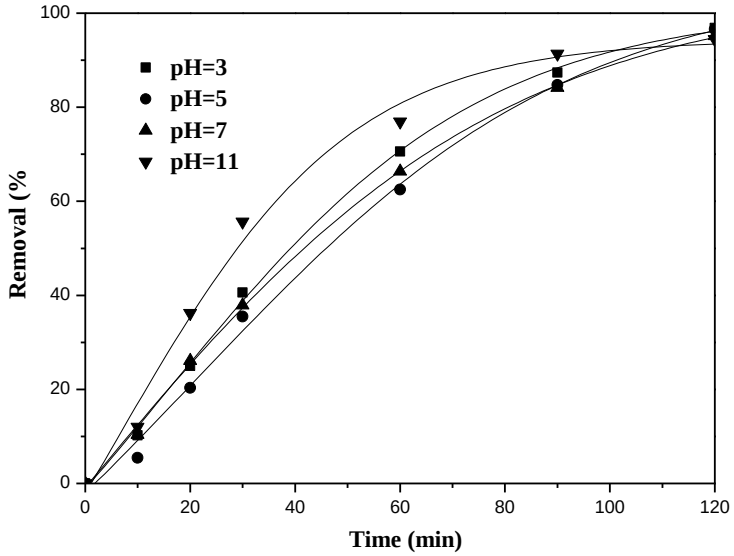


Figure 5. Effect of pH on tetracaine hydrochloride removal

3.6 Degradation mechanism

The degradation mechanism of electrochemical oxidation process could be divided as the direct oxidation and indirect oxidation. While for doped and undoped PbO_2 electrode, the oxidation organics is mainly through indirect oxidation and the hydroxyl radicals play the key role in the organics degradation. The reaction mechanism could be named as anodic O-transfer reactions based on the formation of hydroxyl radicals [21-22, 25-31].

$$PbO_2 + H_2O \rightarrow PbO_2(\cdot OH) + H^+ + e^- \quad (2)$$

Meanwhile, the oxidation reaction was in competition with the side reaction of hydroxyl radicals, which would react with each other to form molecular oxygen to complete the electrolysis of

the water molecules.

$$PbO_2\ (\cdot OH) \rightarrow PbO_2 + O_2 + 2H^+ + 2e^- \quad (3)$$

Also, due to the presence of chloride in tetracaine hydrochloride, there would lead to the formation of active chlorine, such as the hypochlorous acid. The active chlorine is a strong oxidant and could greatly improve the overall electrochemical abatement of organic pollutants [32-35].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (5)$$

4. CONCLUSION

In this study, the Al/Zn doped PbO_2 electrode was prepared by the thermal deposition and electrodeposition. The degradation of tetracaine hydrochloride by electrochemical oxidation using undoped and doped PbO_2 electrode was studied and compared. The results showed that the organic degradation could be enhanced with the doped electrode. The effects of different factors were studied and the optimal removals of tetracaine hydrochloride and COD were above 97.35% and 59.56% after 120min treatment. The results of the paper showed that relatively satisfied results could be achieved using Al/Zn doped PbO_2 electrode for the treatment of tetracaine hydrochloride wastewater. And this study could provide the basic data of electrochemical oxidation for the tetracaine hydrochloride and other pharmaceutical wastewater pollution control.

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