



Electrochemical oxidation of reverse osmosis concentrate using a novel electrode: Parameter optimization and kinetics study



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HIGHLIGHTS

- Typical transition metal Co doped PbO₂ electrode was prepared
- The catalytic activity of PbO₂ electrode was enhanced after Co doped
- Electrochemical oxidation technology work is proved to be a useful way for the treatment of reverse osmosis concentrates using a Co doped PbO₂ anode

ARTICLE INFO

Article history:

Received 10 April 2016

Received in revised form 25 July 2016

Accepted 1 August 2016

Available online xxx

Keywords:

Reverse osmosis concentrates

Electrochemical oxidation

Degradation mechanism

Co doped PbO₂ electrode

ABSTRACT

Pharmaceutical wastewater is difficult to be treated efficiently by the conventional biological wastewater treatment plant and reverse osmosis is a solution for this kind of wastewater pollution control. One limitation for RO application in pharmaceutical wastewater treatment is the treatment of RO concentrate. This work prepared a Co doped PbO₂ anode and assessed the treatment of reverse osmosis concentrates with electrochemical oxidation process using this Co doped PbO₂ anode. The operational parameters which have an influence on the electrochemical oxidation of quinoline, including the current density, the initial concentration of quinoline and the initial value of pH, were studied. The results revealed that the electrochemical degradation of quinoline followed the pseudo-first-order kinetics and the optimal removals of quinoline and COD were 100% and 59.35% after 120 min. The EE/O was calculated among all the experiments which showed that the Co doped electrode would greatly reduce the EE/O value. The degradation mechanism and kinetics were analyzed and the intermediates including kinds of organic acids generated during the process of electrolysis were analyzed. This paper can provide a technique reference for the reverse osmosis concentrate pollution control.

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1. Introduction

Pharmaceutical wastewater is a kind of industrial wastewater which is difficult to be degraded due to its environment toxic, variable compositions, complex mixtures [1]. Hundreds of tons of pharmaceuticals are discharged into the environment every year. Many of these pharmaceutical active compounds (PhACs) are persistent organics and could not be treated completely by the conventional wastewater treatments and would cause ecological risks to the environment [2,3]. Their presence in water can have potential health effects on humans through drinking water or consumption of food irrigated by polluted water. And the aquatic ecosystems may be affected in an unpredictable way [4]. Therefore, the release of organic contaminants into the environment from pharmaceutical wastewater has been considered as a serious environmental problem and attracted extensive attention [5].

The treatment of pharmaceutical wastewater has emerged as an important concern during the latest decade. Reverse osmosis (RO) is an effective way for the pharmaceutical wastewater treatment, which can separate many compounds from the wastewater and for desalination [6–8]. One limitation for RO application in pharmaceutical wastewater treatment is the treatment of RO concentrate. The concentrations of the organic and inorganic contaminants or pathogens in RO concentrates can be 6–7 times higher than those in the original wastewater. This kind of wastewater would result in the environment pollution if discharged into surface water without sufficient treatment [9]. As a consequence, the treatment of these concentrates is necessary for minimizing the environmental impacts. The organics and biological constituents are difficult to be treated efficiently by the conventional biological method due to the presence of salts. Electrochemical oxidation is a promising technology in industrial wastewater pollution control, which utilizes in-situ generated highly reactive hydroxyl radicals, and it is also an attractive option for treating RO concentrate [10,11]. High salinity which provides an excellent electric conductivity that could

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reduce the energy consumption. Specifically, high chloride content in the concentrates could facilitate the indirect oxidation of organics and improve the current efficiency through the electrogeneration active chlorines (Cl_2 , HOCl , OCl^-) [12,13].

Electrode material is crucial for electrochemical processes. Various anode materials have been tested for the electrochemical oxidation of organic pollutants. Lead dioxide electrode is an effective anode material and has received much attention in the field of water treatment due to the high oxygen evolution potential, strong corrosion resistance, good conductivity and low cost [14]. Studies have shown that adding some elements, such as Co [15], Al [16], Ni [17], can significantly improve electrocatalytic oxidation properties and its stability of lead dioxide electrode. It was also found that the nanometer materials would exhibit an obviously enhanced catalytic activity [18–21]. So, if the transition metal doped PbO_2 with nanometer grain sizes was prepared, it would be promising for the application of electrochemical oxidation in RO concentrates treatment. However, few studies on the doping of transition metals into PbO_2 electrodes have been reported.

So in this study, Co was selected as the doping material to prepare the different content of Co doped PbO_2 electrode. The aim of this work was to assess the treatment of reverse osmosis concentrates through electrochemical oxidation process using Co doped PbO_2 (Co- PbO_2) anode with nanometer grain sizes. Quinoline is a typical nitrogen-containing heterocyclic compounds and exists widely in pharmaceutical wastewater, thus was selected as the model organic pollutant. Co- PbO_2 electrode was prepared by the method of thermal decomposition and electrochemical deposition, and was used to degrade quinoline to research the removal of quinoline and COD. The experimental parameters, including the current density, initial quinoline concentration and initial value of pH, which influencing the removal of quinoline and COD were studied. Moreover, the degradation mechanism of quinoline in electrochemical oxidation was analyzed. This paper can provide basic data and technique reference for the reverse osmosis concentrate pollution control.

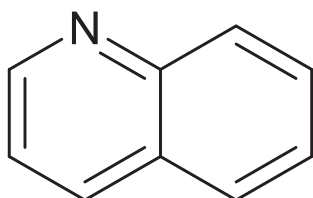
2. Experimental

2.1. Materials and reagents

Quinoline was analytical reagent and purchased from J&K Chemicals (Beijing, China). The chemical structure is given in Scheme 1. High-purity titanium plate (TA1) was selected as the metal matrix to prepare Co- PbO_2 electrode. All other reagents are analytical grade. Solutions were prepared using deionized water.

2.2. Electrode preparation characterization

Co is a typical transition metal element and it has the advantages in catalytic oxidation, which can be used as a doping element to enhance the catalytic efficiency in catalytic oxidation. So in this study, Co was selected as the doping material to prepare the different content of Co doped PbO_2 electrode. The Co- PbO_2 working electrode is composed of four layers: (1) the Ti substrates which were preperated: First, the Ti substrates were degreased in NaOH solution at room temperature for 30 min, then etched in H_2SO_4 solution at 60 °C for 20 min and oxalic acid solution at 80 °C for 3 h; (2) the SnO_2 - Sb_2O_5 bottom layer with



Scheme 1. The chemical structure of Quinoline.

the disposed of thermal decomposition at 515 °C for repeated 10 times in the air, in the first nine times the baking was annealed for 16 min and the last time was 66 min; (3) α - PbO_2 intermediate layer after being alkaline electroplated. The electrolyte consisted of 3.5 mol/L NaOH and 0.08 mol/L PbO and the electroplated was conducted at 60 °C for 1 h with the current density of 6 mA/cm²; (4) Co- PbO_2 active layer through the processing of acidic electroplating. The electrolyte contained 0.3 mol/L $\text{Pb}(\text{NO}_3)_2$, 0.01 mol/L NaF, 3 mL/L polytetrafluoroethylene (PTFE) and amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the electroplated was conducted at 80 °C with the current density of 50 mA/cm² for 150 min.

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, Netherlands), using Cu K α radiation at 40 KV and 40 mA.

2.3. Electrochemical experiments

Electrochemical degradation experiments were conducted in galvanostatic mode at room temperature with the help of magnetic stirring. The simulation RO concentrate compositions were based on those of the concentration in actual RO concentrate, which contains 150 mg/L chloride, 13 mg/L nitrate and 12 mg/L phosphate [9]. And 0.1 mol/L sodium sulfates were added additionally to increase the conductivity of the solution. The Co- PbO_2 electrode was used as the anode and a titanium plate with the same area was used as the cathode. Quinoline was selected as the model organic pollutant. The experiment parameters, which influencing the removal of quinoline and COD, were researched, including the current density (20–80 mA/cm²), initial quinoline concentration (20–150 mg/L) and the initial pH value (3.0–11.0).

2.4. Analytical methods

The concentration of quinoline was determined by High-performance liquid chromatography (HPLC; 1200, Agilent Technologies, USA) with an ultraviolet (UV) detector (SPD-10AV) and a C18 column (250 mm \times 4.6 mm, 5 μm) at the column temperature of 25 °C. The methanol and ultrapure water with the ration of 60:40 (v/v) was used as a mobile phase at a flow rate of 1.0 mL/min, the injection volume was 20 μL and absorbance detection was 280 nm. The determined of chemical oxygen demand (COD) was used fast digestion-spectrophotometer method (DRB200, Hach, USA). Ion Chromatograph (ICS-200, Dionex, USA) was used to identify the intermediate organic acids generated during the process of electrochemical oxidation. The pH value was detected by pH meter (pHs-3E, Leici, China).

The instantaneous current efficiency (ICE) was calculated on the basis of the values of chemical oxygen demand of the wastewater, using the following equation:

$$\text{ICE} = \frac{(\text{COD}_0 - \text{COD}_t)}{8It} FV \times 100\% \quad (1)$$

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 (96,487 C/mol), V is the volume of the solution (dm^3), I is the current (A) and t is the reaction time (s).

A great quantity of electrical energy is needed in the process of electrochemical oxidation and the associated costs are significant. The definition of electrical efficiency per log order (EE/O) is the electrical energy according to reduce of the concentration of quinoline. It can be calculated using the following equation [22]:

$$\text{EE/O} = \frac{P \times t}{V \times \log(C_i/C_f)} \quad (2)$$

where EE/O is the electrical efficiency per log order reduction (kWh/m^3), P is the lamp power output (kW), t is the reaction time (h), V is

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