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Mechanism and kinetics of electrochemical degradation of isothiazolin-ones using Ti/SnO_2–Sb/PbO_2 anode

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ABSTRACT

This study investigated the electrochemical degradation of isothiazolin-ones in aqueous solution on a Ti/SnO_2–Sb/PbO_2 electrode. 1-Nitro-2-crylic-acetone, acetic acid and formic acid were the main degradation intermediates identified by tandem mass spectrometry (MS/MS) and the pathway for electrochemical degradation of isothiazolin-ones was proposed. Kinetic analyses indicated that electrochemical degradation of isothiazolin-ones was a pseudo-first-order reaction. The influences of operating parameters, such as electrolysis time, initial concentration of isothiazolin-ones, current density, initial pH and electrolyte flow rate on electrochemical degradation of isothiazolin-ones were investigated. Electrochemical degradation of isothiazolin-ones as well as COD_{cr} (chemical oxygen demand determined by potassium dichromate) was controlled by mass transport.

1. Introduction

Isothiazolin-ones are used worldwide as a bactericide [1]. Bactericide wastewater contains a number of different kinds of pollutants such as greases, organic acids, sulfide, salts and isothiazolin-ones. The concentration of isothiazolin-ones in the wastewater typically reaches as high as 200 mg L^{-1}. Conventional treatments of wastewater include biological degradation [2], incineration [3], and resin adsorption [4]. The cost of biological treatment of wastewater is lower than the others. Nevertheless, isothiazolin-ones in wastewater are very difficult to break down biologically, due partly to the toxicity of the isothiazolin-ones to microbes. Incineration is an expensive procedure, and the hazardous wastes incinerating in incinerators may bring about new toxic wastes. Resin adsorption is applied for the recycling and recovery of valuable resources. In an attempt to find approaches that do not have the aforementioned drawbacks, attention has been focused on electrochemical methods.

In recent years, there has been increasing interest in the use of electrochemical methods for the treatment of recalcitrant toxic wastes [5,6]. Electrochemical oxidation is a promising environmental remediation technology due to its easy operation and environmental compatibility. The organic matters and toxic pollutants can usually be destroyed by electrochemical oxidation. Electrochemical processes generally have lower temperature requirements than those of other equivalent non-electrochemical treatments, such as wet air oxidation. Electrochemical methods have been successfully applied to treat various refractory pollutants such as petroleum refinery wastewater [7], textile dyes and dyehouse effluents [8], olive oil mill wastewater [9], and textile wastewater [10]. However, few reports have been published on the degradation of isothiazolin-ones by the electrochemical method. Generally, platinum-coated titanium electrodes are suitable for the oxidation of organic substances [11], but their cost poses a major restriction for their widespread use. On the other hand, cheaper substitutes such as titanium electrodes coated with active oxides (e.g., SnO_2 [12], RuO_2 [13], and PbO_2 [14]) have been successfully used in the electrochemical method. PbO_2 electrodes are widely used for the electrochemical oxidation of the organics because of its lower price compared to noble metals, and better electrochemical stability, as well as high oxygen evolution potential [15].

The mechanism for the electrochemical oxidation of organic compounds can be detailed as shown below for PbO_2 anode [5,16,17], where $PbO_2[\ ]$ represents the active sites of the anode, and RO represents the oxidized organic matter.

$$PbO_2[\,] + H_2O_{ads} \rightarrow PbO_2[\bullet OH]_{ads} + H^+ + e^-$$

$$R + PbO_2[\bullet OH]_{ads} \rightarrow PbO_2[\,] + RO + H^+ + e^-$$

The first step is the anodic discharge of the water, forming hydroxyl radicals which are absorbed on the active sites of the electrode surface. After this, the absorbed hydroxyl radical oxidizes the organic matter. Due to their high oxidation potential, the radicals [•OH] can oxidize organic compounds (i.e., direct oxidation). On the other hand, the hydroxyl radical can be decomposed to other oxidants (such as O_2, O_3, and H_2O_2), which diffused into the water away from the anode, thus continuing the oxidation process (i.e., indirect oxidation). Direct

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oxidation is effective in pollutant degradation, because it is able to convert totally the organic species into water and carbon dioxide. So the PbO_2 electrodes can be highly effective for complete degradation of organic.

The objective of this work was to investigate the kinetics and mechanism of electrochemical degradation of isothiazolin-ones in aqueous solution using Ti/SnO_2–Sb/PbO_2 anode.

2. Materials and methods

2.1. Preparation of Ti/SnO_2–Sb/PbO_2 anode

Titanium plates (99.5%, 50 mm × 80 mm) were pretreated by the following procedures. The titanium sheets were mechanically polished with different abrasive papers to a mirror-like finish and ultrasonically cleaned in twice-distilled water and acetone successively. They were then etched in 18% HCl at 80 °C for 60 min, and then etched in boiling aqueous solution of oxalic acid (20%) for 120 min.

The SnO_2–Sb coating deposited onto the pretreated titanium substrate was prepared by the sol–gel technique. Afterwards, PbO_2 was deposited on the SnO_2–Sb interlayer of the Ti substrate by electrochemical anodization [18,19].

2.2. Electrochemical degradation of isothiazolin-ones

A diagram of the experimental setup was shown in Fig. 1. The electrolytic cell was a cylindrical vessel containing 450 mL solution. The Ti/SnO_2–Sb/PbO_2 electrode was used as the anode. The stainless steel plate with the same surface area was used as the cathode, and the distance between the electrodes was 2 cm. The electrodes were connected to an electrical DC power supply. The isothiazolin-one solution was continuously fed to the electrolytic cell in a desired flow rate using a digital peristaltic pump. So the isothiazolin-one solution circulated between the electrolytic cell and the circulation vessel (550 mL) through a peristaltic pump. Samples were periodically taken from the reactor. The concentrations of isothiazolin-ones and COD_{cr} were analyzed to investigate the behavior of electrochemical oxidation of isothiazolin-ones. The effects of electrochemical oxidation time, initial isothiazolin-one concentration, current density, initial pH and electrolyte flow rate on isothiazolin-ones and COD_{cr} degradation were investigated.

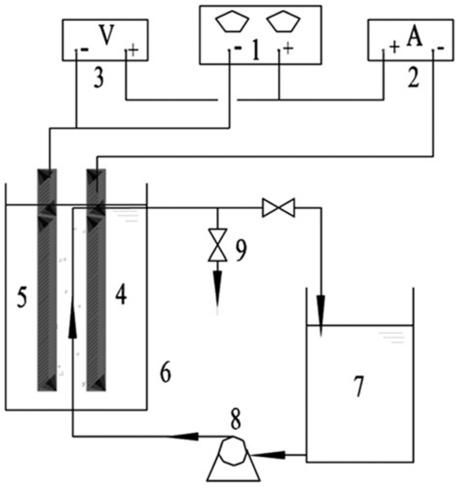

Fig. 1. Diagram of electrochemical oxidation system. (1) Direct current manostat; (2) amperemeter; (3) voltmeter; (4) anode; (5) cathode; (6) electrolytic cell; (7) circulation vessel; (8) pump; (9) sample.

2.3. Analytical methods

The mechanism of isothiazolin-one degradation was analyzed by tandem mass spectrometry (MS/MS). The mass spectrometer (TSQ Quantum Ultra AM, Thermo Finnigan, USA) was equipped with an electrospray ionization (ESI) source. The concentrate of isothiazolin-ones was analyzed by UV–visible spectrophotometer at a wavelength of 273 nm. COD_{cr} was determined by potassium dichromate according to standard methods [20].

The instantaneous current efficiency (*ICE*) and the efficiency of oxidation for isothiazolin-ones (η) were calculated using the relations [21,22].

$$ICE = \frac{(COD)_t - (COD)_{t+\Delta t}}{8 \cdot i \cdot S \cdot \Delta t} \cdot F \cdot V$$

$$\eta = FV \frac{C_t - C_{t+\Delta t}}{i \cdot S \cdot \Delta t}$$

where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$ (in mg O_2 dm^{-3}), respectively, i is current density (A cm^{-2}), S is the electrode area (cm^2), F is the Faraday constant (96,487 C mol^{-1}), V is the volume of the electrolyte (dm^3), and C_t and $C_{t+\Delta t}$ are the concentrations of isothiazolin-ones at times t and $t + \Delta t$ (in mg O_2 dm^{-3}).

3. Results and discussion

3.1. The mechanisms of isothiazolin-one degradation

3.1.1. UV-spectrophotometer analyses of the degradation intermediates

The UV–visible spectrum of isothiazolin-one degradation solution at different electrolysis times was presented in Fig. 2. The peak observed in the UV region at 273 nm was the characteristic peak of the isothiazolin-ones. Fig. 2 also showed the disappearance of this characteristic peak during the electrolysis, inferring that the ring of isothiazolin-ones was possibly open. It was clear that the peak at 210 nm grew in the initial period, and then went down. This could be due to the production of degradation intermediates.

It has been reported that the half-life was found to be 4.6 days at 40 °C and pH 7. Moreover, the half-life was 46 days at 24 °C and pH 8.5 [23]. In our studies, the isothiazolin-one removal efficiency in the artificial wastewater containing 200 mg L^{-1} isothiazolin-ones and 10 g L^{-1} Na_2SO_4 could reach 86.1% at 25 °C and pH 7.0 with an applied

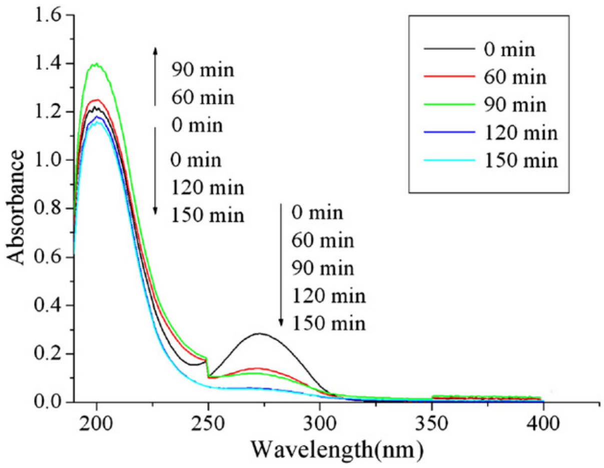

Fig. 2. UV spectrum of isothiazolin-ones during electrolysis: current density, 15 mA cm^{-2}; concentration of supporting electrolyte (Na_2SO_4), 10 g L^{-1}; initial concentration of isothiazolin-ones, 200 mg L^{-1}; electrolyte flow rate, 100 mL min^{-1} and initial pH, 7.0.