Chemical Engineering Journal 350 (2018) 960–970

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrochemical removal of thiamethoxam using three-dimensional porous PbO_2-CeO_2 composite electrode: Electrode characterization, operational parameters optimization and degradation pathways

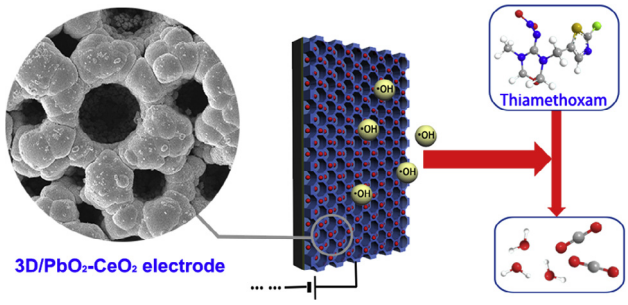
Yingwu Yao*, Chunjiao Huang, Yang Yang*, Mengyao Li, Bingli Ren

Hebei University of Technology, School of Chemical Engineering and Technology, Tianjin 300130, PR China

HIGHLIGHTS

- A novel three-dimensional porous PbO_2-CeO_2 composite electrode was prepared.
- Electrochemical method was used to remove thiamethoxam by novel composite electrode.
- The influence of operating conditions on thiamethoxam degradation was studied.
- Thiamethoxam can be fully removed using novel electrodes by electrochemical method.
- The electrochemical degradation intermediates and pathway of thiamethoxam were proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Electrochemical oxidation
3D/PbO_2-CeO_2 composite electrode
Thiamethoxam
Operating parameters
Degradation mechanism

ABSTRACT

Highly performed electrode is one of the key factors affecting the efficiency of electrochemical oxidation toward organic pollutants. In the present work, three-dimensional porous PbO_2-CeO_2 composite electrodes (3D/PbO_2-CeO_2) were fabricated by composite electrodeposition method using oxygen bubbles as template, to eliminate neonicotinoid thiamethoxam in aqueous solution. The surface morphology, structure, and composition of the 3D/PbO_2-CeO_2 electrodes were well characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersive spectrometer (EDS). Then the influence of the applied current density, the initial concentration of thiamethoxam, the concentration of supporting electrolyte, and initial pH value on the thiamethoxam removal ratio were also optimized. Amount to twenty deductive intermediates of thiamethoxam degradation were identified by HPLC-MS analysis, and dechlorination, hydrogen abstraction, denitration, and hydroxylation were observed in electrochemical oxidation process of thiamethoxam. Based on these identified byproducts, a hypothetical degradation mechanism has been proposed, which was divided into two parallel pathways according to the different initial oxidation position on thiamethoxam, such as chlorine atom on thiazole ring and nitro group on 1,3,5-oxadiazinane ring. All the intermediates were ultimately mineralized into H_2O and CO_2. The electrochemical oxidation based on 3D/PbO_2-CeO_2 electrodes in this work is a promising approach to effective removal of thiamethoxam.

* Corresponding authors.
E-mail addresses: yaoyingwu@hebut.edu.cn (Y. Yao), yangyang0410@hebut.edu.cn (Y. Yang).

https://doi.org/10.1016/j.cej.2018.06.036
Received 6 February 2018; Received in revised form 14 May 2018; Accepted 8 June 2018
Available online 14 June 2018
1385-8947/

1. Introduction

Thiamethoxam is the representative second-generation neonicotinoid insecticides, which has been widely used for pest control in foliar, soil and seed treatments [1,2]. It plays an active role in the control of numerous sucking and chewing insect pests [3]. However, thiamethoxam has become a potential contaminant of the surface and underground waters which might seriously threat aquatic organisms and public health owing to its low soil adsorption, poor biodegradability, high leaching capability, and high solubility in water [4]. Therefore, decontamination techniques for thiamethoxam with high efficiency are highly in emergent demand. In recent years, series of treatment methods, including ozonation [5], photocatalytic degradation [6,7], electro-Fenton reactions [8], adsorption [9], and dielectric barrier discharge treatment [10], have been employed to remove thiamethoxam in aqueous solution.

Electrochemical oxidation has been proposed as an effective approach to the degradation of refractory organic pollutants in wastewaters [11–14]. Thereinto, the anode materials play significant roles in the electrochemical oxidation process. Recently, quantities of anode materials have been fabricated, such as SnO_2 [15,16], PbO_2 [17], BDD [18–22], *etc*. Among these anode materials, PbO_2 has been considered as a remarkable metal oxide anode materials for its low cost, facile preparation, and remarkable electrochemical stability, which has been widely applied to remove the organic pollutants in wastewaters [23–31].

For the purpose of further improvement on the electrochemical properties of PbO_2 electrode, cerium ions [32–34] or CeO_2 particles have been added into the electrodeposition solution during the preparation process of PbO_2 electrode. Especially, the codeposition of CeO_2 particles into the lead dioxide matrix has drawn much attention due to its high catalytic activity, thermal stability, and electrical conductivity. Song et al. [35] electrodeposited PbO_2-CeO_2 electrodes on the stainless steel, which was applied to treat wastewater containing antibiotics. Chen et al. [36] prepared Al/α-PbO_2/β-PbO_2 composite electrodes doped with CeO_2 particles by anodic oxidation method. The results show that the doping of CeO_2 can enhance the electro-catalytic activity of PbO_2 electrodes. Our group [37] also fabricated PbO_2-CeO_2 composite electrodes by composite electrodeposition methods in the lead nitrate solution containing CeO_2 particles. All these reported literatures proved that the incorporation of CeO_2 particles could effectively improve the electro-catalytic oxidation activity of PbO_2 electrode. However, the reported preparation of PbO_2-CeO_2 composite electrodes were only restricted to planar structure, and PbO_2-CeO_2 composite electrode with three-dimensional structure has not been reported.

In this study, we incorporated CeO_2 particles into PbO_2 by composite electrodeposition using oxygen bubbles as template to fabricate a novel three-dimensional porous PbO_2-CeO_2 composite electrode (3D/PbO_2-CeO_2). Gas bubble dynamic template is a novel green and promising technology, which can form three-dimensional porous structures in electrode materials, and enlarge the specific surface area of PbO_2 electrodes [38,39]. The prepared 3D/PbO_2-CeO_2 composite electrodes were used as anode materials to eliminate thiamethoxam in aqueous solution by electrochemical degradation methods. The influence of experimental parameters, such as applied current density, initial concentration of thiamethoxam, the concentration of electrolyte solution, and the initial pH value, were investigated and optimized. Finally, the degradation intermediates during the electrochemical degradation process of thiamethoxam were analyzed based on the experimental results from HPLC-MS, and the dominant degradation pathways were proposed.

2. Experimental

2.1. Materials

Thiamethoxam was purchased from Raw Material Medicin Reagent Co., Ltd. China, and its physicochemical characteristics were summarized in Table S1 in the Supplementary Materials. The CeO_2 particles (VK-Ce01, purity > 99.9%) were supplied by Wanjing Co., Ltd. China. The particles diameter is about 40 nm. Methanol (HPLC grade) was obtained from Kermel Int. China. All other chemicals were analytical grade and used as received without further purification. Deionized water was used as solvent throughout all the experiments.

2.2. Preparation and characterization of 3D/PbO_2-CeO_2 electrode

Composite electrodeposition method was employed for the preparation of 3D/PbO_2-CeO_2 composite electrodes on Ti/SnO_2-Sb_2O_3 interlayers using oxygen bubbles as template, applying the potential at 5 V (vs. SCE) for 10 min. The plating solution was composed of 0.2 mol L^{-1} lead nitrate, 0.01 mol L^{-1} nitric acid, and 2 g L^{-1} CeO_2 particles. Ti/SnO_2-Sb_2O_3 interlayers were applied as the substrates [37]. CeO_2 particles in the solution were dispersed by ultrasonic for 180 min before electrodeposition. As a contrast, we also prepared 3D/PbO_2 electrodes at 5 V (vs. SCE) for 10 min in the same solution without CeO_2 particles, and planar structural (2D) PbO_2-CeO_2 composite electrodes in the same solution at the current density of 30 mA cm^{-2}, based on our previous work [37,40].

The morphology of 3D/PbO_2-CeO_2 composite electrodes were examined by scanning electron microscopy (SEM, Nova NanoSEM 450, Thermo Fisher Scientific, USA) equipped with the energy dispersive spectrometer (EDS) for elemental analysis. X-ray diffraction (XRD, D8 Focus, Bruker, USA) was applied for the analysis of the crystal structure of 3D/PbO_2-CeO_2 composite electrodes.

2.3. Electro-catalytic degradation process

The electro-catalytic degradation of thiamethoxam was performed in a cylindrical single compartment cell containing 500 mL initial volume of reaction solution. 3D/PbO_2-CeO_2 composite electrode was anode and Ti sheet was cathode. The working area of anode was 6 cm^2, and the electrode gap was set as 1 cm. The effects of operation parameters on thiamethoxam degradation were investigated, including applied current density (10–50 mA cm^{-2}), initial thiamethoxam concentration (10–50 mg L^{-1}), the concentration of supporting electrolyte (Na_2SO_4) (0.05–0.25 mol L^{-1}), and initial pH values (2.0–10.0). In the degradation process, samples (2 mL) were extracted from the cell at certain intervals for monitor on the degradation process.

2.4. Analytical methods

Chemical oxygen demand (COD) was measured by the reported standard methods [41]. The measurement methods about instantaneous current efficiency (ICE), energy consumption (Ec), electrodes service life, Pb ion leaching, hydroxyl radicals detection, and cyclic voltammetry were presented in detail in Supplementary Materials.

The variation of thiamethoxam concentration in the degradation experiment was monitored by high performance liquid chromatography (HPLC) (Shimadzu LC-30AD) with a reversed phase C18 column (InertSustainAQ-C18 column, 250 mm × 4.6 mm, 5 μm). The mobile phase was water and methanol with the ratio of 75:25 (v/v) with a flow rate of 1.0 mL min^{-1}. The injected volume of the sample was 20 μL, and the detection wavelength was 251 nm. The column temperature was maintained at 25 °C. After data collection, the concentration was calculated using the standard curve equation of peak area, and the removal ratio of thiamethoxam could be obtained. The identification of intermediates in thiamethoxam degradation process was performed on