



Electrochemical oxidation of acid orange 7 dye with Ce, Nd, and Co-modified PbO₂ electrodes: Preparation, characterization, optimization, and mineralization

Qicheng Qiao^a, Seema Singh^b, Shang-Lien Lo^{b,*}, Ya Li^a, Jierong Jin^a, Lizhang Wang^c

^aSchool of Environment and Biological Engineering, Nantong College of Science and Technology, Nantong City, Jiangsu 226007, PR China

^bGraduate Institute of Environmental Engineering, National Taiwan University, 71, Chou-Shan Rd., Taipei 106, Taiwan

^cSchool of Environment Science and Spatial Informatics, China University of Mining and Technology, Xuzhou City, Jiangsu 221116, PR China

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ABSTRACT

Present study proposed the preparation, characterization and application of cobalt (Co), neodymium (Nd), and cerium (Ce) modified lead (PbO₂) electrodes. Morphological and structural properties of as-prepared electrodes were determined by SEM, XRD, and XPS. Linear sweep voltammetry (LSV) and accelerated life test were used to determine the electrocatalytic activity and stability of as-prepared electrodes. Higher oxygen evolution potentials (OEP) and longer service life were used to confirm the maximum electrocatalytic activity of Nd and Ce–PbO₂ electrodes. The electro-oxidation ability was examined with Acid Orange 7 (AO 7) treatments. Cyclic voltammetry (CV), UV–visible, and fluorescence spectrophotometric analysis of AO 7 treatment were confirmed that Nd and Ce–PbO₂ have excellent oxidation ability, higher AO 7 removal efficiency and higher total organic carbon (TOC) with a good correlation of instantaneous current efficiency (ϵ_{inst}) and higher hydroxyl radical ($^{\bullet}\text{OH}$) generation rate, respectively. The effect of removal parameters was optimized with Ce–PbO₂ electrode. Results of AO 7 and TOC removal were reached up to 100% and 93.7%, respectively, after 180 min of electrolysis at the optimum condition of 0.2 M Na₂SO₄ concentration, 100 mg L⁻¹ initial dye concentration, solution pH 7.0 and 20 mA cm⁻² applied current density. Reusability and safety test analysis were used to detect the best results of AO 7 degradation with Ce–PbO₂ electrode. Mass spectroscopy and ion chromatography (IC) were used to detect the formation of intermediates by-products. Finally, based on the detection of reaction by-products, a plausible degradation pathway including radical reactions, ring opening and de-nitrification was proposed.

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1. Introduction

Synthetic and natural dyes are extensively used in various industries, such as textile and printing leather, tanning and food industry [1,2]. It is predicted that higher than 60% worldwide dyes are manufactured in China [3]. Due to the rapid growth of dyes industry in China, it has become a challenging to control the discharge of highly concentrated dyeing effluents into the local water body. Many treatment technologies including chemical, physical and biological remediation [3,4–8] of dye wastewater treatment could not progressively meet the strict discharge standard of dye wastewater treatment, therefore a number of alternative treatment technologies have been investigated [6–8].

Recently, electrochemical oxidation (EO_x) is an emerging and promising technology and has been widely used in various field

of recalcitrant pollutants degradation due to its versatility, strong oxidation ability, environmental compatibility, energy efficiency, cost effectiveness and easy implementation ability [9,10]. The EO_x degradation ability is directly influenced by the nature of electrode materials [11]. Thus, a lot of research affords have been paid more attention for increase the chemical stability and electrocatalytic activity of anode materials [12]. Moreover, after the invention of the dimensionally stable anode (DSA), research has focused on the synthesis and development of anode materials which exhibited both higher electrochemical stability and electrocatalytic activity [12]. Many types of noble metal and/or their oxides of anode materials such as Pt, Au, Ir, IrO₂, RuO₂, SnO₂, PbO₂ and boron-doped diamond (BDD) have been studied [8,11,12]. However, the higher cost of these electrodes is a major challenge for their industrial applications [13].

Among them, PbO₂ has attracted a great deal of consideration due to its high OEP, low cost, high anodic oxidation ability and chemical stability [14]. However, sometimes flake on PbO₂

* Corresponding author.

E-mail address: slo@ntu.edu.tw (S.-L. Lo).

layer diminished its activity and stability during the electrolytic [12,15]. Therefore, the research has been paid more attention to solving the stability and activity of PbO_2 by incorporate the different internal layer between the active PbO_2 layer and substrate such as $\alpha\text{-PbO}_2$ [11] and Sb-doped SnO_2 [16]. Additionally, some foreign metal cations such as Co^{2+} , Cu^{2+} , Fe^{3+} , Ag^+ , Bi^{3+} , and Ru^{3+} have already been introduced by electro-deposition method [11,12]. However, some challenges still required to making the effective and more suitable doped PbO_2 anode. Recently, rare earth metal/metal oxides such as Ce, La, Y, and Dy etc. have been extensively used as a more attractive dopant on PbO_2 [17] by using the electro-deposition method [12] because of their special metal/metal oxides characteristics.

In recent years, the research concerning the roles of various types of electrode materials on the performance of electrochemical advanced oxidation processes (EAOPs) including AO; AO- H_2O_2 ; AO- H_2O_2 and electro-Fenton (EF), photo-electro Fenton and ultraviolet A (PEF-UVA) had been focused by various researchers for the treatment of persistent pollutant such as dye wastewater. For example, AO 7 has been treated by AO [18], AO- H_2O_2 , EF [19], AO- H_2O_2 , EF, PEF-UVA [20] etc.

Present study proposed the modification on $\beta\text{-PbO}_2$ by Ce, Nd and Co. Analysis techniques such as SEM, XRD, and XPS were used to characterize the modification of electrodes. LSV and accelerated life test were used to determine the electrochemical stability. UV-visible, TOC, and fluorescence measurements were used to investigate the dye removal and mineralization. The effect of operating parameters of AO 7 treatment with Ce- PbO_2 electrode was optimized via the AO process. GC-MS and IC was used to identify the degradation by-products and possible degradation pathways. In addition, the safety and reusability of the Ce- PbO_2 electrode was also discussed.

2. Experimental and methodology

2.1. Materials

All analytical grade chemicals without further purification were used for the present study. AO 7 was purchase from Shanghai Ji-aying Chemical Co. Ltd. Mercuric sulfate, cerium and niobium trinitrate, cobalt and lead di-nitrate, sodium chloride, oxalic acid, silver sulfate, tertiary butanol, potassium dichromate, phosphoric acid and sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd. All solutions were prepared prior to use in double distilled water. The main characteristics of AO 7 dye are summarized in Table S1.

2.2. Electrode preparation and characterization

The detail procedure of PbO_2 electrode preparation has been described in our previous study [21]. Firstly, Ti plates ($2.5\text{ cm} \times 2.0\text{ cm}$) were polished by grit sand paper then clean plates puts in 40 wt% NaOH solution at 333 K for 2 h after that 10 wt% oxalic acid was used for etching to attaining the uniform roughness on the surface of electrode. After pretreatment, an interlayer of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_3$ electrode was prepared by using the dip-coating plus thermal deposition of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, SbCl_3 /butanol, and hydrochloric acid with a nominal composition of Sn:Sb=9:1. Pretreated Ti plates were painted, dried and sintered at 773 K in a muffle furnace. This procedure was repeated for ten times. The final interlayer of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_3$ electrode was obtained by last baking at 773 K for 1 h. Lastly, electrodepositing of $\beta\text{-PbO}_2$ films was done on as-prepared $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_3$ electrode. 0.5 M Pb (NO_3)₂, 0.1 M HNO_3 , 0.2 M Cu (NO_3)₂ and 40 mM NaF were used as an electrolytes for pure PbO_2 electrode, whereas 0.01 M of $\text{Nd}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$, respectively, were used for

Nd, Ce, and Co deposition on PbO_2 . Finally, pure and doped PbO_2 films were deposited on the electrode within a 120 min at 333 K and 20 mA cm^{-2} current density.

Scanning electron microscope (SEM: Quanta 250, USA) and X-ray diffraction (XRD: D8 Advance, GER) with Cu $K\alpha$ radiation at 40 kV and 30 mA were used to examine the morphology and composition, respectively. X-ray photoelectron spectroscopy (XPS: ESCALAB 250XiX, UK), with Al $K\alpha$, monochromatized radiation X-ray source was used to determine the atomic valence state. Electrochemical workstation (CHI 660D, China) with three-electrode configuration i.e., saturated calomel electrode (SCE), PbO_2 electrodes and platinum foil were used as a reference, working electrode and cathode, respectively. CV at 50 mV s^{-1} sweep rates and LSV at 10 mV s^{-1} scanning rates between 0 and 2.5 V vs. SCE (0.5 M H_2SO_4 electrolyte) were used for AO 7 degradation. Accelerated life test at $j=2.0\text{ A cm}^{-2}$ in 1.0 M H_2SO_4 at 333 K was used to determine the stability of electrodes.

Fluorescence spectroscopy (RF-5301PC, Japan) was used to investigate the quantity of hydroxyl radical ($\cdot\text{OH}$) production in terephthalic acid (TA) solution during the electrolysis with different anodes [21]. TA had a known reaction with hydroxyl radical to form of fluorescent 2-hydroxyterephthalic acid. As a result, TA was used as a probe for $\cdot\text{OH}$ detection during the fluorescence analysis with pure and doped PbO_2 anodes and stainless steel sheet as a cathode were employed in 50 mL solution of 0.25 M Na_2SO_4 , 0.5 g L^{-1} NaOH and 0.5 mM TA. The electrolyzed solutions were tested via the spectrofluorimetry at different time. The production of OH radical was detected at a current density of 30 mA cm^{-2} at 30 °C. During the treatment, the samples were collected from the reactor after a regular interval than this solution was 20 times diluted with deionized water and finally used for the analysis. Fluorescence emission spectrums were recorded from the range of 370 nm to 520 nm, with an excitation wavelength at 315 nm.

2.3. Experiment method and analysis

A batch reactor connected with a DC power supply (APS3500Si, China) was used for the electrochemical oxidation experiments. As-prepared electrodes ($2.0\text{ cm} \times 2.0\text{ cm}$) and Ti plate with the same area were used as anode and cathode, respectively by keeping a 1.0 cm inter-electrode gap. For each experiment, 50 mL solution of 100 mg L^{-1} AO 7 was placed in a batch reactor at a continuous stirring of 450 rpm on a magnetic stirrer. Samples were analyzed after drawn a certain intervals. The EO_x process was optimized with Ce- PbO_2 at a varied range of parameters such as initial dye concentration (C_0) (50–200 mg L^{-1}), initial solution pH (pH_0) (2–11), current density (j) (5–200 mA cm^{-2}) and electrolyte concentration (m) (0.05–0.3 M Na_2SO_4), respectively, at the room temperature. The solution of 0.5 M H_2SO_4 and NaOH were used for adjusting the solution pH during the treatment.

UV-vis spectrophotometer analyzer (TU-1901, China) at $\lambda_{\text{max}}=485\text{ nm}$ and TOC (TOC-L CPH, Japan) based on the combustion-infrared method were used to determine the removal rate of AO 7 (Eq. (1)) and (Eq. (2)),

$$\text{Decolorization rate} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the initial and final absorbance of AO 7.

$$\text{TOC removal (\%)} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \quad (2)$$

where TOC_0 and TOC_t are the initial and final TOC (mg L^{-1}) of the solution.

Instantaneous current efficiency ($\varepsilon_{\text{inst}}$) (Eq. (3)) and average current efficiency (ACE) (Eq. (4)) were calculated from the TOC results

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