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Electrochemical oxidation of 2,4,5-trichlorophenoxyacetic acid by metal-oxide-coated Ti electrodes

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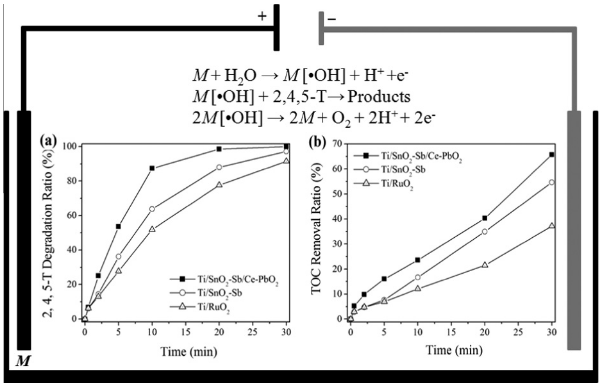
HIGHLIGHTS

- Metal-oxide-coated Ti anodes are applied to eliminate 2,4,5-T from water.
- A high degradation efficiency of 2,4,5-T is obtained on Ti/SnO_2–Sb/Ce–PbO_2 anode.
- TOC removal ratio obtains >65% on PbO_2 electrode after 30 min of electrolysis.
- An energy efficiency and 2,4,5-T degradation by-products are determined.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical oxidation of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) over metal-oxide-coated Ti anodes, i.e., Ti/SnO_2–Sb/Ce–PbO_2, Ti/SnO_2–Sb and Ti/RuO_2, was examined. The degradation efficiency of over 90% was attained at 20 min at different initial concentrations (0.5–20 mg L^{-1}) and initial pH values (3.1–11.2). The degradation efficiencies of 2,4,5-T on Ti/SnO_2–Sb/Ce–PbO_2, Ti/SnO_2–Sb and Ti/RuO_2 anodes were higher than 99.9%, 97.2% and 91.5% at 30 min, respectively, and the respective total organic carbon removal ratios were 65.7%, 54.6% and 37.2%. The electrochemical degradation of 2,4,5-T in aqueous solution followed pseudo-first-order kinetics. The compounds, i.e., 2,5-dichlorohydroquinone and 2,5-dihydroxy-*p*-benzoquinone, have been identified as the main aromatic intermediates by liquid chromatography-mass spectrometry. The results showed that the energy efficiencies of 2,4,5-T (20 mg L^{-1}) degradation with Ti/SnO_2–Sb/Ce–PbO_2 anode at the optimal current densities from 2 to 16 mA cm^{-2} ranged from 8.21 to 18.73 kW h m^{-3}.

1. Introduction

Chlorophenoxy herbicide, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), has been used extensively in a large quantity in agriculture to protect the growth of cereal crops from weeds (Chaudhary et al., 2009; Wang and Chu, 2011). Chlorophenoxy compounds are also detected as one of the major pollutants with contamination levels up to mg L^{-1} in natural waters (Aaron and Oturan, 2001; Brillas et al., 2004). Usually, water pollution with organic compounds such as chlorophenoxy acids can occur through cropland runoff, industrial effluent, and chlorination of wastewater. Several studies have been reported in recent years concerning the possible health effects of exposure to 2,4,5-T and

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its by-products (Boffetta et al., 2011; USEPA, 2012). Thus the removal of these organic pollutants from wastewater is an important issue.

As a refractory organic pollutant, 2,4,5-T is resistant to biodegradation in aqueous solution (Wang and Chu, 2011). Recently, the removal of 2,4,5-T from contaminated water with various techniques such as adsorption, biological degradation and advanced oxidation processes (AOPs) has received increasing attention. AOPs are comparatively considered as effective technologies in wastewater treatment system due to their high efficiency to mineralize various organic pollutants by the generation of hydroxyl radicals ($^{\cdot}OH$). Thus, several kinds of AOPs have been established to eliminate 2,4,5-T from water including electro-Fenton process (Brillas et al., 2004), photoelectro-Fenton process (Boye et al., 2003a), photolytic–electrolytic system (Chaudhary et al., 2009) and UV/TiO_2 (Singh et al., 2007). Although the above processes are very efficient for the degradation of organic pollutants besides 2,4,5-T, some are relatively less cost effective and can produce highly toxic by-products during the reaction (Latch et al., 2003; Zhang et al., 2008). Electrocatalytic oxidation process has been effectively used in decomposing various organic contaminants due to several unique characteristics, i.e., versatility, cost effectiveness, amenability to automation and high energy efficiency (Yang et al., 2009; Panizza, 2010; Lin et al., 2012; Niu et al., 2013a, 2013b). It is well-known that the electrode materials with good stability, high oxygen evolution over-potential and low cost are the key factors for the efficient and cost-effective degradation of organic pollutants (Rodrigo et al., 2001; Flox et al., 2009; Lin et al., 2013). Moreover, the electrode configurations with different metal-oxide-coatings are the other important factors that can affect the electro-catalytic characteristics and stability of the electrodes. Recently, some metal-oxide-coated Ti electrodes have been produced and their efficiency toward electro-oxidation of refractory organic pollutants was demonstrated. The electrodes including Ti/SnO_2–Sb, Ti/SnO_2–Sb/PbO_2 (Houk et al., 1998; Lin et al., 2012; Niu et al., 2013a,b), Ti/Pt (Szczepankiewicz et al., 2000), Ti/boron-doped diamond (BDD) (Chen et al., 2003; Wang and Li, 2012) are the most typical dimensionally stable electrodes and extensively applied in recent wastewater treatment processes. However, only a few investigations have been found regarding the efficiency of these electrodes in the electrochemical oxidation of chlorophenoxy compounds such as 2,4,5-T. Previously, it was reported that 2,4,5-T can be rapidly degraded by peroxi-coagulation process using an iron (Fe) anode and an O_2-diffusion cathode, while the degradation efficiency of 2,4,5-T was higher than 90% within 10 min over an Fe anode and a graphite cathode by the electro-Fe(II)/oxone process (Boye et al., 2003b; Wang and Chu, 2011). Besides, 2,4,5-T can also be efficiently degraded by the anodic oxidation and electro-Fenton process using a high oxygen over-potential BDD anode (Brillas et al., 2004). Although the BDD electrode has an excellent performance toward the oxidation of organic pollutants by the electro-Fenton process, its high cost and the difficulty in finding an appropriate substrate for the deposition of the diamond layer limit the large-scale application (Qu and Zhao, 2008; Panizza and Cerisola, 2009). Interestingly, it has been proven that the Ti/SnO_2–Sb/PbO_2 electrode can be effectively used in water purification plants because of its high stability, high energy efficiency and long life time (Schümann and Grundler, 1998; Kong et al., 2007; Lin et al., 2012, 2013). The addition of different metal oxides such as Bi^{4+}, Co^{3+}, Fe^{3+} and Ce^{4+} into the PbO_2 coating can possibly enhance its catalytic activity (Panizza, 2010). Recently, CeO_2 is preferentially used as an active catalyst in the electro-oxidation of organic pollutants for its diffusivity and high degradation capability (Zhang et al., 2006; Liu et al., 2011; Lin et al., 2013). Thus, in this present study, we prepared the Ce-doped porous nanocrystalline PbO_2 on Ti/SnO_2–Sb base electrode and then determined the electro-catalytic degradation efficiency of 2,4,5-T in aqueous solution.

In this study, different metal-oxide-coated Ti electrodes, i.e., Ti/SnO_2–Sb, Ti/SnO_2–Sb/Ce–PbO_2 and Ti/RuO_2 were applied to eliminate 2,4,5-T from aqueous solution. The effects of operating parameters such as initial 2,4,5-T concentration, initial pH, plate distance, and applied current density on the degradation kinetics of 2,4,5-T were determined. The removal of total organic carbon (TOC) was investigated to reveal the oxidation of 2,4,5-T over different electrodes. In addition, the degradation by-products of 2,4,5-T were also detected during the electro-oxidation process.

2. Materials and methods

2.1. Chemicals

Analytical grade 2,4,5-T was purchased from Sigma–Aldrich (USA). Sodium hydroxide, sodium perchlorate, sodium sulfate, acetic acid, phosphoric acid and hydrochloric acid were obtained from Sinopharm (Beijing, China). All solutions were prepared in Milli-Q deionized water and the pH value was adjusted by adding HCl (5%, v/v) and NaOH (5%, w/w). HPLC-grade acetonitrile was used for the sample analyses.

2.2. Preparation and characterization of electrodes

The Ti sheets were rectangular in shape with a dimension of 5 cm × 5 cm and a thickness of 1.0 mm. Initially, Ti plates were immersed in NaOH solution (5%, w/w) at 90 °C for 1.0 h to remove dirt and grease from the surface. The sheets were then etched in boiling oxalic acid (10%, w/w) for 3.0 h to produce a gray surface with uniform roughness. The Ti/SnO_2–Sb electrode was prepared by the sol–gel method as described in detail elsewhere (Lin et al., 2012; Niu et al., 2013a). Briefly, citric acid and ethylene glycol were firstly mixed and agitated at 60 °C until complete dissolution, and then the solution was heated to 90 °C under stirring. The mixture of $SnCl_4{\cdot}4H_2O$ and $SbCl_3$ was added to the solution at the molar ratio of 140:30:9:1 (citric acid:ethylene glycol:$SnCl_4{\cdot}4H_2O$:$SbCl_3$). The mixture was heated at 90 °C for 30 min to obtain a glue type substance. And then, the glue/sol–gel solution was uniformly coated on the surface of the Ti sheets by dip-coating method. The Ti sheets were oven-dried for 10 min and then sintered at 500 °C in a muffle furnace to decompose the coating thermally. The above procedure was repeated at least 20–22 times to fabricate the smooth and thicker electrodes. Furthermore, electro-deposition method was used to deposit Ce-doped porous nanocrystalline PbO_2 on the surface of the Ti/SnO_2–Sb electrode (Lin et al., 2013). The Ce-doped porous nanocrystalline PbO_2 layer was prepared by polarizing Ti/SnO_2–Sb electrode at a constant electrode current density of 250 A m^{-2} for 20 min in 0.1 M HNO_3 containing 200 g L^{-1} $Pb(NO_3)_2$, 0.4 g L^{-1} $Ce(NO_3)_3$, and 0.5 g L^{-1} NaF. Similarly, the Ti/RuO_2 electrode was prepared using the methods reported by Motheo and Pinhedo (2000). The surface structure of the electrodes was observed by a scanning electron microscopy (SEM; S4800, Hitachi, Japan) with accelerating voltage of 5.0–20.0 kV.

The electrochemical behavior of the Ti/SnO_2–Sb/Ce–PbO_2 anode was examined using CHI 660D electrochemical workstation with a conventional electrochemical reactor (Shanghai Chenhua instrument Co., Ltd., China). In the experiments, the Ti/SnO_2–Sb/Ce–PbO_2 electrode (10 mm × 20 mm) was used as the working electrode, while a platinum electrode (10 mm × 20 mm) and an Ag/AgCl electrode were employed as the counter electrode and reference electrode, respectively. Linear sweep voltammetry (LSV)