Chemosphere 195 (2018) 63–69

Contents lists available at ScienceDirect

Chemosphere

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

Electrosorption enhanced electrooxidation of a model organic pollutant at 3D SnO_2-Sb electrode in superimposed pulse current mode

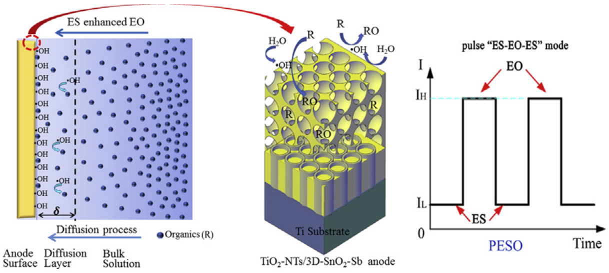
Yong Chen*, Yong Tu, Yonggang Bai, Jun Li, Jilai Lu

Jiangsu Provincial Key Laboratory of Environmental Engineering, Jiangsu Provincial Academy of Environmental Science, Nanjing 210036, China

HIGHLIGHTS

- Superimposed pulse current mode was created in PESO process.
- The pulse "ES-EO-ES" mode is successfully developed for treating organic pollutant.
- The synergism and mutual promotion effect between ES and EO is embodied.
- ES contributed to the great enhancement of degradation efficiency in PESO process.
- Mechanism of enhanced electrochemical degradation by PESO process was analyzed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 August 2017
Received in revised form
10 December 2017
Accepted 11 December 2017
Available online 12 December 2017

Handling Editor: E. Brillas

Keywords:
Electrosorption
Enhanced electrooxidation
3D SnO_2-Sb electrode
Superimposed pulse current

ABSTRACT

In this work, the novel pulse "electrosorption-electrooxidation-electrosorption" (PESO) mode is developed in the superimposed pulse current system for benzoic acid oxidation. Due to the synergistic effect of electrosorption and electrooxidation at TiO_2-NTs/3D-SnO_2-Sb electrode in PESO mode, the enhancement of removal efficiency, improvement in mass transport and decrease of energy consumption were significantly obvious. The mechanism for the great enhancement of the mode is analyzed in details. The strengthened interaction between electrode and organics, increased instantaneous currents and lower intermediate accumulation contributed to the significant enhancement of electrochemical performance of the superimposed pulse system. The pulse PESO mode was an efficient and promising method for treating organic pollutants.

1. Introduction

Industrial processes generate large amount of wastewater. The wastewater is a very complex mixture of different organic and inorganic pollutants, which is mainly treated by conventional technologies such as aerobic and anaerobic biological degradation (Panizza and Cerisola, 2009; Särkkä et al., 2015). However, the refractory organic pollutants have high resistance to the biological treatment and can exert considerable negative impacts on ecosystems. Electrochemical oxidation (EO) treatment has attracted a

---

* Corresponding author.
E-mail address: yong.chen@hotmail.com (Y. Chen).

https://doi.org/10.1016/j.chemosphere.2017.12.074
0045-6535/

great deal of attention in environmental remediation and refractory organics oxidation in recent years (Chatzisymeon et al., 2009; Fernandes et al., 2014; Ridruejo et al., 2017). EO is a promising technology for treating the wastewater due to the relatively simple equipment, amenability to automation, powerful oxidation ability and wide application (Comninellis, 1994; Martínez-Huitle, and Brillas, 2009; Cho et al., 2014). EO treatment could also be called "green technology" process because little or no chemicals are needed for the technology (Panizza et al., 2008; Thiam et al., 2015). Hydroxyl radical (•OH) generated from water discharge (physically adsorbed on anode's surface): $H_2O \rightarrow {}^{\bullet}OH_{ads} + e^- + H^+$, is considered the principal oxidizing species for the electrochemical degradation of organics (Comninellis, 1994; Ridruejo et al., 2017).

The metal oxide anodes including Pt (Vlyssides et al., 2005; Bagastyo et al., 2013), SnO_2 (Chen et al., 2010; Xu et al., 2017), IrO_2 (Chung et al., 2016), RuO_2 (Liang et al., 2005; Fukunaga et al., 2008), PbO_2 (Shmychkova et al., 2013; Chen et al., 2014), and BDD (Koparal et al., 2007; Brillas et al., 2010; El-Ghenymy et al., 2014) have been investigated for treating refractory organic pollutants. Porous structured anode has high surface area, and provides more electrochemical sites to accelerate the generation of •OH and improve the electrocatalytic activity towards oxidation of organics (Chai et al., 2014; Zanin et al., 2014). Recently, the TiO_2 nanotubes based three-dimensionally macroporous SnO_2 with mesoporous walls (TiO_2-NTs/3D-SnO_2-Sb) have been fabricated using the dual-templating strategy (Chen et al., 2017). This 3D porous SnO_2-Sb anode has large surface area and high electrocatalytic performance (Chen et al., 2017). Furthermore, EO treatment in conventional direct-current (DC) electrolysis is a diffusion control process under normal operating conditions, which may result in concentration polarization and consequently lead to higher energy consumption (Ren et al., 2011; Särkkä et al., 2015). It is generally accepted that the introduction of pulse technology bring a positive impact on the electrolysis processes (Ren et al., 2011; Grygolowicz-Pawlak et al., 2012). Hence, a growing amount of research on typical pulse ("off-on-off" power supply) mode for the EO system has been reported (Ren et al., 2011; Wei et al., 2011; Huang, 2013). In comparison with DC electrolysis under normal operating conditions, the pulse current mode can reduce the concentration polarization and obtain higher pollutant degradation efficiency (Wei et al., 2011; Karimi and Foulkes, 2012; Huang, 2013), but the mass transfer of ions is interrupted in the off-pulse time. Electrosorption (ES), which is generally defined as potential-induced adsorption of molecules on the electrode surface, is also a promising technology for faster pollutants removal especially with the porous electrode (Li et al., 2011; Bharath et al., 2017).

In this work, superimposed pulse current system was created for organics oxidation. First, the superimposed pulse is the pulse mode plus a low current, which prevents interruption of mass transfer of ions when the conventional pulse is switched off. Second, refractory organics could be enriched to the 3D porous SnO_2-Sb (TiO_2-NTs/3D-SnO_2-Sb) by electrosorption (ES) in the plus low current. Herein, pulse "ES-EO-ES" mode is developed in the superimposed pulse current system. The synergism and mutual promotion effect between ES and EO will be embodied more evident in this mode.

Therefore, the present study aimed at investigating the feasibility of setting up the pulse "ES-EO-ES" mode in the 3D porous SnO_2-Sb system for treating benzoic acid (BA), which is a model organic pollutant representative of the aromatic fraction commonly found in industrial effluents (Yan et al., 2007). This provides a new idea for exploring the 3D porous anode and electrolysis mode, which has important significance for the research and application on electrochemical degradation of contaminants. The mechanism for the great enhancement of electrochemical performance is analyzed by the instantaneous pulse current and accumulated degradation intermediates.

2. Material and methods

2.1. Preparation of the 3D porous SnO_2-Sb anode

The 3D porous SnO_2-Sb anode was prepared according to our previous study (Chen et al., 2017). The details are listed in SM1 of the Supplementary Materials. Briefly, the inner layer of TiO_2 nanotubes (TiO_2-NTs) was introduced on the Ti sheet, and the out layer of 3D porous SnO_2-Sb was fabricated using the dual-templating strategy on the TiO_2-NTs substrate.

2.2. Electrochemical degradation of benzoic acid

The electrolysis experiments were performed in a cell with working volume of 100 mL. The TiO_2-NTs/3D-SnO_2-Sb electrode with an area of 4 cm^2 was used as the anode. A stainless steel with the same size was used as the cathode. The concentration of benzoic acid was 120 mg L^{-1}, with 50 mM Na_2SO_4 as supporting electrolyte. The same mass transfer condition for stirring was maintained in the electrolysis cell (The experiments were done with constant stirring at 300 rpm using a magnetic stirrer). The 3D-SnO_2-Sb electrode system was performed using a Pulse Current Supply (PCS-FN, Shandong Electrical Co., Ltd, China). During the "off-on-off" pulse mode (named as PEO) for the system, a pulse cycle time T (set at 1 ms) is comprised of T_{on} and T_{off}, which is the power-on time and power-off time, respectively. The pulse frequency of 1000 kHz is equal to 1/T. The current density I_{on} is set at 25 mA cm^{-2} in the T_{on} period. The pulse duty cycle determined by T_{on}/T is controlled to be 1/2 (i.e., 50%). So the mean current density I_{mean} is 12.5 mA cm^{-2} for PEO mode. The superimposed pulse current mode (named as PESO) is the PEO mode plus a base direct current, which allows the electrosorption reaction when the PEO mode is switched off. The base current density I_L is set at 1.25 mA cm^{-2} for the electrosorption reaction in the system, and other conditions for PESO process were the same as those in PEO process.

For comparison, single electrooxidation (SEO) and single electrosorption (SES) process for treating BA was carried out in DC electrolysis at current density of 12.5 mA cm^{-2} and 1.25 mA cm^{-2}, respectively.

2.3. Desorption experiment

Desorption experiment was conducted in a bottle containing 100 mL distilled water. The TiO_2-NTs/3D-SnO_2-Sb electrodes at the same reaction intervals during different electrolysis processes were respectively soaked into 100 mL distilled water for 48 h to desorption. Finally, the sample was withdrawn from the bottle for benzoic acid (BA) and COD analysis.

2.4. Analytical methods

The microstructure and morphology of the 3D porous SnO_2-Sb anode were examined by field-emission scanning electron microscopy (FE-SEM, Quanta 250 FEG), transmission electron microscopy (TEM, JEM-200CX) and X-ray diffraction (XRD, Bruker D8) using Cu Ka radiation (0.154 nm).

Benzoic acid and degradation intermediates were quantified by high-performance liquid chromatography (HPLC, Agilent 1200) fitted with an Extend-C18 column (4.6 mm × 150 mm). 85% $HClO_4$ and 15% methanol (v/v) were employed as the mobile phase. GC-MS (Varian Saturn 2000, USA) was also used to determine the