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Enhanced electrochemical degradation of ibuprofen in aqueous solution by PtRu alloy catalyst

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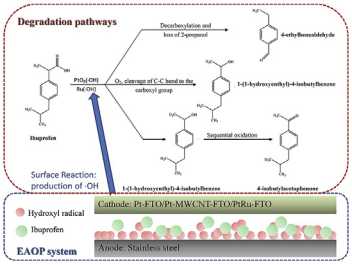
HIGHLIGHTS

- Effective anodes were successfully synthesized and applied to ibuprofen treatment.
- Addition of MWCNTs effectively reduces the grain size of electrocatalyst.
- Usage of PtRu electrocatalysts effectively enhances the surface activity.
- Bimetallic PtRu nanoparticles possess the greatest electroactivity in EAOPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical advanced oxidation processes (EAOPs) regarded as a green technology for aqueous ibuprofen treatment was investigated in this study. Multi-walled carbon nanotubes (MWCNTs), Pt nanoparticles (Pt NPs), and PtRu alloy, of which physicochemical properties were characterized by XRD and X-ray absorption spectroscopy, were used to synthesize three types of cheap and effective anodes based on commercial conductive glass. Furthermore, the operating parameters, such as the current densities, initial concentrations, and solution pH were also investigated. The intermediates determined by a UPLC-Q-TOF/MS system were used to evaluate the possible reaction pathway of ibuprofen (IBU). The results revealed that the usage of MWCNTs and PtRu alloy can effectively reduce the grain size of electrocatalysts and increase the surface activity from the XRD and XANES analysis. The results of CV analysis, degradation and mineralization efficiencies revealed that the EAOPs with PtRu-FTO anode were very effective due to advantages of the higher capacitance, CO tolerance, catalytic ability at less positive voltage and stability. The concentration trend of intermediates indicated that the potential cytotoxic to human caused by 1-(1-hydroxyenthyl)-4-isobutylbenzene was completely eliminated as the reaction time reaches 60 min. Therefore, EAOPs combined with synthesized anodes can be feasibly applied on the electrochemical degradation of ibuprofen.

1. Introduction

Pharmaceuticals are widely detected in the aquatic environment and have raised increasing concerns due to the possibly chronic toxicity and interference in the reproduction of regulators (Han et al., 2010). Non-steroid anti-inflammatoy drugs (NSAIDs)

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are antipyretic analgesic drugs and normally given over dose to the adults (Buser et al., 1999). Among NSAIDs, ibuprofen (IBU) is the mostly used and detected in waters (Buser et al., 1999; Verlicchi et al., 2010), and one of the high priority pharmaceuticals in water management (de Voogt et al., 2009). IBU has been approved to cause general stress on clam (i.e., *Corbicula fluminea*) at environmental relevant concentrations of 0.1–1 μg L^{-1} (Aguirre-Martinez et al., 2015). It has been reported that IBU was detected in the bile of two wild fish species, which were caught downstream of a wastewater treatment plant (WWTP) (Brozinski et al., 2013a). The bioconcentration factors (BCFs) of IBU determined in the bile of rainbow trout were found to be ranged from 14,000 to 49,000 under the exposure concentration of sub μg L^{-1} (Brozinski et al., 2013b). However, the very low BCFs of 0.08–1.4 were discovered in fathead minnow and channel catfish instead (Brozinski et al., 2013b). Moreover, even though the low concentration of single IBU in the aquatic environment caused low ecotoxicity, the very steeper dose-response effects possibly existed in the mixtures of NSAIDs, in which the individual compounds were at non-effective concentrations (Cleuvers, 2004). Obviously, the removal of NSAIDs by WWTPs, which are regarded as the hotspots of NSAIDs for aquatic environment, demands immediate attention.

Physicochemical processes are often superior in the treatment of refractory organic compounds for the treatment of wastewater, especially advanced oxidation processes (AOPs). The main purpose of AOPs is to produce the strong oxidant of hydroxyl radical which can non-selectively attract and then mineralize the organic compounds in the aquatic solution. Several investigators have studied the photodegradation of IBU via direct and indirect photolysis (Xu et al., 2011; Szabo et al., 2011; Ruggeri et al., 2013; Li et al., 2014). Moreover, the transformation intermediates were approved to be more harmful than the parent compound IBU during photolysis (Ruggeri et al., 2013; Li et al., 2014). UV/H_2O_2 and UV/peroxydisulfate (UV/PS) have been investigated to degrade IBU in the simulated wastewater, in which the degradation efficiency was strongly inhibited by co-ions in the solution and less amount of IBAP was generated during oxidation in the case of the UV/PS (Kwon et al., 2015). Photocatalytic and Fenton-like processes have been also considered to degrade IBU with superior ability (Sun et al., 2013; Bian et al., 2014). However, the usage auxiliary agents, such as photocatalysts, ferric ions and PS, need the subsequent treatment before discharge.

Electrochemical advanced oxidation processes (EAOPs) has been regarded as a green technology for wastewater treatment due to the dispensable agents used in the process. Suitable anodes material are necessarily required to effectively degrade and mineralize IBU under suitable conditions, such as Pt (Thokchom et al., 2015), Ti/Pt/PbO_2 and Si/BDD (boron doped diamond) (Ciriaco et al., 2009; Garcia-Segura et al., 2015), and multi-walled carbon nanotubes-epoxy composite electrode (Motoc et al., 2013). In addition, new types of anodes were also developed for the degradation of 1-hydroxy-2,4-dinitrobenzene, such as Pb/PbO_2, Ti/SnO_2 and Ti/Ir_x-$Ru_y$$SnO_2$ (Quiroz et al., 2014). Also effective anodes were used to enhance the Fenton (Skoumal et al., 2009; Loaiza-Ambuludi et al., 2013) and photoelectro-Fenton processes (Skoumal et al., 2009), even for other drugs of paracetamol and diclofenac (Garcıá-Montoya et al., 2015). In the meanwhile, photocatalysts of TiO_2 combined with EAOPs for degradation of diclofenac and acetaminophen was also investigated to improve the removal efficiency (Peralta-Hernández et al., 2016). Our previous study has demonstrated new, easy, flexible and effective anodic materials which can be feasibly applied to degrade naproxen (Chin et al., 2014). The degradation and mineralization efficiencies of naproxen via Pt/MWCNT-FTO (platinum nanoparticles/multi-walled carbon nanotube- Fluorine-doped tin oxide conductive glass) anode at a reaction of 2 h can reach 96% and 51%, respectively. Due to the low energy consumption and high treatment efficiency, the obtained anode material possesses high potential to serve as an AOP to further remove NSAIDs and their intermediates. However, the mineralization efficiency and the possible harmful intermediates generated during EAOP are necessary to be improved and identified to well understand the feasibility of the obtained anode materials. PtRu (platinum – ruthenium) nano-alloy at an atomic ratio equal to 1 used as an electrocatalyst have been proved to be the optimal performance and effectively enhance the oxidation efficiency of CO to CO_2 at lower potentials for direct methanol fuel cell (DMFC) (Long et al., 2000; Liu et al., 2006).

Therefore, the main objective of this study was to degrade and mineralize IBU in aquatic environment by electrochemical oxidation process. Anodes based on commercial FTO conductive glass, MWCNTs, Pt NPs, and PtRu NPs were synthesized in this study. The physicochemical properties of Pt NPs, Pt/MWCNT and PtRu alloy were characterized by XRD and X-ray absorption spectroscopy. Furthermore, the operating parameters, such as the current densities, initial concentrations of IBU, and solution pH values were also investigated. The degradation and mineralization efficiencies of IBU were examined to judge the feasibility of obtained anodes. In the meantime, the intermediates obtained from the EAOPs were determined by a UPLC-Q-TOF/MS system to evaluate the possible reaction pathway of IBU.

2. Materials and methods

2.1. Materials and chemicals

The commercial FTO glass at a thickness of 2.2 mm was purchased from the Solaronix (Aubonne, Switzerland) and subsequently cut into the size at a length of 3 cm and width of 1 cm. The chemicals of $H_2PtCl_6{\cdot}(H_2O)_6$ (98.0 wt%), $RuCl_3$ (98.0 wt%), and ethylene glycol (EG, 99.5 wt%) are reagent grade from Showa Chemical Industry Co., Ltd, Tokyo, Japan. Poly(N-vinyl-2-pyrrolidone) (PVP-40, 99.0 wt%) and ibuprofen (98.0 wt%) are reagent grade from Sigma-Aldrich, Denmark). Acetone (99.8%, Analytic grade, Merck, Darmstadt, Germany), ethyl alcohol (99.5%, reagent grade, Shimakyu's pure chemicals, Osaka, Japan), and multi-walled carbon nanotubes (99.5%, FloTubeTM9000, Industrial-grade, Cnano, Beijing, China) were also used in this study for the synthesis of various anodes.

2.2. Synthesis of electrodes

2.2.1. Preparation of Pt-FTO and Pt/MWCNT-FTO

The as-received MWCNTs needed pretreatment of acidic purification before preparing Pt/MWCNT. The preparation of Pt NPs followed the polyol process. The Pt/MWCNT were obtained by the addition of MWCNTs into Pt NPs suspension. The spin coating method was use to load the Pt NPs, Pt/MWCNT on the FTO glass to obtain the anodic type of Pt-FTO and Pt/MWCNT-FTO. After spin coating, the anodes were calcinated at a heating rate of 10 K min^{-1} to the temperature of 393 K for the soaking time of 30 min. Sequentially, the temperature was further increased to a final temperature of 603 K for the soaking time of 30 min to obtain the final anodes for EAOPs. Details of the synthesizing procedures are described elsewhere (Chin et al., 2014).

2.2.2. Preparation of PtRu alloy and PtRu-FTO

The preparation of PtRu NPs adopted the polyol process as well,