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Maximization of current efficiency for organic pollutants oxidation at BDD, Ti/SnO_2-Sb/PbO_2, and Ti/SnO_2-Sb anodes

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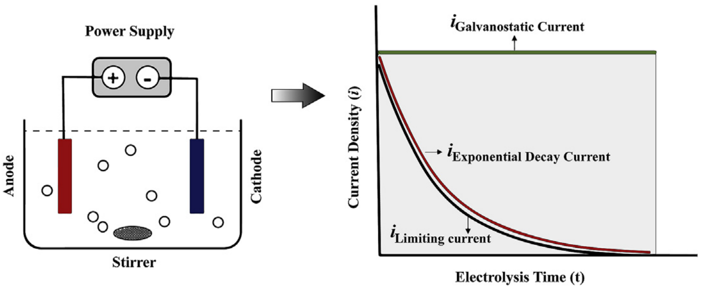
HIGHLIGHTS

- Possible highest ICE at different anodes relevant to hydroxyl radical forms.
- Wisely designed exponential decay current mode for PHICE maintenance.
- Solution provided for expected D_{COD} and E_{sp} with increase of retention time.
- Over 70% energy-saving in electrochemical oxidation of phenol at BDD anode.

GRAPHICAL ABSTRACT



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ABSTRACT

Whereas electrochemical oxidation is noted for its ability to degrade bio-refractory organics, it has also been incorrectly criticized for excessive energy consumption. The present paper rectifies this misunderstanding by demonstrating that the energy actually consumed in the degradation process is much less than that wasted in the side reaction of oxygen evolution. To minimize the side reaction, the possible highest instantaneous current efficiency (PHICE) for electrochemical oxidation of phenol at Boron-doped Diamond (BDD), Ti/SnO_2-Sb/PbO_2 (PbO_2), and Ti/SnO_2-Sb (SnO_2) anodes has been investigated systematically, and found to reach almost 100% at the BDD anode compared with 23% at the PbO_2 anode and 9% at the SnO_2 anode. The significant discrepancy between PHICE values at the various anodes is interpreted in terms of different existing forms of hydroxyl radicals. For each anode system, the PHICEs are maintained experimentally using a computer-controlled exponential decay current mode throughout the electrolysis process. For applications, the minimized energy consumption is predicted by response surface methodology, and demonstrated for the BDD anode system. Consequently, almost 100% current efficiency is achieved (for a relatively meagre energy consumption of 17.2 kWh $kgCOD^{-1}$) along with excellent COD degradation efficiency by optimizing the initial current density, flow rate, electrolysis time, and exponential decay constant. Compared with galvanostatic conditions, over 70% of the energy is saved in the present study, thus demonstrating the great potential of electrochemical oxidation for practical applications.

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1. Introduction

Many industrial processes generate bio-refractory organic effluent, such as coking processes (Lai et al., 2009; Zhu et al., 2009), oil refining(Wei et al., 2010), textile dyeing(Abdessamad et al., 2013; Sathishkumar et al., 2017; Shi et al., 2018), the production of pharmaceutics (Wang et al., 2017), pesticide (Wee and Aris, 2017), herbicide (Allan et al., 2017), heavy metal removals (Li et al., 2016), pulp and paper (Fang et al., 2017), plastics and detergents (Hermabessiere et al., 2017). Such wastewaters usually contain many kinds of bio-refractory organic compounds, and so cannot be degraded efficiently by conventional biological methods. Instead, advanced oxidation processes (AOPs) including Fenton oxidation (Gupta and Garg, 2018), ozonation (Chacana et al., 2017), wet air oxidation (Li et al., 2013), photocatalytic oxidation (Uyguner-Demirel and Bekbolet, 2011), supercritical water oxidation (Yang et al., 2017) and electrochemical oxidation (Zhu et al., 2009; Li et al., 2010; Yi et al., 2010; Zhu and Ni, 2011; Xing et al., 2012) have been widely investigated to treat these wastewaters.

Electrochemical oxidation is one of the most promising AOPs techniques because of its low use of chemicals, fast oxidization rate, and lack of secondary pollution (Wang et al., 2015; Fan et al., 2016; Chai et al., 2017). However, the electrochemical oxidation method has long been criticized for its poor current efficiency (CE) and high energy consumption, and so has not been widely applied. To remedy these defects, a considerable body of research has been undertaken on combinations of various oxidation methods (Brillas et al., 2004; Cañizares et al., 2009; Borràs et al., 2011; Garcia-Segura et al., 2012) and the enhancement of mass transfer processes (Lindermeir et al., 2003; Zhao et al., 2008). However, many problems persist such as the need of extra chemicals, dependence on specialized equipment, formation of complex substances, etc., and no satisfactory results have been obtained to date.

Anode materials are critical for electrochemical oxidation processes and have a significant influence on CE. Over the past few decades, various anodes have been tested including Pt (Zhao et al., 2008), IrO_2 (Martínez-Huitle et al., 2004), RuO_2 (Zhou et al., 2011), PbO_2 (He et al., 2018), SnO_2 (Guo et al., 2016), and boron-doped diamond (BDD) anodes (Panizza and Cerisola, 2005; Li et al., 2010; Zhu et al., 2010a, 2011b; Wei et al., 2011). According to the oxidation mechanism, these anodes can be divided into two groups, i.e. active and non-active anodes (; Zhu et al., 2007, 2008; Zhu et al., 2007). During electrolysis, water molecules initially oxidize on the anode surface (MO_x) leading to the formation of hydroxyl radicals (MO_x(•OH)). At active anodes, such as Pt, IrO_2 and RuO_2, the hydroxyl radicals oxidize the oxide lattice and form higher oxides (MO_{x+1}) that participate in the electrochemical conversion of organic pollutants. At non-active anodes, such as SnO_2, PbO_2 and BDD, the hydroxyl radicals are mainly physically adsorbed and react with organics directly. Besides oxidizing organics, oxygen is evolved through further oxidation of the hydroxyl radicals. This decomposition process wastes energy during electrolysis and this worsens the longer the duration of the process. Hence, it can be speculated that if the side reaction of oxygen evolution can be prevented or minimized, then energy consumption would be substantially reduced. Recently, a multi-step modulation method involving complicated adjustment to the applied current has been proposed (Panizza et al., 2008) to enhance CE in a BDD anode system. Simplification of this method would make it attractive for use in practical applications.

In the present study, the possible highest instantaneous current efficiency (PHICE) of three typical systems with non-active anodes of BDD, Ti/SnO_2-Sb/PbO_2 (PbO_2), and Ti/SnO_2-Sb (SnO_2) is investigated by reducing the side reaction. Using a computer-controlled exponential decay current mode, the PHICE is successfully maintained throughout the electrolysis process without being affected by the electrolysis time. System optimization using response surface methodology (RSM) is conveniently undertaken by altering the following operating parameters: initial current density, electrolysis time, flow rate, and exponential decay constant *k*. The optimization technique is demonstrated for phenol (Yi et al., 2010; Wei et al., 2011; Zhu and Ni, 2011) electrochemical oxidation in a BDD anode system.

2. Experimental section

2.1. Electrochemical system

A diagram illustrating the electrochemical installation is given in Figure SM-1, which is constant with previous study (Zhu et al., 2010b). The three anodes respectively comprise BDD (purchased from CONDIAS GmbH, Germany), PbO_2 and SnO_2 electrodes (purchased from the General Research Institute for Nonferrous Metals, Beijing, China), each with a working area of 24 cm^2 (3 cm × 8 cm). A piece of stainless steel of the same dimensions is used as the cathode. The gap between the electrodes is set to be 1.55 cm, and thus the working volume of the system is 37.2 mL. The anode system is operated in continuous mode at room temperature for phenol simulated wastewater. During the electrochemical oxidation process, the water contaminated with phenol is pumped from a tank at a constant flow rate through the reactor. At regular intervals, samples are drawn from the tank for chemical analysis.

2.2. Analytical methods

Phenol concentration is measured by an Agilent HP1100 HPLC instrument with a ZORBAX SB-C^{18} column and a DAD detector. The UV detector is set at 217 nm for phenol detection. The mobile phase is methanol: water (50:50), with a constant flow rate of 1.0 mL min^{-1}. Initial chemical oxygen demand (COD) of the phenol simulated wastewater is controlled at 500 mg L^{-1} with 0.1 M Na_2SO_4 as the electrolyte. COD is measured by a titrimetric method using dichromate as the oxidant in an acidic solution at 150 °C for 2 h (Hachi, USA). The instantaneous current efficiency (*ICE*) for the anodic oxidation of phenol is determined from:

$$ICE = \frac{[COD_t - COD_{\Delta t}]FV}{8I\Delta t} \tag{1}$$

where COD_t and $COD_{t+\triangle t}$ are the COD (g O_2 m^{-3}) at times *t* and $t+\triangle t$ (s), respectively. F is the Faraday constant (96,487 C mol^{-1}), *V* is the volume of the electrolyte (L), *I* is the current (in A), and the number 8 is a dimensional factor for consistency of units (32 g O_2/4 mol e^{-1} O_2).

The time-averaged current efficiency (*CE*) is calculated using the mean - value theorem from:

$$CE = \frac{\int_0^\tau ICE(t)dt}{\tau} \tag{2}$$

where τ is the electrolysis duration (s) necessary to reach a target COD conversion.

Degradation efficiency (D_{COD}) is calculated using:

$$D_{COD} = \frac{COD_0 - COD_t}{COD_0} \times 100\% \tag{3}$$

where COD_0 is the initial concentration, COD_t is the concentration after electrolysis time t (h).