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Research article

Boron-doped diamond electrooxidation of ethyl paraben: The effect of electrolyte on by-products distribution and mechanisms

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ABSTRACT

Ethyl paraben (EP), a representative emerging pollutant of the parabens family, was subject to electrochemical oxidation over a boron-doped diamond (BDD) anode. Experiments were carried out in a single-compartment cell at 10–70 mA cm⁻² current density, 200–600 µg L⁻¹ EP concentration, initial solution pH 3–9 and 0.1 M electrolyte concentration. The degradation rate is favored at increased current densities and in the presence of NaCl as the supporting electrolyte, while the pH effect is inconsiderable. For instance, the first order rate constant for the degradation of 200 µg L⁻¹ EP at 30 mA cm⁻² was 0.25, 0.1 and 0.07 min⁻¹ with NaCl, Na₂SO₄ and HClO₄, respectively. Degradation in secondary treated wastewater was faster than in pure water presumably due to the action of chloride ions present in the effluent.

Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) was employed to determine major transformation by-products (TBPs). The route of EP degradation with Na₂SO₄ involves hydroxylation and demethylation reactions, signifying the role of electrogenerated hydroxyl radicals in the process. Twenty one TBPs were identified with NaCl as the electrolyte, including several chlorinated and non-chlorinated dimers and trimers; these findings suggest that indirect oxidation mediated by chlorine radicals and other chlorine active species also takes place. In this view, the role of the supporting electrolyte is crucial since it can influence both reaction kinetics and pathways.

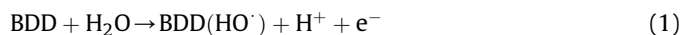
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1. Introduction

In recent years, electrochemical oxidation has attracted considerable attention as a remediation technology for the treatment of industrial wastewaters, disinfection of drinking water, and the removal of emerging micro-pollutants from various aqueous matrices (Sarkka et al., 2015). Although several operating factors are likely to determine process efficiency, this strongly depends on the anodic material, as well as the type of the supporting electrolyte.

In this context, various types of anodes have been tested such as graphite, Pt, TiO₂, IrO₂, PbO₂ and several Ti-based alloys (Sires and Brillas, 2012). Boron-doped diamond (BDD) has recently emerged as a very promising anodic material for environmental applications since it can promote the degradation and mineralization of organic

compounds. Using this anode at high potential, highly reactive hydroxyl radicals are generated on its surface:



The radicals are weakly adsorbed on the surface and can readily react with organic matter, R, leading to its mineralization (Sarkka et al., 2015; Sires and Brillas, 2012):



Besides direct anodic oxidation, indirect oxidation mediated by primary and secondary oxidants can also take place; the most striking effect is associated with the action of Cl-containing active species that are formed electrochemically from chloride ions; the latter may either be inherently present in the matrix (e.g. in drinking water or secondary treated wastewaters) or released when a Cl-containing electrolyte (e.g. NaCl) is used (Sarkka et al., 2015; Sires and Brillas, 2012). In this case, process characteristics

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may be strongly affected in terms of degradation kinetics, reaction pathways and mechanisms, and matrix toxicity.

Parabens, esters of 4-hydroxybenzoic acid with an alkyl or benzyl group, have been employed for about a century as preservatives in foodstuff, cosmetics and personal care products and they have recently been classified as emerging pollutants by the US Environmental Protection Agency. Although their endocrine disrupting potency is rather moderate (Papadopoulos et al., 2016), they are frequently detected in environmental matrices (e.g. freshwater, marine water, sediments) due to their high usage worldwide (Haman et al., 2015). Larsson et al. (2014) reported that ethyl paraben (EP) was detected in levels above the detection limit ($0.4 \mu\text{g L}^{-1}$) in the 95% of samples taken from mothers and 77% of samples taken from children in a campaign where early-morning urine samples were collected from mother-child pairs living in either a rural or an urban area. Application of paraben-containing products on skin was related in the past with breast cancer (Darbre et al., 2004) or even with DNA damage in the sperm of male animals (Oishi, 2002). Therefore, efficient treatment processes are necessary to eliminate parabens in the environment and, thus, to avoid their accumulation.

Interestingly, treatment of parabens by electrochemical (and, indeed, other) advanced oxidation processes has received mere attention. To the best of our knowledge, there is only one journal publication (Gomes et al., 2016) on butyl paraben employing Pt and glassy carbon electrodes and only two dealing with BDD oxidation of methyl paraben (Steter et al., 2014a; 2014b). In the first study, Gomes et al. reported that the degradation of butyl paraben on glassy carbon electrode in $\text{K}_4\text{P}_2\text{O}_7$ (0.1 M) and cetyltrimethylammonium chloride ($40 \mu\text{M}$) was more efficient in acidic media (pH 5) reaching paraben conversion values up to 90%. In the other two studies (Steter et al., 2014a; 2014b), the degradation and mineralization of 100 mg L^{-1} methyl paraben (an unrealistically high concentration for environmental samples) was studied at current densities between 1.35 and 21.6 mA cm^{-2} using K_2SO_4 as the supporting electrolyte by means of electrochemical oxidation alone or a hybrid sonoelectrochemical process. The hybrid process (Steter et al., 2014b) was conducted with the application of ultrasound at a frequency of 20 kHz and a power intensity of 523 W cm^{-2} . The hybrid process was more efficient for paraben and total organic carbon removal than the individual ones, thereby confirming the synergistic role of process integration.

In this study, the feasibility of BDD electrochemical oxidation to degrade ethyl paraben at the $\mu\text{g L}^{-1}$ concentration level was assessed. The scope was two-fold: (i) to investigate how various operating parameters can affect degradation kinetics, and (ii) to identify major TBPs and elucidate reaction pathways with two different electrolytes (NaCl and Na_2SO_4), thus shedding light on the respective reaction mechanisms.

2. Experimental and analytical

2.1. Chemicals

Ethyl paraben (EP) ($\text{HO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{CH}_2\text{CH}_3$, CAS no: 120-47-8) was supplied by Sigma-Aldrich. Ultrapure water (UPW, pH = 6.5) was taken from a water purification system (EASYPureRF-Barnstead/ThermoLyne, USA), while secondary treated wastewater (WW) was taken from the University of Patras campus treatment plant (pH = 8, COD = 21 mg/L). Humic acid (HA, CAS number 1415-93-6), used as a model of the organic fraction typically found in natural waters, was purchased from Sigma-Aldrich. NaCl , Na_2SO_4 and HClO_4 , used as the supporting electrolyte, were supplied by Sigma-Aldrich.

2.2. Reactor setup and procedures

Electrochemical experiments were conducted in a batch type, laboratory-scale electrochemical reactor made of pyrex glass. This single-compartment, squared cell comprised a BDD anode (Adamant Technologies SA, Switzerland; B/C 1000 ppm) with an active working area of 7 cm^2 and a stainless steel cathode of 7 cm^2 , while the distance between the electrodes was 2.2 cm.

To assess the effect of operating conditions on EP degradation, experiments were performed at $10\text{--}70 \text{ mA cm}^{-2}$ current density, $200\text{--}600 \mu\text{g L}^{-1}$ EP concentration and 0.1 M electrolyte concentration, while the liquid holdup was 150 mL. The pH of the solution was unbuffered at its inherent value in all cases except the experiments shown in Fig. 3; in this case, the initial pH value was adjusted to acidic or alkaline conditions adding the appropriate volume of acid or alkali. To identify TBPs, experiments were performed at an increased EP concentration of 20 mg L^{-1} and current density of 133 mA cm^{-2} , while the electrolyte concentration was 0.1 M.

2.3. Determination of EP and TBPs

High performance liquid chromatography (HPLC: Alliance 2695, Waters) was employed to monitor the concentration of EP. Separation was achieved on a Kinetex XB-C18 100A column ($2.6 \mu\text{m}$, $2.1 \text{ mm} \times 50 \text{ mm}$) and a $0.5 \mu\text{m}$ inline filter (KrudKatcher Ultra) both purchased from Phenomenex. The mobile phase consisting of 75:25 water:acetonitrile eluted isocratically at 0.35 mL min^{-1} and $45 \text{ }^\circ\text{C}$, while the injection volume was $40 \mu\text{L}$. Detection was achieved through a photodiode array detector (Waters 2996 PDA detector, detection $\lambda = 254 \text{ nm}$).

TBPs were identified using a Dionex Ultra-HPLC system connected to a microTOF Focus II time of flight mass spectrometer from Brüker Daltonics (Germany). Chromatographic separation was performed on a C18 Acclaim™ RSLC 120 column, $100 \text{ mm} \times 2.1 \text{ mm}$, $2.2 \mu\text{m}$ particle size (Thermo Scientific) protected by a column guard by Waters, using MS grade water with 0.01% formic acid and acetonitrile as a binary mobile phase. Elution started with 1% acetonitrile and increased linearly to 99% at 15 min and then reverted to 1% acetonitrile at 18 min with a constant flow rate of 0.3 mL min^{-1} . The adopted ESI-source parameters in negative ionization mode are described in detail elsewhere (Papadopoulos et al., 2016).

3. Results and discussion

3.1. Effect of operating conditions on degradation

3.1.1. Effect of applied current

Fig. 1 shows the effect of varying applied current density in the range $10\text{--}70 \text{ mA cm}^{-2}$ on $200 \mu\text{g L}^{-1}$ EP degradation. Conversion increases with increasing current density and complete removal can be achieved within 20 min at 70 mA cm^{-2} . The kinetics of the electrochemical degradation in the aqueous phase can be described by the Langmuir-Hinshelwood kinetic model:

$$r = -\text{d}C/\text{d}t = k[\text{KC}/(1 + \text{KC})] \quad (3)$$

where r is the rate of degradation, k is the intrinsic reaction rate constant and K is the Langmuir adsorption equilibrium constant. For those systems where (i) the substrate concentration is low, and (ii) adsorption onto the anode surface is weak (as we can safely assume in the case of ethyl paraben on a non-active anode), Eq. (3) is reduced to:

$$-\text{d}C/\text{d}t = k\text{KC} = k_{\text{app}}C \Leftrightarrow \ln(\text{Co}/C) = k_{\text{app}}t \quad (4)$$

where k_{app} is a pseudo-first order kinetic constant.

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