

# Electrochemical oxidation route of methyl paraben on a boron-doped diamond anode



Juliana R. Steter, Robson S. Rocha, Dawany Dionísio, Marcos R.V. Lanza, Artur J. Motheo\*

Universidade de São Paulo–Instituto de Química de São Carlos Avenida do Trabalhador Sancarlenense 400, Centro, CP 780 São Carlos - SP, CEP 13560-970, Brazil

## ARTICLE INFO

### Article history:

Received 21 August 2013  
Received in revised form  
18 November 2013  
Accepted 19 November 2013  
Available online 4 December 2013

### Keywords:

Endocrine disruptor  
Electrochemical oxidation  
Boron-doped diamond anode  
Mineralization route

## ABSTRACT

Parabens have been widely used in different industries and can be found in health and personal care products. They are esters of *p*-hydroxy-benzoic acid associated with breast tumors and classified as endocrine disruptors. This study describes the galvanostatic electrochemical oxidation of methyl paraben (MePa) on a boron-doped diamond anode using current densities in the 1.35 to 21.6 mA cm<sup>-2</sup> range. The degradation process can be controlled by either charge transfer or mass transport, according to the experimental conditions and rate of mineralization of MePa increased by the current density. The concentration variation as a function of electrolysis time showed that the degradation kinetics follows a pseudo first-order law. A mechanism for the MePa degradation based on reactive intermediates determined by gas chromatography mass spectrometry (GC-MS) is also proposed.

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## 1. Introduction

In recent years, probably no issue concerning environmental toxicology has drawn more attention from the scientific community and regulatory authorities than endocrine disruptors. According to the U.S. Environmental Protection Agency (EPA), an endocrine disruptor is any exogenous substance that interferes with the synthesis, secretion, transport, conjugate activity, metabolism or elimination of the natural hormones responsible for the homeostasis regulation, reproduction, development and behavior of living species [1–4].

Endocrine disruptors can be classified as persistent, lipophilic and bio-accumulative and are low-vapor-pressure compounds, characteristics that facilitate their accumulation in the environment. These substances are often found in industrial effluents and/or domestic sewage and are only partially removed by the conventional sewage treatment [5–10].

Several natural and synthetic substances have been classified as endocrine disruptors: phenolic compounds, pesticides, pharmaceutical and therapeutic agents, natural estrogens, phytoestrogens, phthalates, parabens, heavy metals, among others [2].

Parabens are a very common class of preservatives widely used in food and pharmaceutical industries and especially in health and personal care products (HPC: health and personal care). Chemically,

they are designated as esters derived from *p*-hydroxy-benzoic acid and the ones most commonly used are methyl paraben, which is more hydrophilic, and butyl paraben, the most soluble. Their solubility properties make them convenient to use [11–13]. The human population is exposed to parabens from different sources because these substances have been used over last 50 years in several industries. They can be found in most of the cosmetic and food products and are used in over 13,200 formulations [12]. Products containing methyl paraben may have direct contact with the skin, lips, hair, nasal and oral mucosal, axillars and their use may be over a period of years. By this via, these industrial products are released in the environment on a daily basis, causing problems as bioaccumulation and affecting the human health. These esters have been found in breast tumors, probably associated to the use of deodorants, lotions or sprays, and several studies have classified them as endocrine disruptors [14–19].

Research and development efforts, as well as the implementation of processes and methods for a more efficient treatment of sewage and wastewater have been conducted [20–22]. These efforts include the development of methods for either the removal or degradation of those endocrine disruptors taking into account the efficiency and cost of those processes for the implementation of such technologies. Advanced oxidation processes (AOP) including chemical, photocatalytic, electrochemical and ozone oxidations, sonolysis, Fenton, photo-Fenton and other techniques which involve the *in situ* generation of the hydroxyl radical (\*OH) have been considered effective technologies in the degradation of a wide variety of organic compounds [23–42].

\* Corresponding author. Tel.: +55 16 3373 9932; fax: +55 16 3373 9952.  
E-mail address: [artur@iqsc.usp.br](mailto:artur@iqsc.usp.br) (A.J. Motheo).

One of the most promising techniques for the oxidation of organic contaminants is the electrochemical process, which offers several advantages, such as versatility, environmental compatibility and easy automation [43–47]. Several anodes have been used for the electrochemical treatment of wastewaters, e.g., dimensionally stable anode (DSA<sup>®</sup>), SnO<sub>2</sub>-Sb, β-PbO<sub>2</sub> and boron-doped diamond (BDD). However, in recent studies, the use of BDD has shown that, because of the electro-generation of larger quantities of ( $\bullet$ OH), strongest oxidant species—Eq. (1), the electrooxidation process is faster and more efficient [48–53].



This study deals with the electrochemical oxidation of MePa using a BDD as anode and the analysis of parameters, such as current density applied, speed and degradation kinetics, mineralization current and energy efficiencies. Based on the determination of the degradation products, as well as aromatic and aliphatic intermediates, a mechanistic route for the degradation of MePa is proposed.

## 2. Experimental

### 2.1. Materials

Methyl paraben from Aldrich (reagent grade), K<sub>2</sub>SO<sub>4</sub> from Mallinckrodt, K<sub>3</sub>[Fe(CN)<sub>6</sub>], K<sub>4</sub>[Fe(CN)<sub>6</sub>] and Na<sub>2</sub>CO<sub>3</sub> from Synth were used as received. Acetonitrile and methanol were chromatographically pure (J.T. Baker). All solutions were prepared with ultrapure water (>18 MΩ, Milli-Q, Millipore Inc.).

### 2.2. Electrochemical setup and conditions

MePa (100 mg L<sup>-1</sup> in 0.05 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> aqueous solution) was oxidized in a one-compartment pyrex cell (400 mL) operated at 25 ± 1 °C in batch mode. A BDD thin film deposited on Nb with single crystal p-type Si wafer (substrate containing 500 ppm of boron), provided by Adamant Technologies (La-Chaux-de-Fonds, Switzerland) was used as anode and its effective working (geometric) area was 9.68 cm<sup>2</sup>. A titanium foil of approximately same area of the anode was used as cathode and an Ag/AgCl electrode was used as reference. The range of the current densities used was 1.35 to 21.6 mA cm<sup>-2</sup> on a galvanostat/potenciostat from Autolab (model PGSTAT30N).

### 2.3. Procedures and analysis

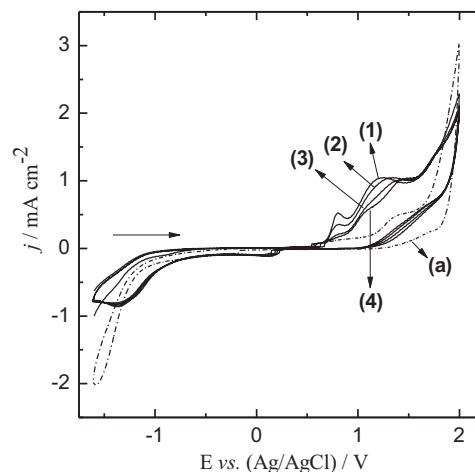
The concentrations of MePa in the solution were determined by HPLC (Shimadzu LC-10AD VP) with a Zorbax SB-C<sub>18</sub> column and a detector set at λ = 254 nm, corresponding to the maximum absorption wavelength of MePa. Samples of 20 μL were injected and a mixture (40:60 (V/V) acetonitrile:water) flowing at 1.0 mL min<sup>-1</sup> was used as the mobile phase. The retention time corresponding to the MePa was 5.3 minutes.

The percentage of mineralization was monitored by the abatement of the total organic carbon (TOC) determined by a TOC-V<sub>CPH</sub> (Shimadzu). UV-Vis absorption spectra were recorded on a MultiSpec-1501-Shimadzu by a temperature accessory model CPS-Controller set at λ = 254 nm.

The current efficiencies (CE) were calculated as

$$\text{CE} = \frac{2.67 [\text{TOC}_0 - \text{TOC}_f] \text{FV}}{8It} \times 100 \quad (2)$$

where (TOC<sub>0</sub>) and (TOC<sub>f</sub>) correspond to the TOC values (g L<sup>-1</sup>) at initial and final times, respectively, F is the Faraday constant (96,487 C mol<sup>-1</sup>), V is the volume of the working solution (L), I is



**Fig. 1.** Cyclic voltammograms of BDD anode in: (a) 0.05 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> (blank solution) and (1 to 4 cycles) 100 mg L<sup>-1</sup> methyl paraben in 0.05 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>. Cyclic voltammograms performed in the potential range -1.6 to +2.0 V vs. Ag/AgCl and scan rate of 50 mV s<sup>-1</sup>.

the current intensity (A), t is the time interval (s) and 2.67 is the conversion factor of the COD (Chemical Oxygen Demand) to TOC [28].

The energy consumption EC (kW h m<sup>-3</sup> and kW h Kg<sup>-1</sup>) defined as the electrochemical oxidation energy for the removal of 1 g of paraben can be calculated as follows [54,56] considering U the potential cell (V), I the current applied (A), V the solution volume (m<sup>3</sup>), m the converted mass (kg) and t the time (h):

$$\text{EC} = \frac{Ult}{1,000(V) \text{ or } (m)} \quad (3)$$

The degradation products of MePa were identified by GC-MS on a Varian CP-3800 Gas Chromatograph equipped with an ion trap Saturn 2200 Mass Spectrometer using Agilent DB-5 capillary column (30 m x 0.25 mm, 0.25 μm film thickness). Methodology applied: 70 °C hold (1 min), rate of 15 °C min<sup>-1</sup> up to 170 °C, hold (2 min), rate of 35 °C min<sup>-1</sup> up to 250 °C. The injector temperature was kept at 80 °C and helium (1 mL min<sup>-1</sup>) was used as the carrier gas. The mass ranged from 40 to 250 m/z. Before injections in GC-MS, the products of the sample solutions degradation were filtrated and extracted six times with methanol by solid phase extraction (SPE) using C<sub>18</sub> filters.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

The BDD electrode was characterized by cyclic voltammetry. Initially, the electrode was subjected to an electrochemical conditioning, i.e., anodic polarization for 30 minutes using a solution of K<sub>2</sub>SO<sub>4</sub> (0.05 mol L<sup>-1</sup>) at constant current of 50 mA cm<sup>-2</sup>, for the removal of any deposits or impurities from the electrode surface. Fig. 1 shows the cyclic voltammograms of the BDD electrode in MePa 100 mg L<sup>-1</sup> in 0.05 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> aqueous solution, potential range of -1.6 to +2.0 V vs. Ag/AgCl electrode and scan rate of 50 mV s<sup>-1</sup>.

There are two oxidation peaks in the potential range applied, one located at +0.75 V and another at +1.25 V. The first anodic peak (+0.75 V) can be assigned to the hydroxyl group present in the molecule, which is easily oxidized based on the peak disappearance after four potential scans. The second peak (+1.25 V) corresponds to the carboxyl group, which is more difficult to be oxidized than the hydroxyl group, because the electron donor effect of the carboxyl group deactivates the aromatic ring and prevents

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