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Research article

Boron-doped diamond oxidation of amoxicillin pharmaceutical formulation: Statistical evaluation of operating parameters, reaction pathways and antibacterial activity

Zacharias Frontistis ^a, Maria Antonopoulou ^b, Danae Venieri ^c, Ioannis Konstantinou ^d, Dionissios Mantzavinos ^{a,*}

^a Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, GR-26504 Patras, Greece

^b Department of Environmental & Natural Resources Management, University of Patras, 2 Seferi St., GR-30100 Agrinio, Greece

^c School of Environmental Engineering, Technical University of Crete, Polytechniopolis, GR-73100 Chania, Greece

^d Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece

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ABSTRACT

The electrochemical oxidation of a commercial amoxicillin formulation over a boron-doped diamond (BDD) anode was investigated. The effect of initial COD concentration (1–2 g/L), current density (30–50 mA/cm²), treatment time (15–90 min), initial pH (3–9) and electrolyte concentration (2–4 g/L NaCl) on COD removal was assessed through a factorial design methodology. For the range of conditions in question, the first three single effects, as well as the interaction between COD and time were the most important ones in terms of mass of COD removed.

Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) was employed to identify major transformation by-products (TBPs); thirteen compounds were detected as TBPs of AMX electrochemical degradation, while several others appear in the original formulation. AMX degradation occurs through the following pathways: (i) hydroxylation mainly in the benzoic ring, (ii) opening of β-lactam ring followed by decarboxylation, hydroxylation and re-arrangement, and (iii) bond cleavage between the carbons of amino and amide groups. Furthermore, the process is accompanied by the release of several ions, i.e. nitrate, sulfate and ammonium.

The antibiotic activity of AMX up to 1000 mg/L was tested against *Klebsiella pneumoniae* and *Enterococcus faecalis* reference strains; both bacteria are completely inactivated at this concentration but the activity is reduced substantially at lower concentrations. Oxidized samples still exhibit some antibacterial activity (50–60%) which is due to TBPs and active chlorine species present in the liquid phase. The latter are generated from chloride ions and enhance considerably AMX degradation rates.

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1. Introduction

In recent years, electrochemical advanced oxidation technologies have gained considerable attention for the destruction of persistent organic compounds (Antonin et al., 2015) and/or the inactivation of pathogens (Long et al., 2015) in wastewaters. In particular, the electrochemical mineralization of organic pollutants, i.e. their rapid conversion to carbon dioxide and water, is a relatively new approach in wastewater management suitable for industrial effluents of moderate concentration, i.e. COD <5 g/L

(Cominellis et al., 2008). This technology is based on the use of high oxidation power anodes and it consumes electrical energy for the mineralization of organic pollutants.

An ideal anode for this type of treatment is the boron-doped diamond (BDD) electrode characterized by high reactivity towards organics oxidation and efficient use of electrical energy. BDD can generate weakly adsorbed hydroxyl radicals on the anode that are used to mineralize various organics, including the relatively refractory short-chain acids. Furthermore, BDD anodes exhibit high stability, low background current and wide potential window (Anglada et al., 2009; Antonin et al., 2015).

The occurrence and fate of emerging micro-pollutants in the environment has attracted enormous attention in the past 15–20

* Corresponding author.

E-mail address: mantzavinos@chemeng.upatras.gr (D. Mantzavinos).

years and this is particularly true for pharmaceuticals in various aqueous matrices such as groundwater, surface waters, hospital effluents and secondary treated municipal wastewaters. Antibiotics constitute an important subset of the scrutinized pharmaceuticals and they are usually detected at the ng/L to µg/L level depending on the matrix (Homem and Santos, 2011). Amoxicillin (AMX) is a semi-synthetic β-lactam antibiotic commonly used in human treatment and veterinary practice and it has been employed in several studies as a model compound representing the antibiotics family. Since AMX is excreted by the body almost unmetabolized (e.g. excretion levels as much as $86 \pm 8\%$ in human urine have been reported (Garcia-Reiriz et al., 2007)), AMX itself rather than a metabolite is likely to be found in environmental samples (Morse and Jackson, 2004). AMX concentrations up to about 85 µg/L have been reported in hospital effluents (Benito-Pena et al., 2006).

Although the advanced treatment of pharmaceuticals/antibiotics at concentrations between several µg/L and mg/L (this is usually a compromise between actual micro-pollutant concentrations found in environmental samples and the availability of analytical techniques to detect very low concentrations) has been studied exhaustively, relatively fewer studies have dealt with higher concentrations that may be found in formulation wastewaters. BDD oxidation has been employed to treat a real pharmaceutical wastewater of initial COD = 12 g/L (Dominguez et al., 2012), as well as various commercial formulations of antihypertensive drugs (Contreras et al., 2015), veterinary drugs (Espinoza et al., 2014) and AMX (Quand-Meme et al., 2015). AMX, as pure compound, has also been treated electrochemically over BDD (Panizza et al., 2014; Sopaj et al., 2015) and other anodes (Jin et al., 2013; Padilla-Robles et al., 2015; Santos et al., 2013; Sopaj et al., 2015).

The goal of this work was to investigate the BDD electrochemical oxidation of commercial AMX formulation at high concentrations (1–2 g/L COD) evaluating the statistically important variables that affect degradation; moreover, issues such as antibiotic activity, formation of by-products and possible pathways, and energy efficiency are also discussed. The novelty of this work is associated with (i) the use of a synthetic formulation wastewater of the actual AMX drug, and (ii) a systematic, inter-disciplinary approach to address various, inter-related issues that can determine treatment efficiency.

2. Materials and methods

2.1. Materials

Commercially available capsules containing amoxicillin trihydrate (Amoxil caps 500 mg, GlaxoSmithKline) were taken from a drug store. According to the manufacturer, the capsule also contains magnesium stearate ($\text{Mg}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$), while chromatographic analysis (see section 3.2) of the dissolved capsule contents showed several peaks corresponding presumably to the excipient and its hydrolysis metabolites. The content of the capsules was dissolved in ultrapure water under magnetic stirring for several hours. Water (pH = 6.5) was taken from a water purification system (EASY-pureRF-Barnstead/Thermolyne, USA). Sodium chloride, used as the electrolyte, was supplied by Sigma–Aldrich. Sulfuric acid or sodium hydroxide was used, as needed, to adjust the initial solution pH to acidic or alkaline conditions.

2.2. Electrochemical oxidation experiments

Batch experiments were performed in a double-wall, cylindrical glass vessel at a liquid holdup of 0.2 L. A rectangular electrode (10 cm^2) made of BDD was used as the anode, while the cathode was made of stainless steel. Electrodes were immersed in the liquid

at a distance of 1.5 cm between them. A temperature control unit was used to keep the temperature constant at $30 \pm 2^\circ \text{C}$. Lower temperatures could not be achieved with the water bath used in this work due to the relatively high heat dissipation rates occurring during electrolysis.

2.3. Analytical methods

2.3.1. Determination of TBPs

The TBPs generated during the electrochemical process were identified by liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS), in positive and negative ionization mode, using an Ultimate 3000 UPLC (Dionex) equipped with a reverse-phase C18 Acclaim™ RSLC 120 analytical column from Thermo Scientific (100 mm × 2.1 mm i.d., 2.2 µm particle size), protected by a guard from Waters. The mobile phase was water with 0.1% formic acid (solvent A) and acetonitrile (solvent B), at a flow rate of 0.3 mL/min. The injection volume was 10 µL. A linear gradient progressed from 1% B (initial conditions) to 99% B in 15 min and returned to the initial conditions after 3 min. The LC system was connected to a time-of-flight mass spectrometer with an electrospray interface operated under the conditions reported in our previous work (Darsinou et al., 2015).

2.3.2. Mineralization

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution containing potassium dichromate, sulfuric acid and mercuric sulfate (Hach-Lange) and the mixture was then incubated for 120 min at 150°C in a COD digester (Model LT200, Hach-Lange). COD concentration was measured colorimetrically using a DR/5000 spectrophotometer (Hach-Lange). Possible interferences of chloride with the COD measurement were checked for and corrected according to the concept described elsewhere (Gotsi et al., 2005).

Determination of NH_4^+ ions, released during the process, was performed by a colorimetric method based on indophenol blue formation (Solorzano, 1969) using a UV–Vis spectrophotometer (Hitachi, U-2000). NO_3^- , NO_2^- , Cl^- and SO_4^{2-} ions were quantified by a Dionex ICS-1500 ion chromatography system equipped with ASRS Ultra II suppressor and an IonPac AS9-HC. The mobile phase was an aqueous sodium carbonate (9 mM) solution at a flow rate of 1 mL/min.

2.4. Calculation of current efficiency and specific energy consumption

The average current efficiency (ACE) of the anodic oxidation was computed as follows (Chatzisyneon et al., 2010):

$$ACE = \frac{COD_0 - COD_t}{8It} FV \quad (1)$$

where COD_0 and COD_t (in mg/L) correspond to concentrations at $t = 0$ and $t = t$ (in s) respectively, I is the applied current (A), F is the Faraday constant (96,487 C/mol), and V is the liquid holdup (m^3).

The specific energy consumption (SEC) in €/kg COD removed was determined as follows:

$$SEC = \frac{UIt}{3600(COD_0 - COD_t)V} P \quad (2)$$

where U is the applied voltage (V) and P is the cost of energy (€/kWh). On average, the cost of energy for industrial use in Greece is 0.05 €/kWh (data for 2016 have been taken from the Public

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