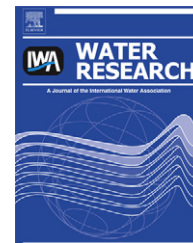




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# Electrochemical incineration of omeprazole in neutral aqueous medium using a platinum or boron-doped diamond anode: Degradation kinetics and oxidation products

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## ABSTRACT

The electrochemical incineration of omeprazole, a widely prescribed gastrointestinal drug which is detected in natural waters, has been studied in a phosphate buffer of pH 7.0 by anodic oxidation with electrogenerated H<sub>2</sub>O<sub>2</sub> (AO-H<sub>2</sub>O<sub>2</sub>) operating at constant current density (*j*). The experiments were carried out in a cell equipped with either a Pt or a boron-doped diamond (BDD) anode and an air-diffusion cathode to continuously produce H<sub>2</sub>O<sub>2</sub>. In these systems, organics are mainly oxidized by hydroxyl radicals formed at the Pt or BDD surface from water oxidation. A partial total organic carbon (TOC) abatement close to 78% for omeprazole was achieved by AO-H<sub>2</sub>O<sub>2</sub> with a BDD anode after consumption of 18 Ah L<sup>-1</sup> at 100 mA cm<sup>-2</sup>, whereas the alternative use of Pt did not allow mineralizing the drug. However, the drug was totally removed using both anodes, although it decayed more rapidly using BDD. In this latter system, increasing *j* accelerated the degradation process, but lowering the mineralization current efficiency. Greater drug content also enhanced the degradation rate with higher mineralization degree and current efficiency. The kinetics for omeprazole decay always followed a pseudo-first-order reaction and its rate constant increased with increasing *j* and with decreasing its concentration. Seven heteroaromatic intermediates and four hydroxylated derivatives were detected by LC–MS, while nine short-linear carboxylic acids were identified and quantified by ion-exclusion HPLC. These acids were largely accumulated using Pt and rapidly removed using BDD, thus explaining the partial mineralization of omeprazole achieved by AO-H<sub>2</sub>O<sub>2</sub> with the latter anode. The release of inorganic ions such as NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> was followed by ionic chromatography. A plausible reaction sequence for omeprazole mineralization involving all intermediates detected is proposed.

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## 1. Introduction

Over the last two decades, drugs have received increasing attention as potential bioactive chemicals in the environment

(Kümmerer, 2009b). They are considered as emerging pollutants in waterbodies because they remain unregulated or their directives and legal frameworks are not yet set-up (Esplugas et al., 2007). A large variety of drugs including analgesics,

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anti-inflammatory, beta-blockers, antimicrobials, blood lipid regulators and so on, has been detected as micropollutants, found in the  $\text{ng L}^{-1}$  or  $\mu\text{g L}^{-1}$  range in soils, surface waters, ground waters and even drinking waters (Tamtam et al., 2008; Kümmerer, 2009a, 2009b; Postigo et al., 2009; McClellan and Halden, 2010). This pollution arises from emission from production sites, direct disposal of overplus drugs in households and hospitals, excretion from urine or faeces after drug administration to humans and animals and water treatments in fish farms (Bound and Voulvoulis, 2005). Pharmaceuticals and their metabolites persist in the environment because of their incomplete elimination in sewage treatment plants (STPs), with 60–90% of the parent molecules still present after the action of biodegradation, deconjugation, partitioning and photodegradation steps (Jones et al., 2005; Vieno et al., 2007; Homem and Santos, 2011). This affects the water quality and drinking water supply and may constitute a long-term potential risk for the ecosystems and the human and animal health (Klavarioti et al., 2009). It has been documented the development of multi-resistant strains of microorganism by some drugs (Jarnheimer et al., 2004; Naviner et al., 2011), the effects of pharmaceuticals on the endocrine systems of fishes and invertebrates (Migliore et al., 1997) and their toxicity on algae and small invertebrates (Crane et al., 2006; Pomati et al., 2008). Research efforts are then needed for the development of powerful methods to remove drugs from waters in order to avoid their potential toxicity and other environmentally undesirable effects.

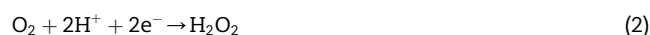
Recently, many advanced oxidation processes (AOPs) have been used to remove pharmaceutical pollutants from waters (Esplugas et al., 2007; Rosal et al., 2008; Brillas et al., 2009; Klavarioti et al., 2009; Panizza and Cerisola, 2009; Rozas et al., 2010; Homem and Santos, 2011; Sirés and Brillas, 2012). AOPs are chemical, photocatalytical and electrochemical methods with the common feature of the in situ generation of hydroxyl radical ( $\cdot\text{OH}$ ), which is the second strongest oxidant known after fluorine due to its high standard reduction potential ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V vs SHE}$ ).  $\cdot\text{OH}$  reacts non-selectively with most organics giving dehydrogenated and hydroxylated derivatives, which can in turn be mineralized, that is, transformed into  $\text{CO}_2$ , water and inorganic ions. Among these treatments, the simplest and most popular electrochemical AOP (EAOP) is electrochemical oxidation or anodic oxidation (AO) where organics contained in a contaminated solution are oxidized by direct charge transfer at the anode (M), or rather destroyed with physisorbed hydroxyl radical ( $\text{M}(\cdot\text{OH})$ ) formed as intermediate of  $\text{O}_2$  evolution from water oxidation at high current densities as follows (Marselli et al., 2003; Panizza and Cerisola, 2009; Sales et al., 2013):



Boron-doped diamond (BDD) thin-film electrodes are currently considered the most potent anodes for AO. BDD possesses technologically important properties like inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high  $\text{O}_2$ -evolution overvoltage. These characteristics enhance strongly the removal of organics with reactive BDD( $\cdot\text{OH}$ ) (Panizza and Cerisola, 2009) and allow the BDD anode to mineralize aromatic pollutants (Brillas et al., 2005; Özcan et al., 2008; Santos

et al., 2010) and byproducts such as aliphatic carboxylic acids (Cañizares et al., 2003, 2008; Garcia-Segura and Brillas, 2011), with much higher oxidation ability than traditional anodes like Pt (Sirés et al., 2006; Hammami et al., 2008; Hamza et al., 2009; Brillas et al., 2010) and  $\text{PbO}_2$  (Sirés et al., 2008).

A variant of the above EAOP, developed in our laboratory, is AO with electrogenerated  $\text{H}_2\text{O}_2$  (AO- $\text{H}_2\text{O}_2$ ) in which an undivided cell with a carbon-polytetrafluoroethylene (PTFE) gas ( $\text{O}_2$  or air) diffusion cathode is used (Flox et al., 2007; Sirés et al., 2007; Guinea et al., 2008, 2010). This electrode minimizes the possible cathodic reduction of organics because it catalyzes efficiently the two-electron reduction of injected  $\text{O}_2$  to continuously supply  $\text{H}_2\text{O}_2$  to the medium by Reaction (2). A quasi-steady content of this species remains in the solution when its electrogeneration rate becomes equal to its destruction one, mainly due to its oxidation at the anode to  $\text{O}_2$  via formation of hydroperoxyl radical ( $\text{HO}_2\cdot$ ) by Reaction (3).



Under these conditions, organic pollutants can be removed by reactive oxygen species (ROS) like  $\text{M}(\cdot\text{OH})$ ,  $\text{M}(\text{HO}_2\cdot)$  and  $\text{H}_2\text{O}_2$ , although the former is always the main oxidizing agent.

In previous work, our group has investigated the effective degradation of several aromatic drugs such as paracetamol (Brillas et al., 2005; Almeida et al., 2011), clofibrac acid (Sirés et al., 2006, 2007), chloroxylenol (Skoumal et al., 2008), salicylic acid (Guinea et al., 2008), ibuprofen (Skoumal et al., 2009), enrofloxacin (Guinea et al., 2010), diclofenac (Brillas et al., 2010) and flumequine (Garcia-Segura et al., 2012) by different EAOPs including AO and AO- $\text{H}_2\text{O}_2$  with either a Pt or BDD anode. It has been found that both anodes lead to the same kinds of oxidation products, although BDD allows reaching greater and faster mineralization. In the case of flumequine, comparative treatments in synthetic waters and a real wastewater matrix yielded similar degradation rates, indicating that natural organic matter (NOM) does not affect the oxidation power of EAOPs. To gain a better knowledge about the possible application of AO to the treatment of wastewaters containing a cocktail of drugs, more research is needed to clarify the degradation kinetics and oxidation products formed from other pharmaceutical families with more complex molecules. In this way, we have undertaken a study on the electrochemical incineration of omeprazole (5-methoxy-2-[[[4-methoxy-3,5-dimethyl-2-pyridinyl)methyl]sulfinyl]-1H-benzimidazole), which is one of the most widely prescribed gastrointestinal drugs. It acts as a proton pump inhibitor used in the treatment of dyspepsia, peptic ulcer disease, gastroesophageal reflux disease, laryngopharyngeal reflux and Zollinger–Ellison syndrome. Omeprazole has been detected in rivers at concentrations up to  $200 \text{ ng L}^{-1}$  (Valcárcel et al., 2011) and in urban wastewaters up to  $2.2 \mu\text{g L}^{-1}$  (Rosal et al., 2010; Verlicchi et al., 2012). It presents low toxicity for algae, crustaceans and fishes (Valcárcel et al., 2011; Dong et al., 2012) and is poorly photolyzed in waters (DellaGreca et al., 2006). However, its degradation by AOPs has not been previously reported, only being described a drastic reduction of its content in STP effluents using ozone (Rosal et al., 2010) and  $\text{O}_3/\text{H}_2\text{O}_2$  (Rosal et al., 2008).

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