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Electrochemical advanced oxidation for cold incineration of the pharmaceutical ranitidine: Mineralization pathway and toxicity evolution

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HIGHLIGHTS

- Ranitidine degraded by anodic oxidation and electro-Fenton using BDD, Pt and DSA anodes.
- Almost total mineralization achieved by both methods with a BDD anode.
- Detection of 11 cyclic organic intermediates with furane moiety and 6 final carboxylic acids.
- Main release of ammonium and sulfate ions, along with nitrate ion in lesser extent.
- Removal of solution toxicity determined by bioluminescence inhibition of *Vibrio fischeri*.

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ABSTRACT

Ranitidine (RNTD) is a widely prescribed histamine H_2-receptor antagonist whose unambiguous presence in water sources appointed it as an emerging pollutant. Here, the degradation of 0.1 mM of this drug in aqueous medium was studied by electrochemical advanced oxidation processes (EAOPs) like anodic oxidation with electrogenerated H_2O_2 and electro-Fenton using Pt/carbon-felt, BDD/carbon-felt and DSA-Ti/RuO_2–IrO_2/carbon-felt cells. The higher oxidation power of the electro-Fenton process using a BDD anode was demonstrated. The oxidative degradation of RNTD by the electrochemically generated $^{\cdot}OH$ radicals obeyed a pseudo-first order kinetics. The absolute rate constant for its hydroxylation reaction was $3.39 \times 10^9\ M^{-1}\ s^{-1}$ as determined by the competition kinetics method. Almost complete mineralization of the RNTN solution was reached by using a BDD anode in both anodic oxidation with electrogenerated H_2O_2 and electro-Fenton processes. Up to 11 cyclic intermediates with furan moiety were detected from the degradation of RNTD, which were afterwards oxidized to short-chain carboxylic acids before their mineralization to CO_2 and inorganic ions such as NH_4^+, NO_3^- and SO_4^{2-}. Based on identified products, a plausible reaction pathway was proposed for RNTD mineralization. Toxicity assessment by the Microtox® method revealed that some cyclic intermediates are more toxic than the parent molecule. Toxicity was quickly removed following the almost total mineralization of the treated solution. Overall results confirm the effectiveness of EAOPs for the efficient removal of RNTD and its oxidation by-products from water.

1. Introduction

Over the last years, pharmaceuticals have been receiving increasing attention as potential bioactive chemicals in the environment (Kümmerer, 2009). They are considered as emerging pollutants because they still remain unregulated or are currently undergoing a regularization process (Esplugas et al., 2007). Their presence in aquatic systems is attributable to pharmaceutical industry wastes, hospital wastes, therapeutical drugs and personal care products. They enter into natural waters due to their incomplete elimination in wastewater treatment plants since they are recalcitrant to conventional processes like biodegradation, coagu-

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lation, sorption and photodegradation (Jones et al., 2005). The presence of drugs and their metabolites affect the quality of water and constitute a potential risk of toxicity for ecosystems and living beings (Klavarioti et al., 2009). Some drugs have been classified as endocrine disrupting compounds and it is usually accepted that some of them cause long-term, irreversible changes to microorganisms genome even at low content, then having more resistance to them (Fent et al., 2006). Moreover, these pollutants often occur as complex mixtures whose toxicity has been seldom predicted (Sirés and Brillas, 2012).

Ranitidine (RNTD) is a H_2-receptor antagonist, very widely prescribed for the treatment of peptic ulcer and gastroesophageal reflux disease. By 1988 it was the largest selling prescription drug (Khetan and Collins, 2007). It is oxidized in liver (30–70%) to *N*-oxide, *S*-oxide and *N*-demethylated metabolites (Martin et al., 1981). It has been detected in European and US surface and wastewaters (Fent et al., 2006; Gros et al., 2007) and sediments (Zuccato et al., 2000). RNTD has been classified as one of the highest risk compounds by a model dealing with the effects of contaminants on human Health (Besse and Garric, 2008).

The development of clean and effective technologies for removing organic pollutants and particularly pharmaceuticals from water has been a major concern of researchers during the last decades. Among these technologies, advanced oxidation processes (AOPs) are known as effective treatment techniques for removing toxic and/or persistent organic pollutants from water (Pignatello et al., 2006; Oturan and Aaron, 2014). Several electrochemical AOPs (EAOPs) are being currently developed for water remediation because of their high oxidation/mineralization efficiency to remove organic pollutants (Brillas et al., 2009; Sirés and Brillas, 2012; Vasudevan and Oturan, 2014; Sirés et al., 2014). EAOPs are based on the in-situ electrochemical generation of hydroxyl radicals ($^{\cdot}OH$) which can non-selectively mineralize organics up to CO_2, water and inorganic ions. The characteristics of EAOPs like anodic oxidation (AO) and electro-Fenton (EF) have been thoroughly reviewed (Brillas et al., 2009; Panizza and Cerisola, 2009; Feng et al., 2013). In AO, heterogeneous $M(^{\cdot}OH)$ radical is formed at the surface of a high O_2-overpotential anode by water oxidation from reaction (1) (Rodrigo et al., 2010; Brillas and Martínez-Huitle, 2011):

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + e^- \quad (1)$$

In the case of EF, $^{\cdot}OH$ radical is produced in the bulk through Fenton's reaction (2) in which H_2O_2 is electrogenerated at a suitable cathode fed with O_2 or air by reaction (3) while a catalytic amount of Fe^{2+} ion (about 0.1–0.5 mM) is added. This ion can be cathodically regenerated from reaction (4) (Oturan, 2000; Brillas et al., 2009; Oturan et al., 2009; Özcan et al., 2009).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (2)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

The EF process has the advantage of producing oxidation reactions in the solution, whereas in AO the reactions are limited to the anode surface. However, AO with a boron-doped diamond (BDD) anode produces powerful heterogeneous $BDD(^{\cdot}OH)$. The use of a BDD anode in EF enhances strongly its oxidation/mineralization power owing to the formation of both, $BDD(^{\cdot}OH)$ and $^{\cdot}OH$ at the anode surface by reaction (1) and in the bulk by Fenton's reaction (2), respectively (Oturan et al., 2012).

Several works have reported the destruction of different drugs by AO and EF using either a BDD or Pt anode with different carbonaceous cathodes (Sirés et al., 2007a,b; Özcan et al., 2008; Panizza and Oturan, 2011; Dirany et al., 2012; Garcia-Segura et al., 2014). In contrast, very few studies have utilized dimensionally stable anodes (DSA) (Ihos et al., 2013) because although these electrodes possess high surface area and excellent mechanical and chemical resistance at high current and in strongly acidic media, they have low ability for $M(^{\cdot}OH)$ generation (Martínez-Huitle and Brillas, 2009).

The degradation of RNTD in aqueous media has been described by direct photolysis (Latch et al., 2003), heterogeneous photocatalysis (Addamo et al., 2005) and ozonation (Rivas et al., 2009). Recently, Radjenović et al. (2010) reported its complete disappearance by photo-Fenton and solar photocatalysis, but only with 55% of total organic carbon (TOC) removal. However, these works have not reported any mechanistic study because the oxidation products of RNTD from $^{\cdot}OH$ attack have not been yet identified.

This work presents a detailed study on the degradation of RNTD by AO with electrogenerated H_2O_2 (AO–H_2O_2) and EF processes using different anodes like Pt, DSA and BDD. The effect of current on drug removal, mineralization rate and mineralization current efficiency (MCE) induced by $^{\cdot}OH$ attack, as well as a toxicity assessment, was comparatively examined. Cyclic intermediates were identified by electrospray ionization-time of flight-mass spectrometry (ESI–TOF–MS), aliphatic acids were quantified by HPLC and released inorganic ions were followed by ion chromatography. Based on detected products, a plausible mineralization pathway for RNTD is proposed.

2. Experimental

2.1. Chemicals

Ranitidine hydrochloride (purity >98%) was of reagent grade from Fluka (Dresden, Germany). Anhydride sodium sulfate used as background electrolyte and heptahydrated iron (II) sulfate used as catalyst in EF were of analytical grade from Acros Organics (Geel, Belgium). All solutions were prepared with ultrapure water from a Millipore Milli-Q system (Molsheim, France) with resistivity >18 MΩ cm. Reagent grade sulfuric acid from Merck (Courbevoie, France) was used to adjust their initial pH to 3.0. All the other chemicals used were either of HPLC or analytical grade from Prolabo (Fontenay-sous-Bois, France), Fluka and Acros Organics.

2.2. Electrochemical treatments

All electrolyses were carried out in an undivided cylindrical cell containing 230 mL solutions under vigorous stirring with a magnetic bar. The anode was a cylindrical Pt mesh of 4.5 cm height and 3 cm internal diameter from Goodfellow (Lille, France) (EF-Pt process), a 25 cm^2 thin-film BDD onto a Nb substrate from Condias Gmbh (Itzehoe, Germany) (EF-BDD process) or a 25 cm^2 DSA-Ti/RuO_2–IrO_2 from Baoji Xinyu GuangJiDian Limited Liability Company (China) (EF-DSA process). The cathode was a carbon felt of 15 cm × 4 cm × 0.5 cm in dimension from Carbon-Lorraine (Paris, France). In all cases, the anode was centered in the cell and was surrounded by the cathode, which covered the inner wall of the cell. The solution was continuously saturated by O_2 at atmospheric pressure by bubbling compressed air at 1 L min^{-1} before 10 min of starting the electrolysis. The EF treatments of 0.1 mM RNTD solutions were assessed in 0.05 M Na_2SO_4 with 0.1 mM Fe^{2+} as catalyst at pH 3.0, room temperature and constant current between 100 and 500 mA provided by a HM8040 triple power supply from Hameg (Mainhausen, Germany). Comparative AO trials were made using a BDD/carbon-felt cell with H_2O_2 generation (AO–H_2O_2–BDD process) but without Fe^{2+} addition.