



Correlation between degradation pathway and toxicity of acetaminophen and its by-products by using the electro-Fenton process in aqueous media



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HIGHLIGHTS

- Coupling ecotoxicity monitoring and chemical analysis during the electro-Fenton process.
- Quantifying the toxicity of every intermediate during the mineralization of ACE.
- Establishing relationship between degradation pathway and global toxicity of the solution.

ARTICLE INFO

Article history:

Received 20 July 2016

Received in revised form

9 December 2016

Accepted 13 December 2016

Available online 21 December 2016

Handling Editor: Xiangru Zhang

Keywords:

Carbon felt

Advanced oxidation process

TOC

Mineralization

By-products

Toxicity

ABSTRACT

The evolution of the degradation by-products of an acetaminophen (ACE) solution was monitored by HPLC-UV/MS and IC in parallel with its ecotoxicity (*Vibrio fischeri* 81.9%, Microtox[®] screening tests) during electro-Fenton (EF) oxidation performed on carbon felt. The aromatic compounds 2-hydroxy-4-(N-acetyl) aminophenol, 1,4-benzoquinone, benzaldehyde and benzoic acid were identified as toxic sub-products during the first stage of the electrochemical treatment, whereas aliphatic short-chain carboxylic acids (oxalic, maleic, oxamic, formic, acetic and fumaric acids) and inorganic ions (ammonium and nitrate) were well identified as non-toxic terminal sub-products. Electrogenerated hydroxyl radicals then converted the eco-toxic and bio-refractory property of initial ACE molecule (500 mL, 1 mM) and subsequent aromatic sub-products into non-toxic compounds after 2 h of EF treatment. The toxicity of every intermediate produced during the mineralization of ACE was quantified, and a relationship was established between the degradation pathway of ACE and the global toxicity evolution of the solution. After 8 h of treatment, a total organic carbon removal of 86.9% could be reached for 0.1 mM ACE at applied current of 500 mA with 0.2 mM of Fe²⁺ used as catalyst.

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1. Introduction

Over the past few years, pharmaceutical drugs have become a severe problem for the domestic wastewater treatment (Schwarzenbach et al., 2006). Pharmaceuticals such as anti-inflammatories, analgesics, lipid regulators, antibiotics, anti-epileptics, betablockers and oestrogens are used extensively for both humans and livestock. When consumed, 10–90% of these

drugs are metabolized. A significant quantity of the active ingredients is therefore excreted, mainly through urine and faeces, and collected in urban sewer systems or discharged directly into the environment by livestock. Many studies have confirmed the presence of a large number of medicinal substances in all environmental compartments: ground and surface water (Andreozzi et al., 2003a,b; Pérez-Estrada et al., 2005), drinking water (Ternes et al., 2002), tap water (Doll and Frimmel, 2003), ocean water, sediment and soil (Halling-Sørensen et al., 1998); this indicates the inefficiency of conventional water treatment processes to remove these kinds of micro-pollutants. Even if the amount of these pharmaceuticals in aquatic media is low, usually with concentrations lower than 10 µg L⁻¹ (Ternes, 1998; Huerta-Fontela et al.,

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2011; Huerta et al., 2016), its continuous input constitutes at long term a real risk for aquatic and terrestrial organisms (Zhou et al., 2013; García-Mateos et al., 2015). Some pharmaceuticals are indeed suspected to affect the endocrine system of fishes, and available data on antibiotics indicate that they can exert toxic effects on algae and invertebrates and may favour the development of multi-drug resistant microbial strains (Zuccato et al., 2000; Balcioglu and Ötker, 2003). Among pharmaceuticals, acetaminophen (ACE) is an analgesic molecule consumed worldwide, and is usually selected by researchers as an emerging contaminant model (García-Mateos et al., 2015). ACE is also called paracetamol, and its chemical name is N-acetyl-p-aminophenol. This drug has been detected in European wastewater treatment plant (WWTP) with a concentration of $6 \mu\text{g L}^{-1}$ (Ternes, 1998), up to $10 \mu\text{g L}^{-1}$ in natural water resource in the USA (Kolpin et al., 2002) and more than $65 \mu\text{g L}^{-1}$ in the Tyne River, UK (Kabdaşlı et al., 1999; Roberts and Thomas, 2006).

Because of the toxicity and persistency of pharmaceuticals, it is necessary to develop powerful methods to ensure complete degradation of pharmaceutical pollutants as well as their potentially toxic degradation by-products. Conventional technologies that are currently used, such as activated carbon adsorption, flocculation, biological degradation, and chemical process like chlorination, have the disadvantages of being poorly efficient for non-biodegradable compounds or to transfer the pollutants into the solid phase (sludge or sorbent). Pollution is, in this case, only displaced and not solved. Advanced oxidation processes (AOPs) (Ozonation, UV/H₂O₂, electro- and photo-Fenton) can be easily incorporated in pre-existing treatment plants and were found to achieve efficient reduction of micropollutant discharge in the aquatic environment (Reungoat et al., 2010, 2012; Eggen et al., 2014; Sirés et al., 2014; Moreira et al., 2017). Because non-selective radicals such as hydroxyl radicals (OH) are generated, AOPs are considered a competitive water treatment technology for the degradation of these refractory organic micropollutants and the improvement of effluent quality from treatment plants (Gerrity et al., 2011; Giannakis et al., 2015). Several publications have highlighted the potentialities of AOPs such as UV/H₂O₂ (Frontistis et al., 2012; Lee et al., 2016); ozonation (Huber et al., 2005; Gerrity et al., 2011; Zimmermann et al., 2011; Reungoat et al., 2012; Margot et al., 2013), Fenton and photo-Fenton (Tekin et al., 2006; Kulik et al., 2008), semiconductor photocatalysis (Molinari et al., 2006; Abellán et al., 2007), and electrochemical separation and degradation technologies (Sirés and Brillas, 2012) to eliminate biorefractory pharmaceuticals. Recently, textural modification of carbon felt (Le et al., 2016) and graphene deposition on graphite substrates (Le et al., 2015a,b) have shown a great potential to enhance mineralization of the azo dye acid Orange 7 and ACE by the electro-Fenton (EF) process. Derived Fenton processes have also already proved to be efficient methods to degrade ACE from water: combined EF and photo-Fenton using a double cathode electrochemical cell (De Luna et al., 2012), coupling adsorption and photo-Fenton using nano-zeolites and cobalt ferrite nanoparticles (Irani et al., 2015), bio-electrochemical degradation in a microbial fuel cell-Fenton system (Zhang et al., 2015), or other methods relevant to the photo-Fenton process (Trovó et al., 2008; Trovo et al., 2012; Cabrera Reina et al., 2015; Rad et al., 2015). As a more detailed example, Sires et al. could totally mineralize ACE in CO₂ after 6 h of treatment by using the catalytic action of Fe²⁺, Cu²⁺ and UVA light to generate hydroxyl radicals. During the electrolysis, several by-products were detected, such as hydroquinone, p-benzoquinone, or short chain carboxylic acids (Sirés et al., 2006). Using the solar photoelectro-Fenton (SPEF) method, ACE was efficiently mineralized in the study of Lucio Cesar Almeida et al. (2011). In particular, after 120 min of electrolysis, total organic carbon (TOC) removal

attained was 75% with an energy cost of 93 kWhkg^{-1} TOC (7.0 kWhm^{-3}) and a mineralization current efficiency of 71%. In addition, many by-products including aromatic compounds as well as carboxylic acids were adequately detected, such as hydroquinone, p-benzoquinone, 1,2,4-trihydroxybenzene, 2,5-dihydroxy-p-benzoquinone and tetrahydroxy-p-benzoquinone, maleic, fumaric, succinic, lactic, oxalic, formic and oxamic acids. In addition, the combination of adsorption and photo-Fenton method by Irani et al. could lead to 99.80% of paracetamol removal in 30 min (Irani et al., 2015).

Depending on the AOP technique used, several degradation pathways of ACE have been identified and already published (Andreozzi et al., 2003a,b; Brillas et al., 2005; Skoumal et al., 2006; Yang et al., 2008a). All authors observed the formation of reactive by-products due to partial oxidation of the initial molecule and reaction with matrix components (Von Gunten, 2003). It is important to track the intermediates generated through degradation reactions and to know their eco-toxicity, with the view to verify the safety of the water treatment process. Unfortunately, very few works were aimed at combining analytical chemistry to individual and global toxicity measurement of both products and solution during AOP treatment (Hamdi El Najjar et al., 2014) as presented in this study.

Research at laboratory and pilot scale clearly demonstrated that AOPs can be applied to improve the quality of effluents from municipal and industrial WWTPs by attenuating trace organic contaminants (micropollutants) (Gerrity et al., 2011; Giannakis et al., 2015). However, a potential disadvantage of these processes is the formation of unknown reactive by-products due to partial oxidation of the targeted compounds and reaction with matrix components (Von Gunten, 2003). Thus, the final toxicity of treated effluent should be determined together with the quantity of targeted compounds in terms of the detection limits of the analytical protocols. In this study, the EF reaction was applied to ACE solution. ACE and its by-products generated during the degradation were monitored by HPLC-UV/MS, IC and TOC analysis. In addition, acute toxicity of the ACE solution under EF treatment as well as individual and mixed intermediate standards were assessed through Microtox[®] toxicity test with *Vibrio Fischeri* marine bacteria. Through this study, the relationship between the ACE degradation pathway, the individual by-product toxicity and the global toxicity of the solution could be newly and clearly established, thus providing a more comprehensive understanding and safety control of the mineralization process of ACE by the EF process.

2. Experimental

2.1. Materials

ACE (acetaminophen: paracetamol), sodium sulphate (anhydrous, 99.0–100.5%), sodium hydroxide (99%), sulphuric acid (95–97%), iron (II) sulphate hepta-hydrate (99%), benzoquinone, benzaldehyde, benzoic acid, oxalic acid, maleic acid, oxamic acid, formic acid, fumaric acid and acetic acid were obtained from Sigma-Aldrich, USA. Bacterial strain of *Vibrio fischeri* NRRL B-11177 involved in toxicity tests was obtained from Hach Lange GmbH, Germany. Osmotic adjusting solution (MilliQ water with 22% NaCl) and diluent (MilliQ water with 2% NaCl) were used for the preparation of the bacterial solution. The carbon felt was purchased from A Johnson Matthey Co., Germany. TOC standard of 1000 mg L^{-1} (Sigma-Aldrich, USA) and sodium hydrogen carbonate ($\geq 99.5\%$, ACS, Karlsruhe, Germany) were used for TOC and inorganic carbon (IC) calibration curves assessments, respectively.

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