



## Improvement of the activated sludge treatment by its combination with electro Fenton for the mineralization of sulfamethazine



Dorsaf Mansour<sup>a,c,d</sup>, Florence Fourcade<sup>a,e,\*</sup>, Samuel Huguet<sup>b,e</sup>, Isabelle Soutrel<sup>b,e</sup>, Nizar Bellakhal<sup>c,d</sup>, Mohamed Dachraoui<sup>c,d</sup>, Didier Hauchard<sup>b,e</sup>, Abdeltif Amrane<sup>a,e</sup>

<sup>a</sup> Université de Rennes 1, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

<sup>b</sup> Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

<sup>c</sup> Laboratoire de Chimie Analytique et Electrochimie, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Tunis, Tunisia

<sup>d</sup> Institut National des Sciences Appliquées et de Technologie, B.P. N° 676, 1080 Tunis Cedex, Tunisia

<sup>e</sup> Université Européenne de Bretagne, 5 Boulevard Laënnec, 35000, France

### ARTICLE INFO

#### Article history:

Received 14 October 2013

Received in revised form

27 November 2013

Accepted 29 November 2013

Available online 18 December 2013

#### Keywords:

Activated sludge

Combined process

Degradation pathway

Drug removal

Electro-Fenton

Sulfamethazine

### ABSTRACT

A combined process coupling an electro-Fenton pretreatment and a biological degradation in order to mineralize sulfamethazine (SMT) was investigated. The electro-Fenton pretreatment of SMT was first examined and the intermediates products were identified for an initial SMT amount of 0.36 mM, after 1 h electrolysis at pH 3, 18 °C, 200 mA. 94.2% SMT was degraded but the level of mineralization remained low (6.5%), ensuring significant residual organic content for a subsequent biological treatment. Two possible degradation reaction pathways involving all the identified and quantified intermediates are proposed. In a second part, biological treatments with fresh activated sludge were performed to complete the mineralization of the electrolyzed solution of SMT, showing an increase of the mineralization yield with time duration of the pretreatment. For an initial SMT concentration of 0.2 mM, a ferrous ions concentration of 0.5 mM, at pH 3, 18 °C and 500 mA, the mineralization yield during the biological treatment increased as follows: 61.4, 78.8 and 93.9% for 0.5, 1 and 4 h pretreatment, confirming the relevance of the proposed combined process.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

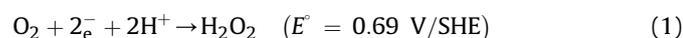
Veterinary antibiotics are largely used for three purposes in animals: to treat sick animals, to prevent infection in animals and as growth promoters to improve feed utilization and production (Barton, 2000). However, these antibiotics can reach the environment when they are excreted by animals through urine and feces and thereafter applied to soils as an organic fertilizer. Since these antibiotics are often found to be recalcitrant after excretion (Kwon-Rae et al., 2011), several researches (Burkhardt et al., 2005; Kay et al., 2005) have proved that these compounds can spread to the groundwater and the surface water by infiltration and runoff, respectively. If these compounds are not eliminated, it can threaten the environment with the potential of adversely affecting aquatic and terrestrial organisms. Consequently and to avoid such

contamination, their removal from wastewater appears to be an important current issue.

A wide variety of processes has been therefore studied in order to remove such pollution. Among destructive processes, advanced oxidation processes (AOP) have received great interest in the recent years (Brillas et al., 2009; Uslu and Balcioglu, 2009; Pérez-Moya et al., 2010, 2011; Saghafiniaa et al., 2011; Batista and Nogueira, 2012; Garcia-Segura et al., 2012; Nasuhoglu et al., 2012; Sirés and Brillas, 2012; Wei et al., 2012). These processes are based on the generation of very reactive, non-selective powerful oxidizing agents such as hydroxyl radicals  $\cdot\text{OH}$  in solution (Ghoneim et al., 2011). Concerning the electro-Fenton process (Jiang and Zhang, 2007; Oturan and Brillas, 2007; Peralta-Hernandez et al., 2009; Muhammad et al., 2010),  $\text{H}_2\text{O}_2$  is produced in an acidic medium from the electrochemical reduction of  $\text{O}_2$  at the cathode (reaction 1). The generated  $\text{H}_2\text{O}_2$  reacts with the added  $\text{Fe}^{2+}$  ions to produce hydroxyl radicals  $\cdot\text{OH}$  and  $\text{Fe}^{3+}$  ions from the Fenton's reaction (reaction 2), which is favored by the catalytic action of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  system, mainly from the regeneration of  $\text{Fe}^{2+}$  by the cathodic reduction of  $\text{Fe}^{3+}$  (reaction 3) (Garcia-Segura et al., 2012). Moreover, the method and the involved reactor are easy to handle and to use.

\* Corresponding author. Université de Rennes 1, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France. Tel.: +33 2 23 23 81 58; fax: +33 2 23 23 81 20.

E-mail address: [Florence.fourcade@univ-rennes1.fr](mailto:Florence.fourcade@univ-rennes1.fr) (F. Fourcade).



Due to a relatively high operational cost of AOP, potential advantage of the strategy of combining chemical and biological processes to treat contaminants in wastewater was previously suggested (Scott and Ollis, 1995, 1997; Oller et al., 2011). AOP constitute a pretreatment in order to increase the biodegradability of the recalcitrant compounds, leading to the formation of non toxic by-products, more readily metabolizable by microorganisms (De La Rochebrochard D'Auzay et al., 2007; Poyatos et al., 2010).

For this purpose, integrated processes including either UV/H<sub>2</sub>O<sub>2</sub> or UV/O<sub>3</sub> (Ledakowicz et al., 2001), photo-Fenton (Farré et al., 2008), photo-Fenton UV/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> (Dominguez et al., 2005) photocatalysis (Parra et al., 2002) or electro-Fenton (Lin and Chang, 2000; Khoufi et al., 2006) followed by biological treatment have been proposed to treat wastewater containing recalcitrant compounds.

The implementation of a direct electrochemical pretreatment and a biological process has been performed in the lab for the treatment of two pesticides, phosmet and 2,4-D, leading to 97% and 85% mineralization, respectively (Alonso salles et al., 2010; Fontmorin et al., 2012).

The feasibility of an electro-Fenton process for the pretreatment of synthetic aqueous solutions of a veterinary antibiotic, sulfamethazine, was previously verified (Mansour et al., 2012). To complete this previous work, the relevance of the combined process for sulfamethazine treatment should be assessed. For this purpose, an aerobic biological treatment was carried out using activated sludge obtained from a local wastewater treatment plant. In parallel, identification and quantification of by products has been carried out in order to propose mechanisms of electro-Fenton degradation of sulfamethazine.

Compounds structurally close to sulfamethazine have been studied using electro-Fenton as degradation process. Wang et al. (2011) have suggested a degradation mechanism for sulfamethoxazole thanks to the research of by-products by LC–MS, but no quantification nor naming have been made. Dirany et al. (2012) have followed the degradation of sulfachloropyridazine with a combination of electro-Fenton and electro-oxidation using a bore doped diamond electrode (BDD). A mechanistic pathway was deduced from the identification of by products and the evolution of the toxicity by means of a test based on *Vibrio fischeri* has been followed. However, no biodegradation has been carried out on the electrolyzed solutions in these two studies.

## 2. Materials and methods

### 2.1. Chemicals

Sufamethazine (C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>S, 4-amino-N-(4,6-dimethyl-2-pyrimidinyl)benzene-sulfonamide – purity 99%) was purchased from Sigma Aldrich (Saint Quentin Fallavier, France). FeSO<sub>4</sub>·7H<sub>2</sub>O (purity 99%) and Na<sub>2</sub>SO<sub>4</sub> (purity 99%) used as a catalyst source and inert supporting electrolyte respectively, were from Acros Organics (Thermo Fisher Scientific, Illkirch, France). Acetonitrile (purity 99.9%) (HPLC grade) was also obtained from Sigma Aldrich. The initial pH of solutions was adjusted to 3 using H<sub>2</sub>SO<sub>4</sub>, the optimal pH value for electro-Fenton process (Diagne et al., 2007), using analytical grade sulfuric acid from Acros. All solutions were

prepared with ultra-pure water and all the other chemicals used for analysis were purchased from Acros Organics and Sigma Aldrich.

### 2.2. Electrochemical reactor and procedures

The degradation of the organic matter by the electro-Fenton process was carried out in duplicate in an undivided cylindrical glass cell equipped with two electrodes; the working volume was 1 L. The dimensions of the carbon felt piece placed on the inner wall of the cell (Le Carbone Lorraine RVG 4000 – Mersen, Paris La Défense, France), which was used as the cathode, were 260 mm × 80 mm. Its specific area, measured by the BET method was 0.7 m<sup>2</sup> g<sup>-1</sup>, its thickness was 12 mm, its density was 0.088 g cm<sup>-3</sup> and its carbon yield was 99.9%. The anode was a cylindrical platinum electrode (50 mm × 20 mm) located in the center of the electrochemical reactor to have a good potential distribution. Prior to electrolysis, compressed air was bubbled for 10 min through the solution at a flow rate of 450 cm<sup>3</sup> min<sup>-1</sup> to saturate the aqueous solution.

The pH of the solutions was adjusted to 3 by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). A catalytic quantity of FeSO<sub>4</sub>·7H<sub>2</sub>O (0.1 mM) was introduced into the cell just before the beginning of the electrolysis. The electrodes were connected to a DC power supply (Metrix, model AX 322, Chauvin Arnoux Group, Paris, France) operating in galvanostatic mode to control the current intensity at a value of 200 mA. The ionic strength was maintained constant by the addition of 0.05 M Na<sub>2</sub>SO<sub>4</sub>. The electrolytic solution was in circulation with the help of a peristaltic pump (flow rate of 2 L min<sup>-1</sup>). The temperature was maintained at 18 °C and the initial sulfamethazine concentration was 0.36 mM.

### 2.3. Analytical procedures

#### 2.3.1. LC–MS/MS method

2.3.1.1. *Ultra-pressure liquid chromatography.* The devices used are detailed in previous works (Gervais et al., 2008; Fontmorin et al., 2012). The analytes were separated by a Waters Acquity UPLC system (Waters, Manchester, UK) consisting of an Acquity UPLC binary solvent manager, an Acquity UPLC sample manager and an Acquity UPLC column heater equipped with a Waters Acquity UPLC BEH C18 column (2.1 mm × 100 mm, 1.7 μm particle size) (Milford, MA, USA). Isocratic LC elution was performed with 0.1% formic acid in acetonitrile as mobile phase A and an ultrapure water 9:1 acetonitrile (v/v) mix, with added 0.1% (v/v) of formic acid as mobile phase B. Separation of the analytes on the column was performed at 0.4 mL min<sup>-1</sup> flow rate.

2.3.1.2. *Tandem mass spectrometry.* A Quattro Premier triple-quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ionization source was used for degradation products detection. MS/MS detection was performed in positive mode. Source conditions were capillary voltage 3 kV, source temperature 120 °C and desolvation temperature 350 °C. The cone and desolvation gas flows (N<sub>2</sub>) were 75 and 750 L h<sup>-1</sup>, respectively. High-purity argon (99.99%, Air Liquid, Paris, France) was used as collision gas. The analytical device was controlled by Micromass MassLynx 4.1 software.

#### 2.3.2. Ion chromatography

Generated carboxylic acids were identified by DIONEX DX120 ion chromatography equipped with a conductivity detector, using an anion-exchange column AS18 (4 × 250 mm) as the stationary phase, and a solution of Na<sub>2</sub>CO<sub>3</sub> (9 mM) in water as the mobile phase. The flow rate was set at 1 mL min<sup>-1</sup> (Yahiat et al., 2011).

Download English Version:

<https://daneshyari.com/en/article/4364909>

Download Persian Version:

<https://daneshyari.com/article/4364909>

[Daneshyari.com](https://daneshyari.com)