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Flow electrolysis on high surface electrode for biodegradability enhancement of sulfamethazine solutions

I. Saidi [a,c,d], I. Soutrel [b,d], F. Fourcade [a,b,d], A. Amrane [a,b,d,*], D. Floner [a,d], N. Bellakhal [c], F. Geneste [a,d,*]

[a] Institut des Sciences Chimiques de Rennes, Université de Rennes 1, UMR-CNRS 6226, Campus de Beaulieu, 35042 Rennes Cedex, France
[b] Institut des Sciences Chimiques de Rennes, Ecole Nationale Supérieure de Chimie de Rennes, UMR-CNRS 6226, Avenue du Général Leclerc, CS 50837, 35042 Renne Cedex 7, France
[c] Laboratoire de recherche de Catalyse d'Electrochimie de Nanomatériaux et leurs applications et de didactique CENAD, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P.N°676, 1080 Tunis Cedex, Tunisie
[d] Université Européenne de Bretagne, 35000 Rennes, France

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ABSTRACT

The main objective of this study was to examine the feasibility of coupling an electrochemical process with a biological treatment for the degradation of sulfamethazine, a biorecalcitrant antibiotic. The electrochemical behavior of sulfamethazine was examined by cyclic voltammetry, showing an electroactivity in oxidation. The pre-treatment was carried out using an electrochemical flow cell involving a graphite felt electrode of high specific area. After a single pass through the cell, the analysis of the electrolyzed solution showed a promising trend in view of the proposed combined process, namely a high degradation of the target compound (more than 90%) while the mineralization level remained low (it did not exceed 20%). The optimization of the operating conditions, viz. flow rate and applied potential, allowed to improve the biodegradability of sulfamethazine solutions. Indeed, under optimal conditions, the biodegradability based on the BOD_5 on COD ratio measurement was improved from 0.08 to 0.58, namely above the threshold limit value (0.4).

1. Introduction

Pharmaceuticals have been widely used as human and veterinary medicinal compounds. Due to their intensive consumption worldwide, their occurrence in aquatic environment (typically in the range of ng to μg/L) has been observed [1–4]. The assessment of the impact to human health from environmental exposure has been the subject of many investigations [5–9]. Even if the amount of pharmaceuticals in aquatic environment is low, indirect effects such as chronic exposure, mixture effects and development of antibiotic resistant bacteria may constitute a risk for aquatic and terrestrial organisms. Thus, several efforts are being made to find out ways of inactivating or eliminating this class of substances in surface or wastewater.

Pharmaceuticals can be removed by physical techniques, such as membrane technologies [10,11] or adsorption processes [12,13]. For example, techniques involving activated carbon [14], reverse osmosis [15], coagulation [16] and flocculation [17] have been applied. However, these techniques are not destructive and the pollutant is only transferred to another phase [18,19]. Consequently, expensive regeneration and post treatment processes are required.

Oxidation processes have also proven their efficiency in the treatment of toxic organic pollutants and biorecalcitrant compounds. Among them, Advanced Oxidation Processes (AOP) have been widely used, since they involve hydroxyl radicals (OH·), which are very reactive and can attack most of the organic molecules [20,21]. Degradation of pharmaceuticals have been reported by oxidation treatments such as ozonation processes [22] and by AOP processes, such as anodic oxidation on Boron Doped Diamond electrode [20,23,24], electro-Fenton [20,23], photo-Fenton [25] and photocatalysis [26]. Although complete mineralization of the pollutant can be achieved by this method, they are expensive and not selective.

Even if biological treatment processes are economical, they can be ineffective for the degradation of recalcitrant compounds such as pharmaceuticals [27,28]. The use of integrated processes, such as the coupling of AOP and biological treatment is therefore an interesting alternative to degrade biorecalcitrant compounds at reduced operating costs [18,19,27–30]. The pre-treatment is carried out to increase the biodegradability of the effluent and to reduce its toxicity, which lets expect a complete mineralization during the subsequent biological treatment.

Direct electrochemical oxidation/reduction of recalcitrant pollutants has also been recently reported as a possible pre-treatment

* Corresponding authors. Address: Institut des Sciences Chimiques de Rennes, Université de Rennes 1, UMR-CNRS 6226, Campus de Beaulieu, 35042 Rennes Cedex, France. Tel.: +33 02 23 23 59 65; fax: +33 02 23 23 59 67.
E-mail addresses: Abdeltif.Amrane@univ-rennes1.fr (A. Amrane), Florence.Geneste@univ-rennes1.fr (F. Geneste).

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before a biological mineralization. This method consists in an electrochemical reaction on electroactive functional groups that are susceptible to be responsible of the non-biodegradability of the molecule. Thus, mild degradation of recalcitrant electroactive compounds, reducing their toxicity and enhancing their biodegradability can be achieved without the intervention of highly reactive hydroxyl radicals. The effectiveness of the method has been demonstrated for recalcitrant molecules such as phosmet an organophosphorous insecticide [31,32], a chlorinated phenoxy herbicide, 2, 4-dichlorophenoxyacetic acid [33,34], and an antibiotic, tetracycline [35].

Sulfamethazine (STM) (Fig. 1) is an antibiotic that belongs to the pharmaceutically important group of heterocyclic sulfonamides. It is widely used in medicine and veterinary practice as antibacterial drug in pharmaceutical preparations [26]. Its structure is presented in Fig. 1. Degradation of sulfamethazine has been studied through different methods. However, all studies deals with Advanced Oxidation Processes, such as photo-Fenton [25] and photo-catalysis with TiO_2 and ZnO as catalysts [26]. A recent study has also shown the efficacy of an integrated process coupling electro-fenton and biological treatment for sulfamethazine removal [27].

In this work, the feasibility of coupling a direct electrochemical process with a biological treatment to degrade sulfamethazine was examined. The pre-treatment was achieved in an electrochemical flow cell using a graphite felt electrode of high specific surface. Such an electrochemical system presents the advantages to transform large amounts of products in a relatively short reaction time. It can be easily automated and therefore adaptable to industry.

The influence of various parameters, such as the flow rate and the applied potential, on the degradation of the molecule and the biodegradability of by-products was investigated. These latter were also identified by UPLC-MS/MS.

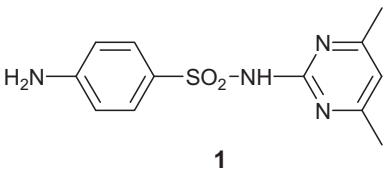
2. Materials and methods

2.1. Chemicals and materials

Sulfamethazine (purity 99%) was obtained from Alfa Aesar (Schiltigheim, France). Inert supporting electrolyte Na_2SO_4 (purity 99%) was purchased from Carlo Erba Reactif-SDS Acetonitrile (purity 99.9%) was HPLC grade obtained from Sigma–Aldrich. Graphite felt (RVG 4000) was supplied by Mersen (France). Its specific area measured by the BET method, its volume density and its carbon content were 0.7 $m^2\ g^{-1}$, 0.088 g cm^{-3} and 99.9%, respectively.

2.2. Materials for the electrochemical pre-treatment

Electrochemical pre-treatment, in continuous system, was performed in a home-made flow cell [33]. Two interconnected PAPYEX carbon papers supplied by Mersen (France) were used as counter-electrodes (85 mm × 85 mm) and the compartments were separated by cationic exchange membranes (Ionac 3470 – Lanxess SAS, Courbevoie, France). The reference electrode (Saturated Calomel Electrode – SCE) was positioned in the middle of the graphite felt (48 mm diameter and 12 mm width) and the potential control was performed using a potentiostat. To ensure a good homogeneity of the potential distribution in the three dimensional working electrode, the felt was located between the two counter-electrodes [36]. The cell was thoroughly rinsed with distilled water before and after each experiment. The solution (50 mg L^{-1} sulfamethazine in 0.1 M Na_2SO_4) percolated the porous electrode at various flow rates monitored by a Gilson minipuls 2 peristaltic pump (Middleton, WI, USA).



1

Fig. 1. Chemical structure of sulfamethazine.

2.3. Analytical procedure

2.3.1. Electrochemical analysis

Electrochemical analysis of sulfamethazine and electrolyzed solutions were performed using a conventional three-electrode cell with a glassy carbon electrode (7 mm^2) as the working electrode and a platinum wire as the counter electrode. All potentials were measured with respect to a saturated calomel electrode (SCE) located near the working electrode. Experiments were performed at room temperature under nitrogen atmosphere to avoid dissolved oxygen. Voltammograms were obtained by cyclic voltammetry using a versaSTAT3 AMETEK Model (Princeton Applied Research) potentiostat/galvanostat. Before each experiment, the glassy carbon electrode was thoroughly polished with Struers waterproof silicon carbide paper.

2.3.2. High Performance Liquid Chromatography (HPLC)

The residual sulfamethazine concentration was determined by HPLC using a Waters 996 system equipped with waters 996 PDA (Photodiode Array Detector) and Waters 600 LCD Pump. The separation was achieved on a Waters C-18 (5 μm; 4.6 × 250 mm) reversed-phase and the mobile phase consisted of a mixture of acetonitrile/ultra-pure water (35/65, v/v) delivered at a flow rate of 1 mL/min. Detection of sulfamethazine was carried out at 268 nm and the retention time was approximately 5 min.

2.3.3. Liquid chromatography–mass spectrometry (UPLC-MS/MS)

2.3.3.1. Ultra-pressure liquid chromatography. The devices used are detailed in a previous work [32]. The analytes were separated by a Waters Acquity UPLC system (Waters Corporation, Milford, MA, USA) 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)) maintained at 45 °C. Isocratic LC elution was performed with 0.1% formic acid in acetonitrile as mobile phase A and an ultrapure water 9.5:0.5 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 with a mobile phase consisting of a mixture of phase A/phase B (5/95, v/v) delivered at a flow rate of 0.4 mL min^{-1}.

2.3.3.2. Tandem mass spectrometry. The separated compounds were detected with a Waters Micromass Quattro Premier (Waters Corporation, Manchester, UK) triple quadrupole mass spectrometer. It was operated with an electrospray source in positive ionization mode with a cone potential of 40 V. The ionization source conditions were: capillary voltage of 3.0 kV, source temperature of 120 °C and desolvation temperature of 350 °C. The cone and desolvation gas flows were 50 L h^{-1} and 750 L h^{-1}, respectively; they were obtained from an in-house nitrogen source. High-purity argon (99.99%, Air Liquid, Paris, France) was used as collision gas and was regulated at 0.1 mL min^{-1}. Analyses were performed in full scan and daughter scan modes. Spectra were acquired between 50 and 300 m/z and the data were treated with Micromass MassLynx 4.1 software.