



Electrochemical degradation of sulfonamides at BDD electrode: Kinetics, reaction pathway and eco-toxicity evaluation

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HIGHLIGHTS

- SNs were electrochemically oxidized at BDD in one compartment reactor.
- The efficiency of SN degradation was the highest in effluents from municipal WWTP.
- The electro-degradation SNs based on oxidation but reduction was also possible.
- Electrochemical oxidation of SNs led in some cases to mixtures toxic to *L. minor*.

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ABSTRACT

The investigation dealt with electrochemical oxidation of five sulfonamides (SNs): sulfadiazine (SDZ), sulfathiazole (STZ), sulfamerazine (SMR), sulfamethazine (SMN) and sulfadimethoxine (SDM) in aqueous solution at boron-doped diamond (BDD) electrode. All studied sulfonamides were degraded according to a pseudo first order kinetics. The structure of SNs had no significant effect on the values of pseudo first order rate constants. Increased degradation efficiency was observed in higher temperature and in acidic pH. Due to the presence of chlorine and nitrate SNs were more effectively oxidized from municipal wastewater treatment plant (WWTP) effluents than from pure supporting electrolyte Na₂SO₄. The intermediates identified by LC–MS and GC–MS analysis suggested that the hydroxyl radicals attack mainly the S–N bond, but also the aromatic ring systems (aniline, pyrimidine or triazole) of SNs. Finally, the toxicity of the SNs solutions and effluents after electrochemical treatment was assessed through the measurement of growth inhibition of green algae (*Scenedesmus vacuolatus*) and duckweed (*Lemna minor*). Toxicity of SMR, STZ, SMN solutions before and after electrochemical oxidation and SDM solution after the process in *L. minor* test was observed. No significant toxicity of studied SNs was observed in algae test.

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1. Introduction

One of the most popular group of antibiotics, which are mainly used in veterinary medicine, are sulfonamides (SNs) [1]. Their production and consumption have been steadily increasing [2]. In the USA 16,000 tons of antibiotics, including 2.3% SNs, are consumed per year. In Europe, this value ranges from 11% to 23% of the total production of antibiotics [3]. This means that every year more than 20,000 tons of these pharmaceuticals are introduced into the biosphere [2,4].

SNs are metabolized incompletely; 75% of sulfamerazine (SMR) is excreted from the body in its parent form [5]. All forms of pharmaceuticals are discharged to wastewater, where they are partially removed by conventional wastewater treatment [6,7]. The average degree of SNs removal by activated sludge was found to be 24% [2]. For this reason, SNs are regularly detected in different environment components [2,8–10]. Although the amount of pharmaceuticals in the aquatic environment is relatively low (ng L⁻¹–μg L⁻¹), its high biological activity, even in trace amounts, could cause significant changes in the biosphere [2,4,11,12]. Additionally a highly toxic effect of SNs on green algae and green plant *Lemna minor* was observed [13–16]. Therefore, pharmaceuticals have been recently classified as particularly dangerous pollutants for the environment [2].

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An effective elimination of SNs from wastewater is a very important stage in preventing water environment pollution. Among all technologies advanced oxidation processes (AOP) are highly effective alternatives to traditional water treatment processes due to degrading toxic and poorly biodegradable organic pollutants [6,17–19]. In recent years an increased interest of electrochemical AOPs (EAOPs) was observed, which is due to their high energy efficiency, versatility and safety, because of the mild conditions of the process and amenability of automation [20,21]. Among all EAOPs the most popular is anodic oxidation of pharmaceuticals [22,23] at boron-doped diamond (BDD) electrodes. BDD is the best known material for electro-oxidation because of its unique properties such as inert surface with low adsorption, high O_2 evolution overvoltage and remarkable corrosion stability, even in strongly acid media [24–27]. BDD possesses much higher oxidation power than common anodes like Pt [8,17], SnO_2 and PbO_2 [13,18] and it is powerful enough to mineralize aromatic compounds like dyes, ionic liquids, pesticides and drugs [26–39].

Recently, EAOPs have been successfully used in SNs removal from water, and different operating conditions of these processes were studied. It was found that the decomposition of sulfamethazine (SMN) in acid conditions, was more effective than oxidation in neutral medium [36]. In contrast to this, natural pH was the most efficient in the direct SMR oxidation [39].

The influence of a reactor construction on kinetics of SMN decay was also studied. The results showed, that oxidation power was greater in the divided for anode and cathode spaces reactor, than in the undivided one, as a result of higher concentration of reactive hydroxyl radicals at the BDD anode space [36]. The filter-press electrochemical reactor was investigated for degradation of sulfamethoxazole (SMX) simultaneously with trimethoprim (TMP). Both antibiotics were virtually all degraded and 90% of both COD and TOC were reduced at the end of only 3 h electrolysis. Although, during the electrolysis, p-benzoquinone was detected as the intermediate, it was completely consumed by the end of the process [38].

For SMX removal, the electro-Fenton process using BDD anode, where H_2O_2 were simultaneously electro-generated at the cathode, was utilized. At low current, the direct oxidation of the drug was predominant; while at high current, the antibiotic was preeminently degraded in the bulk following pseudo first order kinetics [38].

SMX was also used as a model substrate for electrochemical oxidation study at a BDD anode in the presence of chloride ions. In the absence of these ions, oxidation of SMX involves mineralization that is initiated by the attack of anode-derived hydroxyl radicals. The rate of disappearance of SMX increased upon the addition of chloride ions, but without inhibiting mineralization in the early stages of oxidation. However, persistent chlorinated by-products were formed in the presence of chloride ions, indicating that chlorides are significant detriments to the success of electrochemical oxidation [37].

As electrochemical treatment of effluents containing antibiotics is quite recent, it has not been well explored. Only a few papers have addressed the electrochemical treatment at BDD electrode of single SNs (mainly SMX, SMT, SMR and sulfachloropyridazine (SCP)) focusing on kinetics and presenting degradation products [33–39]. The detailed study of SN structure effect on electrochemical removal efficiency and, what is more important, the evaluation of the toxicity of effluents from electrochemical process on plants have not yet been discussed. In this paper, a detailed study of EAO treatment of five most commonly found or detected in the highest concentration in environment, SNs: sulfadiazine (SDZ), sulfathiazole (STZ), SMR, SMN and sulfadimethoxine (SDM) solutions using a BDD is presented. In order to study oxidation of SNs efficiency in real conditions experiments were carried out in the mixture of SNs

in water solution and in effluent from Gdańsk municipal wastewater treatment plant (WWTP) in Poland. The influence of pH on the temperature, and current density was investigated. The kinetics of SNs decay were followed by a reversed-phase high-performance liquid chromatography (HPLC). Aromatic intermediates were identified by two techniques: gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS). From the detected intermediates, a reaction sequence for SNs decomposition by EAOP at BDD was proposed. Furthermore, the toxicity of SNs solutions after electrochemical oxidation for duckweed *L. minor* and green algae *Scenedesmus vacuolatus* were discussed.

2. Experimental

2.1. Materials

Standards of SDZ, STZ, SMR, SMN and SDM were purchased from Sigma–Aldrich (Steinheim, Germany). Methanol (MeOH) and acetonitrile (ACN) were both HPLC grade and sodium sulfate, sodium chloride, methylene chloride, ammonium acetate, acid acetate, potassium phosphate, sodium nitrate and sodium hydroxide were obtained from POCH S.A. (Gliwice, Poland). Trifluoroacetic acid 99% (TFA) and salts used for the culturing media were purchased from Sigma–Aldrich (Steinheim, Germany).

The effluent was collected from mechanical–biological wastewater treatment plant (WWTP) “Wschod” in Gdansk Poland (Appendix Table S1).

2.2. Electrochemical experiments

Cyclic voltammetry (CV) was carried out in a typical three-electrode system on a potentiostat/galvanostat PGSTAT-30 Autolab. A Si/BDD electrode of the surface area 10 cm^2 (Adamant Technologies, 500 ppm of boron) was used as the working electrode, an Ag/AgCl/0.1 M KCl electrode as the reference electrode and stainless steel as the counter electrode. The concentrations of SNs in 6.1 g L^{-1} Na_2SO_4 supporting electrolyte (SE) were: 10 mg L^{-1} , 50 mg L^{-1} , 100 mg L^{-1} and 200 mg L^{-1} . All measurements were performed at room temperature ($25 \pm 2^\circ\text{C}$) in a thermostatic reactor ($V = 100\text{ mL}$). CV was reported using a scan rate of 100 mV s^{-1} .

The electrochemical decomposition experiments were carried out in an undivided electrolytic cell ($V = 100\text{ mL}$) with magnetic stirring and thermostatic (Thermostat Julabol, GmbH, Germany). The cell contained three electrodes as it was described above. The distance between the electrodes in all experiments was 1.0 cm. The solutions and mixtures of SNs were prepared in SE (Na_2SO_4 , 6.1 g L^{-1}) and in effluent from WWTP (Table S1). The effect of operating parameters such as: pH (from 2.0 to 7.4), temperature (from 25 to 60°C), and current density (from 0.05 to 15 mA cm^{-2}) on electrochemical oxidation efficiency was studied in 50 mg L^{-1} SMR solution and in the mixture of five SNs (each compound in 50 mg L^{-1}). The influence of effluent from WWTP and the presence of inorganic ions – NO_3^- (8 mg L^{-1}), PO_4^{3-} (0.31 mg L^{-1}) and Cl^- (160 mg L^{-1}) – was also investigated. All experiments were repeated twice. The oxidation of SNs was monitored by HPLC for 3 h. The intermediates were identified by GC–MS and LC–MS in the mixture after electrochemical oxidation.

2.3. Instrumental analysis

Concentration of the selected antibiotics was determined by a HPLC with UV detector (Perkin Elmer, Series 200) equipped with a Phenomenex Gemini-NX C-18 column ($150\text{ mm} \times 4.6\text{ mm}$, $5\text{ }\mu\text{m}$). Optimization conditions of HPLC–UV method were described by Białk-Bielińska et al. [40] (Table S2 in Appendix).

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