

Performance and Kinetic-Mechanistic Aspects in the Electrochemical Degradation of Sulfadiazine on Boron-Doped Diamond Electrode

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O desempenho eletroquímico de eletrodos de diamante dopado com boro (BDD) na degradação eletroquímica de efluentes contendo sulfadiazina (SDZ) usando um reator filtro-prensa é apresentado e discutido. A eletrooxidação da SDZ (volume de 0,5 L, com uma concentração inicial de 250 mg L⁻¹) obtida sob condições otimizadas (densidade de corrente de 36 mA cm⁻², pH 7,0 e velocidade de fluxo de 5,0 L min⁻¹) mostraram que ao final da eletrólise (correspondente a uma carga circulada por unidade de volume de solução de 5,2 Ah L⁻¹) a SDZ foi totalmente eliminada. A redução da carga orgânica, monitorada por sua demanda química de oxigênio (COD) mostrou que o antibiótico foi praticamente todo mineralizado. Sob condições otimizadas, os compostos intermediários foram devidamente identificados por cromatografia gasosa-espectrometria de massas (GC-MS) e um mecanismo de oxidação foi proposto. Claramente, o eletrodo de BDD mostrou-se muito eficiente tanto para a degradação como para a mineralização de SDZ.

The electrochemical performance of boron-doped diamond (BDD) electrode in the electrochemical degradation of wastewaters containing sulfadiazine (SDZ) using a filter-press reactor is presented and discussed. The electrooxidation of the SDZ (volume of 0.5 L, with a SDZ initial concentration of 250 mg L⁻¹) obtained at optimized conditions (current density of 36 mA cm⁻², pH 7.0 and volume flow rate of 5.0 L min⁻¹) showed that at the end of only 2 h of electrolysis (corresponding to a charge passed through the cell per unit volume of the wastewater of 5.2 Ah L⁻¹) SDZ was totally eliminated. The reduction of the wastewater organic load, monitored by its chemical oxygen demand (COD) showed that the antibiotic was virtually all mineralized. Under optimized conditions the intermediate compounds were properly identified by gas chromatography-mass spectrometry (GC-MS) and a SDZ oxidation pathway was elucidated. Clearly the BDD electrode proved to be quite efficient for both degradation and mineralization of SDZ.

Keywords: sulfadiazine, boron-doped diamond electrode, electrochemical wastewater treatment, reaction pathway, antibiotics

Introduction

The growing concern with environmental contamination by toxic substances has increased interest in developing technologies directed not only to detect these substances but also to degrade them. Conventional treatment methods such as biological, chemical or incineration can only partially remove these contaminants,¹⁻⁵ which from an environmental standpoint represents a disadvantage. In addition, there are other major problems regarding these conventional treatment methods such as the low degradation rates in biological treatment processes, handling and storage risks of chemical substance during chemical treatment processes

and also no absolute assurance of air contamination during the incineration processes.

Thus, electrochemical methods have been proposed for the treatment of many pollutants, especially those hardest to degrade by conventional methods, such as aromatic organic molecules. The use of electrochemical processes allows transforming organic molecules into biodegradable products and then converted directly to CO₂ and H₂O (electrochemical combustion).⁶ The main advantage is that during this process there is practically no chemical consumption and no sludge production.

Sulfonamides are antibiotics used primarily in the treatment of urinary tract infections. As these compounds are excreted in its original form or as a metabolite, they can contaminate the environment if not biodegraded, photolyzed

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or efficiently removed from the sewage treatment plants. Sulfadiazine (SDZ, Figure 1) belongs to this group of substances and is widely used as an antibacterial drug in the prevention and treatment of various diseases.

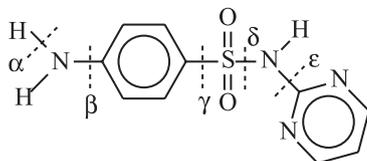


Figure 1. Chemical structure of SDZ with the potential cleavage sites.

Much attention has been given to the contamination of this therapeutic class of antibiotics in the environment, especially because the real risks to human health and to the environment are not yet fully understood. One of the main problems regarding the presence of antibiotics in wastewater is that some microorganisms acquire resistance to these drugs⁷⁻¹⁰ and also the fact that these drugs are used in large quantities in both human and veterinary medicine.¹⁰⁻¹⁵ For instance, studies dating back for more than a decade estimated that the world market has already consumed about 100,000 t to 200,000 t of antibiotics *per year*.¹⁶ Moreover, because they are biologically active substances these drugs can alter the pharmacodynamic effects on aquatic organisms with compatible enzymatic receptors, modifying the biodiversity and balance in the profiles of aquatic ecosystems.¹⁷⁻¹⁹

Studies of the biodegradation of various antibiotics using conventional activated sludge systems have reported that biodegradability occurs incompletely or quite slowly.²⁻⁶ For instance, studies about the degradation of SDZ also using an activated sludge biodegradation system showed that 50% of the SDZ initial concentration was removed after ca. 20 and 50 days.^{5,6} Similarly, it was found that trimethoprim, a drug often used in combination with sulfonamides to increase its antibacterial activity, showed high resistance to biological degradation as it required three days for its complete degradation.²

The use of boron-doped diamond (BDD) electrodes for anodic oxidation of toxic and biologically refractory pollutants has received much attention in recent years.²⁰⁻⁴⁴ However, not much attention has been given to the use of BDD electrodes (or any other electrode) in the electrochemical treatment of wastewater containing sulfonamides as well as to their electrochemical degradation mechanisms.^{27,41-48}

Thus, as the electrochemical treatment of effluents containing antibiotics is quite recent it has not been well explored so far. Therefore, scientific studies about the degradation of antibiotics as well as of its mechanism using

electrochemical methods have become very attractive, especially because of the great investigative range offered by the subject matter. Therefore, the main goal of this work is to develop an efficient system for electrochemical degradation of SDZ using a BDD electrode, as well as discuss a reaction mechanism pathway based on the identification of the intermediates formed during its degradation.

Experimental

Chemicals

All solutions were prepared using deionized water (Millipore, Brazil). Chemicals, including Na₂SO₄ (PA, Synth), K₂HPO₄ (PA, Synth), SDZ (99.9%, Sigma Aldrich) and methanol (J. T. Baker, Philipsburg, USA) were used as received.

Equipments

A Shimadzu high performance liquid chromatography (HPLC) equipment with an SPD-20A detector system was used to monitor the electrochemical degradation kinetics of SDZ. Under optimized conditions (pH, flow rate and current density) the intermediates were identified using an Agilent gas chromatography-mass spectrometry (GC-MS) analyzer (7820A GC System) equipped with an HP-5MS column (30 m × 0.25 mm × 0.25 μm).

The electrolyses were carried out using an Instrutherm (model FA-3005) power supply in order to control the applied current. The pH of the solutions was monitored using a PG 1800 GEHAKA pHmeter.

SDZ electrooxidation

Conventional electrochemical cell

Electrolyses were initially carried out using a conventional glass electrochemical cell (capacity of 200 mL) containing a BDD electrode (2000-4000 ppm in boron doping level) supplied by Condias GmbH Conductive Diamond Products (Germany), which was used as anode (14.7 cm²). Two stainless steel plates were used as counter electrodes. Before each electrolysis, the BDD electrode was anodically pre-treated in a 0.1 mol L⁻¹ Na₂SO₄ solution by applying 50 mA cm⁻² for 10 min to clean the anode surface. All the wastewater solutions (150 mL) contained 250 mg L⁻¹ SDZ in 0.1 mol L⁻¹ Na₂SO₄ and were kept at 25 °C. Accordingly, SDZ was first dissolved in 1.5 mL of 1.0 mol L⁻¹ NaOH and then diluted in the Na₂SO₄ solution. The pH of the solutions was adjusted using 1.0 mol L⁻¹ H₂SO₄ solution.

The purpose of these experiments was to investigate the influence of pH (3, 5 and 7) on the kinetics of SDZ degradation and choose the most suitable pH condition to apply in the filter-press electrochemical reactor. These experiments were carried out by keeping the total electrolysis time and current density at 60 min and 50 mA cm⁻², respectively. When necessary, before and during each electrolysis the pH was adjusted with aqueous solution of 1.0 mol L⁻¹ NaOH or 1.0 mol L⁻¹ H₂SO₄ in order to keep the pH value unchanged. The SDZ concentrations were continuously monitored using only the HPLC technique.

Filter-press electrochemical reactor

The SDZ electrooxidations using a one-compartment filter-press electrochemical reactor (Supplementary Information Figure S1) in batch recirculation system ($V = 500$ mL) were carried out under the same conditions previously described for the conventional electrochemical cell. In this case, the BDD electrode area was 36 cm². The distance between the BDD and stainless steel electrodes in the filter-press reactor was 5.3 mm.

The current density values investigated were chosen based on the value of the limiting current density obtained for the system (i_{lim}). The limiting current and the mass transfer coefficient (k_m) values were obtained from chronoamperograms performed under flow regime (1.0 L min⁻¹ at 5.0 L min⁻¹) for the [Fe(CN)₆]⁴⁻ oxidation.⁴⁸ Thus, the value of the limiting current density where the largest k_m value was obtained (considering the chemical oxygen demand (COD) value of 350 mg L⁻¹, [SDZ]₀ = 250 mg L⁻¹) was 13.5 mA cm⁻² at a flow rate of 5.0 L min⁻¹ (Supplementary Information Table S1).

The SDZ oxidation was considered at three different situations: (i) 9.0 mA cm⁻² ($i_{apl} < i_{lim}$), (ii) 18 mA cm⁻² ($i_{apl} > i_{lim}$) and (iii) 36 mA cm⁻² ($i_{apl} \gg i_{lim}$). These experiments were carried out by keeping the total electrolysis time and flow rate at 180 min and 5.0 L min⁻¹, respectively.

SDZ monitoring

The mobile phase used in the HPLC technique was a mixture of 0.01 mol L⁻¹ potassium monohydrogen phosphate (pH adjusted to 5.0) and methanol in the volumetric proportion 75:25. The flow rate used was 1.0 mL min⁻¹ and detection was monitored at $\lambda = 265$ nm. The analytical column (150 mm × 4.6 mm i.d.) used was packed with Luna[®] octyl silica (10 μm, 120 Å; Phenomenex, Torrance, CA, USA).⁴⁹ Sample analyses were carried out at time zero and then at different electrolysis times (15, 30, 60, 90, 120, 150 and 180 min). For each analysis, aliquots (100 μL) were removed from the wastewater reservoir and then diluted to 10 mL using the mobile phase, in order to

attend the limits of quantification of the method. Finally, a volume of 20 μL of each solution was injected in the analytical column.

The GC-MS analysis was carried out using a temperature ramp of 70 °C for 2.0 min and 20 °C min⁻¹ up to 270 °C. The helium (carrier gas) flow rate was 1.0 mL min⁻¹ and the time of each analysis was 17 min. Analyses of these samples were carried out at different electrolysis times (0, 15, 30, 60, 120 and 180 min) using the solid phase extraction (SPE) technique. Before each analysis, the C18 cartridge (DSC 18, Supelco) was conditioned with dichloromethane (2.0 mL), methanol (2.0 mL) and deionized water (5.0 mL). Next, a 500 mL volume was removed from the wastewater reservoir and then percolated through the C18 cartridge followed by drying with N₂ for 20 min. Finally, the aliquot of each extract was eluted through the cartridge with 2.0 mL volumes of methanol, dichloromethane and acetone (in this sequence) and then stored separately in three different portions for injection (in triplicate).

The chemical oxygen demands (COD) of the wastewater solutions were determined at different times (up to different amounts of charge passed through the cell) using a Hach DR 890 analyzer at a wavelength of 620 nm.

Results and Discussion

Influence of pH

Electrolyses of SDZ were performed at three different pH values (3, 5 and 7) in order to understand the influence of pH on its electrochemical degradation. Figure 2 shows the results of these measurements.

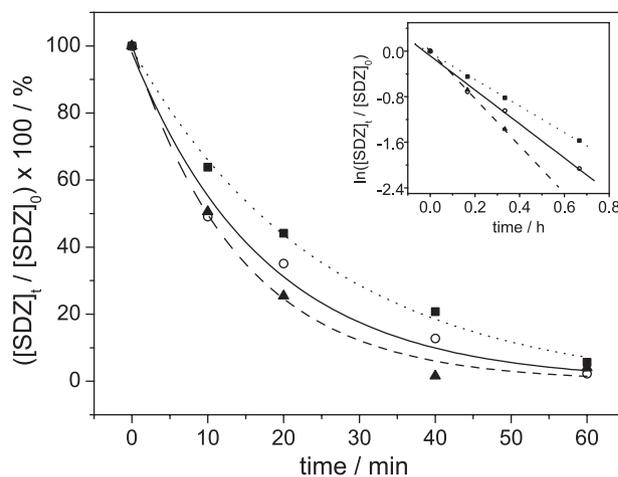


Figure 2. Normalized concentration vs. time for the electrochemical degradation of SDZ at (■) pH 3, (○) pH 5 and (▲) pH 7. Inset: natural logarithm of the normalized SDZ concentration vs. time. [SDZ]₀ = 250 mg L⁻¹, [Na₂SO₄] = 0.1 mol L⁻¹, flow rate = 5.0 L min⁻¹ and $i = 50$ mA cm⁻².

The results in Figure 2 show a first order exponential decay of the SDZ normalized concentration with the electrolysis time for all pH values investigated, which is typical of mass-transport controlled processes. This decay profile is demonstrated by considering the derivation of the rate law for first order reactions, that is, the linear dependence expected between $\ln[\text{SDZ}]_t / [\text{SDZ}]_0$ vs. time (Figure 2 inset).

At the end of each electrolysis, the results showed that 96, 98 and 100% of the initial SDZ concentration could be degraded at pHs of 3, 5 and 7, respectively, and the corresponding apparent reaction rate constants determined for these pHs were 2.33, 2.99 and 3.14 h^{-1} .

Considering the results obtained at 60 min, the SDZ removal percentages are virtually all equivalent. On the other hand, the different apparent reaction rate constants calculated showed that the pH parameter plays an important role with respect to the kinetic of the SDZ electrochemical degradation. One possible explanation for this phenomenon can be proposed considering the chemical nature of the SDZ molecule at each pH condition employed in the electrolyses. SDZ is characterized by having two acid equilibrium constant values ($\text{pK}_{a1} = 2.49$ and $\text{pK}_{a2} = 6.48$). While the lowest pK_a (pK_{a1}) refers to the protonation of the amino group in the *para*- position of the benzene ring, the highest (pK_{a2}) refers to the deprotonation of the SO_2NH group in the SDZ molecule (Figure 3). For instance, if an electrolysis is carried out at pH conditions where the $\text{pH} < \text{pK}_{a1}$, the SDZ molecule could be predominantly in its protonated form and, therefore, less susceptible to the electrophilic attack by the hydroxyl radicals ($\bullet\text{OH}$). On the other hand, when the pH is higher than pK_{a1} and pK_{a2} the predominant species are the non-protonated amine and its ionized form, respectively, which could in turn increase the SDZ reactivity.

It could then be expected that an increase in the pH of the solution contributed to increase the SDZ electrochemical degradation rate, as shown by the results in Figure 2. Thus, the use of neutral pH ($\text{pH} 7$ and higher than the pK_{a2} of SDZ molecule) was considered the most appropriate for the electrochemical degradation of SDZ. The choice was based not only on the kinetics of SDZ electrochemical degradation (larger values of k_{ap} obtained) but also because it provides a condition that is closer to the direct disposal of wastewater.

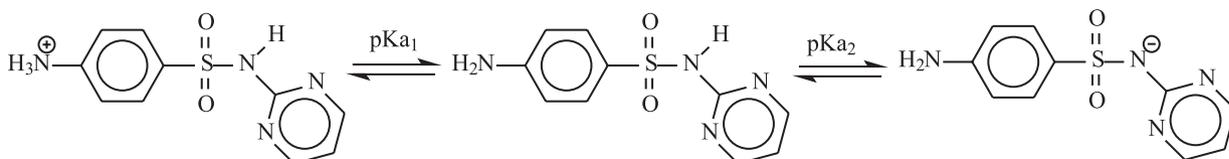


Figure 3. SDZ ionization equilibria.

Filter-press electrochemical reactor

To make these systems more attractive, from a practical perspective, implementing new technologies for the degradation of pollutants requires not only an efficient method but also an optimized energy consumption process to minimize operating costs. Specifically for electrochemical methods, these parameters are strongly related to the type of hydrodynamic regime of the system, as well as choosing suitable electrode materials. Thus, important parameters such as limiting current density and flow rate must be optimized in order to satisfy these criteria. The limiting current is based on the current value in which the oxidation/reduction process is entirely controlled by mass transport. Under limiting current conditions, the process operates at the maximum rate and minimum costs. Therefore, to obtain this kind of information the use of electrochemical reactors coupled to systems that allow the recirculation of the solution is fundamental.

So, after determining the best hydrodynamic condition for the system (see Experimental section and Supplementary Information), the influence of the current density on the SDZ oxidation was investigated. At these measurements, SDZ oxidation was considered at three different situations: (i) 9.0 mA cm^{-2} ($i_{\text{apl}} = 2/3 i_{\text{lim}}$), (ii) 18 mA cm^{-2} ($i_{\text{apl}} = 4/3 i_{\text{lim}}$) and (iii) 36 mA cm^{-2} ($i_{\text{apl}} = 8/3 i_{\text{lim}}$). While the first situation represents a condition in which a charge transport control is expected ($i_{\text{apl}} < i_{\text{lim}}$), the other ones correspond to mass transport controlled conditions ($i_{\text{apl}} > i_{\text{lim}}$). According to Figure 4a it can be clearly seen that the degradation kinetics of SDZ is favored at higher current densities. The corresponding times for the total elimination of SDZ were 180 min for a current density of 9.0 mA cm^{-2} and 120 min for both current densities applied at 18 and 36 mA cm^{-2} . The fact that the time for the total elimination of SDZ does not change when the current density is increased from 18 to 36 mA cm^{-2} indicates mass transport limitations. However, the k_m values obtained for the electrolyses carried out at 9.0, 18 and 36 mA cm^{-2} were 1.24, 1.71 and 2.27 h^{-1} , respectively.

A similar behavior to that seen in Figure 4a was confirmed by taking into account the values of the respective COD decays shown in Figure 4b. At the end of each electrolysis the COD removal percentage was 88,

95 and 100% for the electrolyses carried out at 9, 18 and 36 mA cm⁻², respectively.

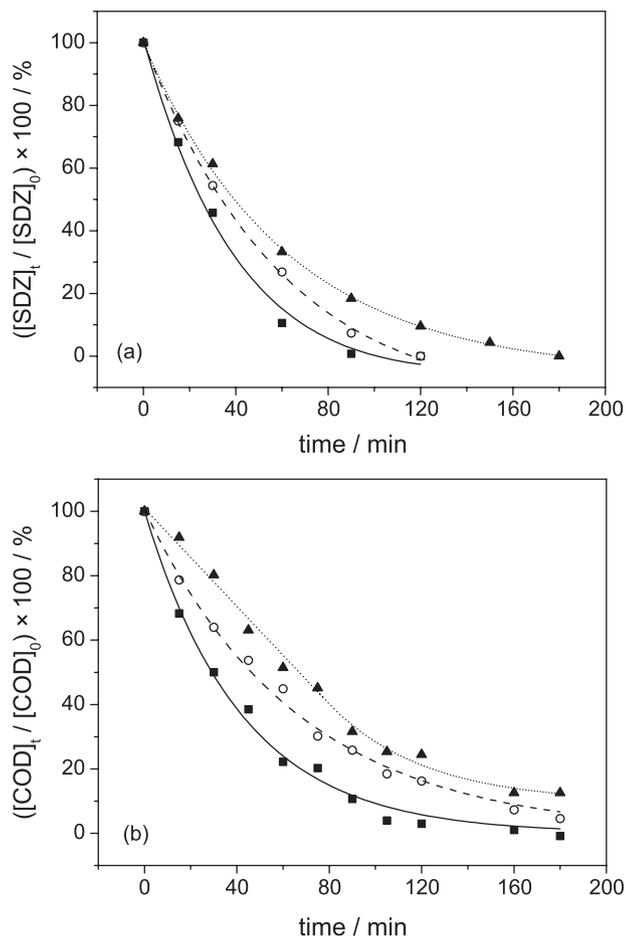


Figure 4. Normalized concentration vs. time for the electrooxidative degradation (at pH 7 and 5.0 L min⁻¹) of SDZ (a) and COD (b) at different current densities: (▲) 9.0 mA cm⁻² (dotted line), (○) 18 mA cm⁻² (dashed line) and (■) 36 mA cm⁻² (full line). $[SDZ]_0 = 250$ mg L⁻¹ and $[Na_2SO_4] = 0.1$ mol L⁻¹.

The total energy consumption (TEC) for the removal of 1 kg of COD (measured in kWh kg⁻¹_{COD}) was calculated using the following equation:

$$TEC = \frac{t \times U \times I}{V \times \Delta COD} \times 1000 \quad (1)$$

where t is the electrolysis time (h), U the average electrolysis cell voltage (V), I the applied electrolysis current (A), V the wastewater volume (L), and ΔCOD the difference in COD (mg L⁻¹).

The average electrolysis cell voltage values measured at 9, 18 and 36 mA cm⁻² were 4.1, 4.5 and 5.4 V, respectively. The corresponding TEC values for these current densities were 19.2, 38.1 and 79.8 kWh kg⁻¹_{COD}. Thus, the process with the lowest TEC value was the one whose applied current density was the lowest. However, from the

practical standpoint, using a current density as low as 9.0 mA cm⁻² does not seem to be advantageous for the SDZ degradation because the time needed to achieve its complete mineralization should be much higher. At this condition, the COD removal percentage is of about 75% after 2 h of electrolysis against 100% of COD removal when a current density of 36 mA cm⁻² was applied. So, although the electrolysis carried out for 36 mA cm⁻² had the highest TEC, the use of this condition was considered the most appropriate one considering not only the lowest electrolysis time for mineralization but also the elimination of by-products. For instance, HPLC chromatograms were obtained at the end of 180 min of electrolysis by direct injection of the undiluted aliquots taken from experiments carried out at 18 and 36 mA cm⁻² (Figure 5a). These HPLC chromatograms clearly show a significant reduction of

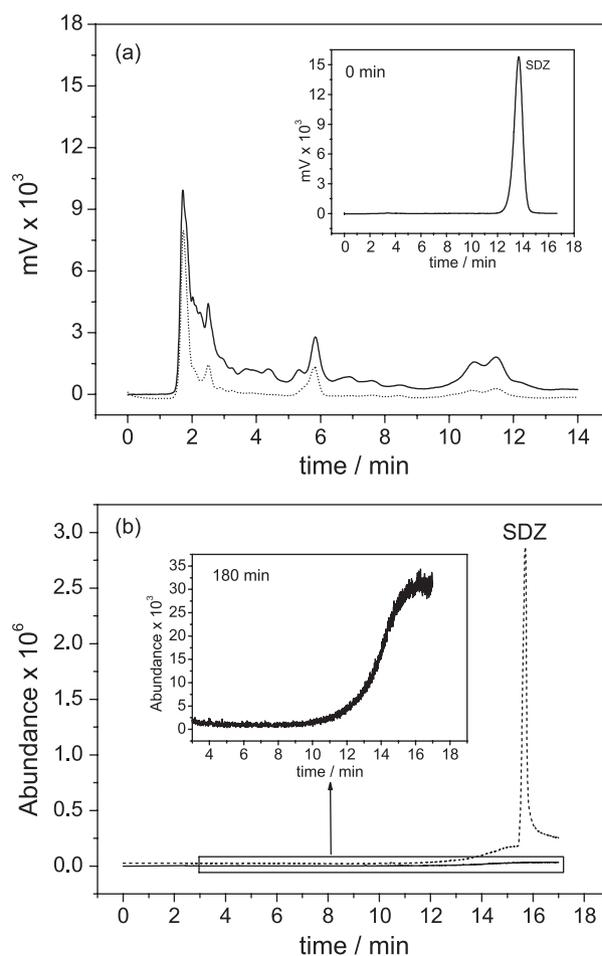


Figure 5. HPLC (a) and GC-MS (b) chromatograms obtained at the beginning and the end of 180 min of electrolysis (pH 7 and flow rate = 5.0 L min⁻¹) by direct injection of the undiluted aliquots. From (a): 18 mA cm⁻² (full line), 36 mA cm⁻² (dotted line) and the inset HPLC chromatogram was obtained before electrolysis (0 min) and from a diluted sample ($[SDZ] = 2.5$ mg L⁻¹). From (b): 0 min (dotted line) and 180 min (full line). The GC-MS chromatogram was obtained from the electrolysis carried out at 36 mA cm⁻².

the remaining chromatogram peaks as well as the total disappearance of other peaks when applying a current density of 36 mA cm^{-2} . It should also be noted that none of these remaining chromatogram peaks is related to the SDZ because the retention time of this antibiotic was of 13.7 min (Figure 5a inset). Also, although the HPLC chromatogram in Figure 5a showed the presence of some small peaks at the end of electrolysis (180 min), no peak was observed in the GC-MS chromatogram (Figure 5b). Therefore, taking into account the better results attained it can be concluded that the use of pH 7, flow rate of 5.0 L min^{-1} and a current density of 36 mA cm^{-2} were considered the most appropriate conditions for the electrochemical degradation of SDZ.

Identification of byproducts and reaction pathway

In order to identify the by-products generated and to propose a possible mechanism for the electrochemical degradation of SDZ, GC-MS total ion chromatograms (TICs) were obtained using the best conditions previously obtained (pH 7, $i = 36 \text{ mA cm}^{-2}$ and flow rate = 5.0 L min^{-1}). All the intermediate compounds identified are shown in Table 1.

The aromatic products identified from the SDZ electrochemical oxidation described in Table 1 were quite consistent with the potential cleavage sites shown in detail in Figure 1. All the intermediate compounds presented here were identified from the aliquots eluted with methanol because the other aliquots eluted with dichloromethane and acetone only confirmed the presence of some peaks already detected by the methanol elution but with very small peak areas. All the m/z ratios presented here correspond to the protonated species ($[M+H]^+$).

The intermediate identified as $\text{C}_4\text{H}_5\text{N}_3$ and with m/z ratio of 96 is consistent with the δ -cleavage of the SDZ molecule. Other fragments of the SDZ molecule ($\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$ and $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$) were identified with 203, 187 and 173 mass units, respectively. The presence of the $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$ intermediate is consistent with the bond breakdown of the carbon located in the ring with two nitrogen atoms substituted. In turn, while the presence of the by-product identified as $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$ confirms the nitrogen-carbon bond breakdown in the γ -position of the SDZ molecule, the origin of the $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$ intermediate molecule possibly refers to a rearrangement of the molecule SDZ after the loss of SO_2 group with the simultaneous

Table 1. Identification of the main aromatic intermediate compounds formed in the electrochemical degradation of SDZ and their respective chemical structures elucidated by the GC-MS technique

| $[M-H]^+$ | Identification | Chemical Structure |
|-----------|--|--------------------|
| 251 | Sulfadiazine ($\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$) | |
| 203 | <i>N</i> -[4-(Hydroxyamino)phenyl]-2-pyridinamine ($\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$) | |
| 187 | 4-Amino- <i>N</i> -methylbenzenesulfonamide ($\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2\text{S}$) | |
| 173 | Sulfanilamide $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$ | |
| 96 | 2-Pyrimidinamine $\text{C}_4\text{H}_5\text{N}_3$ | |

replacement of the hydrogen bonded to the nitrogen of the primary amine ($\text{H}_2\text{N}-$) by a hydroxyl group in the α -position of the SDZ molecule.

Some systematic studies in the literature related to the degradation mechanism of SDZ have been found only by using other degradation methods.^{50,51} For example, Wang *et al.*⁵⁰ investigated the photochemical degradation mechanism of SDZ (pH 3.5) and identified the formation of the 4-*OH*-sulfadiazine and 4-[2-iminopyrimidine-1(2*H*)-yl]aniline intermediates (detected by HPLC-MS), 2-aminopyrimidine (detected by GC-MS), acetic and formic acids (ion chromatography). The authors concluded that the degradation mechanism of SDZ involved the formation of the 2-aminopyrimidine from the cleavage of the SDZ molecule in the δ -position. The presence of the 4-[2-iminopyrimidine-1(2*H*)-yl]aniline was consistent with the breakdown in the γ -position of the SDZ molecule resulting in the sulfanilic acid formation, which in turn reacts with 2-aminopyrimidine to form 4-[2-iminopyrimidine-1(2*H*)-yl]aniline. Neafsey *et al.*⁵¹ investigated the degradation mechanism of SDZ (pH 5.1) by advanced oxidation processes (Fenton process) and suggested two possible mechanisms from the intermediates identified by HPLC-MS. The first mechanism involved the oxidation of the SDZ group with elimination of the SO_2

group to form a byproduct with m/z ratio of 187 followed by a hydroxyl radical attack on the C–N bond located in the ring with two nitrogen atoms substituted. Then, there was the formation of two intermediates with mass units of 109 and 97. On the other hand, the second mechanism involved the attack of the hydroxyl radicals to the C–C bond located in the benzene ring of the byproduct with m/z ratio of 187 to form other byproducts with mass units of 96 and 109.

The results reported here are different from those previously cited.^{50,51} However, it is important to emphasize that the results reported here were obtained under different degradation conditions (flow regime, pH 7 and a different degradation method) and because of this it seems to play an important role with respect to the differences found. Nevertheless, an electrophilic attack by the hydroxyl radicals on the preferential cleavage sites of the SDZ molecule can be expected and the main reaction pathways are summarized in Figure 6.

According to the mechanism shown in Figure 6, the first step for the electrochemical oxidation of SDZ involves the formation of the 2-pyrimidinamine (m/z 96) after 15 min of electrolysis, which was originated from the S–N bond breakdown in the δ -position of the SDZ molecule. The presence of the 4-amino-*N*-metilbenzenosulfonamide (m/z 187) and sulfanilamide (m/z 183) intermediates were

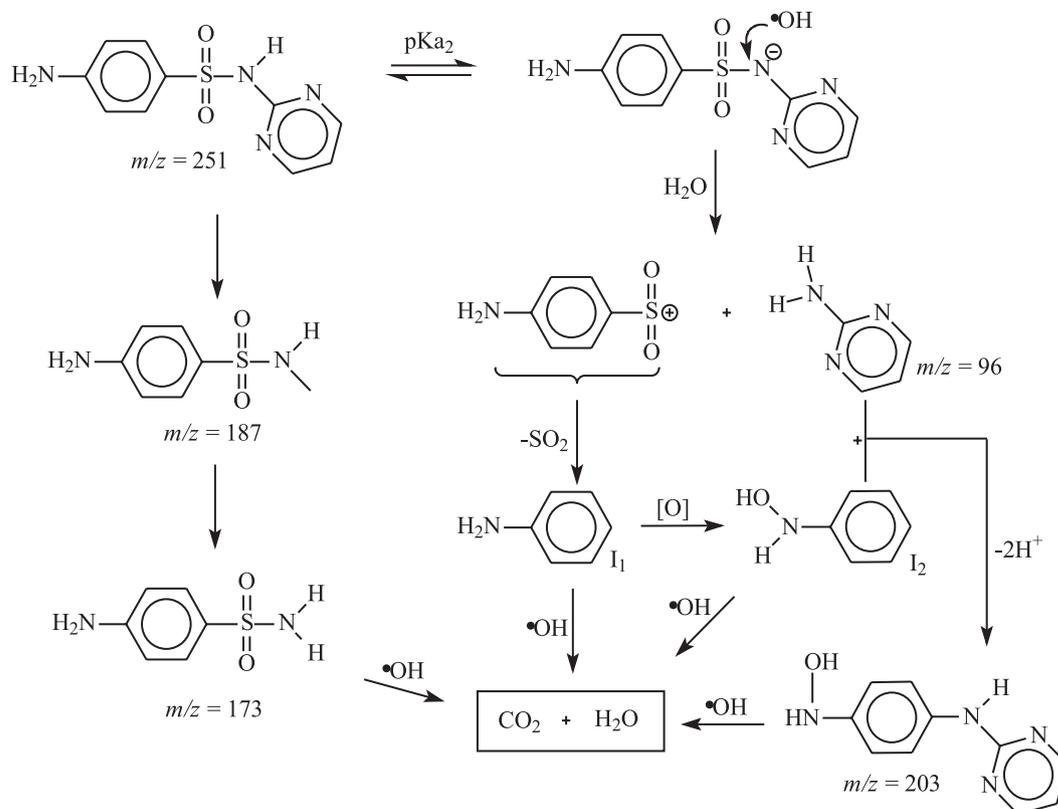


Figure 6. Main reaction pathway proposed for the SDZ electrochemical degradation. $[\text{SDZ}]_0 = 250 \text{ mg L}^{-1}$, pH 7, $i = 36 \text{ mA cm}^{-2}$ and flow rate = 5.0 L min^{-1} . The m/z ratio corresponds to the protonated species.

detected after 30 min of reaction, which were consistent with the successive oxidations of the SDZ molecule from the cleavage of the carbon located in the ring with two nitrogen atoms substituted and the subsequent N–C bond breakdown in the ϵ -position of the SDZ molecule. These intermediates could be converted directly to CO₂ and H₂O (both deduced by the decrease in COD) or, more likely, first converted into aliphatic molecules (not detected) before mineralization. The origin of the *N*-[4-(hydroxyamino)phenyl]-2-pyridinamine (*m/z* 203) intermediate could be justified considering the reaction between 2-pyrimidinamine (*m/z* 96) with *N*-aryl-hydroxylamine (I_b), formed from the oxidation of aniline (I_a). Aniline (I_a) was originated after the loss of the SO₂ group from the C₆H₆NSO₂⁺ species.

It should be mentioned that although I_a and I_b intermediates have only been deduced as possible byproducts of the SDZ degradation (no measurable peak areas), the proposed mechanism can be substantiated by considering that they were quickly consumed (mineralized) by the hydroxyl radicals, thereby preventing their accumulation in the system. The same argument can be considered in order to justify the absence of probable aliphatic byproducts in the electrochemical degradation of SDZ.

Conclusions

The results obtained allowed to conclude that the BDD electrode is quite efficient in the degradation of the SDZ antibiotic.

The effects of both the current density, pH and flow rate in the degradation kinetics of SDZ were properly optimized and interpreted. The electrolyses carried out under different pH conditions showed that the degradation of SDZ was favored at neutral conditions due to the chemical nature of the SDZ molecule (pH > pK_a).

From the environmental standpoint, excellent results were achieved by applying better electrolysis conditions (pH 7, *i* = 36 mA cm⁻² and flow rate = 5.0 L min⁻¹). Under these conditions, both SDZ and COD were totally consumed at the end of only 2 h of electrolysis.

An oxidation pathway of the SDZ electrochemical degradation was proposed taking into account the five aromatic organic intermediate compounds properly identified by GC-MS technique. All these intermediate byproducts were consistent with the potential cleavage sites of the SDZ molecule.

Supplementary Information

Supplementary information is available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgements

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References

- Drillia, P.; Dokianakis, S. N.; Fountoulakis, M. S.; Kornaros, M.; Stamatelatou, K.; Lyberatos, G.; *J. Hazard. Mater.* **2005**, *122*, 259.
- Perez, S.; Eichhorn P.; Aga, D. S.; *Environ. Toxicol. Chem.* **2005**, *24*, 1361.
- Carballa, M.; Omila, F.; Lema, J. M.; Llompert, M.; Garcia-Jares, C.; Rodríguez, I.; Gomez, M.; Ternes, T.; *Water Res.* **2004**, *38*, 2918.
- Larcher, S.; Yargeau, V.; *Appl. Microbiol. Biotechnol.* **2011**, *91*, 211.
- Galan, M. J. G.; Diaz-Cruz, M. S.; Barceló, D.; *Anal. Bioanal. Chem.* **2012**, *404*, 1505.
- Li, B.; Zhang, T.; *Environ. Sci. Technol.* **2010**, *44*, 3468.
- Comminellis, C.; *Electrochim. Acta* **1994**, *39*, 1857.
- Bower, C. K.; Daeschel, M. A.; *Int. J. Food Microbiol.* **1999**, *50*, 33.
- Guardabassi, L.; Wong, D. M. A. L.; Dalsgaard, A.; *Water Res.* **2002**, *36*, 1955.
- Miranda, C. D.; Castillo, G.; *Sci. Total Environ.* **1998**, *224*, 167.
- Bila, D. M.; Dezotti, M.; *Quim. Nova* **2003**, *26*, 523.
- Ingerslev, F.; Toräng, L.; Loke, M. L.; Halling-Sorensen, B.; Nyholm, N.; *Chemosphere* **2001**, *44*, 865.
- Loke, M. L.; Ingerslev, F.; Halling-Sorensen, B.; Tjornelund, J.; *Chemosphere* **2000**, *40*, 759.
- Rabolle, M.; Spliid, N. H.; *Chemosphere* **2000**, *40*, 715.
- Kumar, R. R.; Lee, J. T.; Cho, J. Y.; *J. Korean Soc. Appl. Biol. Chem.* **2012**, *55*, 701.
- Kümmerer, K.; *Chemosphere* **2009**, *75*, 417.
- Wise, R.; *J. Antimicrob. Chemother.* **2002**, *49*, 585.
- Fent, K.; Weston, A. A.; Caminada, D.; *Aquat. Toxicol.* **2006**, *76*, 122.
- Bound, J. P.; Voulvoulis, N.; *Chemosphere* **2004**, *56*, 1143.
- Pereira, G. F.; Rocha-Filho, R. C.; Bocchi, N.; Biaggio, S. R.; *Chem. Eng. J.* **2012**, *198*, 282.
- Melo, S. A. S.; Trovó, A. G.; Bautitz, I. R.; Nogueira, R. F. P.; *Quim. Nova* **2009**, *32*, 188.
- Alfaro, M. A. Q.; Ferro, S.; Martínez-Huitle, C. A.; Vong, Y. M.; *J. Braz. Chem. Soc.* **2006**, *17*, 227.
- Martinez-Huitle, C. A.; Andrade, L. S.; *Quim. Nova* **2011**, *34*, 850.
- Panizza, M. In *Synthetic Diamond Films: Preparation, Electrochemistry, Characterization and Applications*;

- Brillas, E.; Martínez-Huitle, C. A., eds.; Wiley: New York, 2011, ch. 14.
25. Zhang, C. Y.; Liu, L. P.; Wang, J. L.; Rong, F.; Fu, D. G.; *Sep. Purif. Technol.* **2013**, *107*, 91.
26. Rabaaoui, N.; Moussaoui, Y.; Ilagui, M. S.; Ahmed, B.; Elaloui, E.; *Sep. Purif. Technol.* **2013**, *107*, 318.
27. Vidales, M. J. M.; Robles-Molina, J.; Domínguez-Romero, J. C.; Cañizares, P.; Sáez, C.; Molina-Díaz, A.; Rodrigo, M. A.; *J. Chem. Technol. Biotechnol.* **2012**, *87*, 1441.
28. Polcaro, A. M.; Vacca, A.; Palmas, S.; Mascia, M.; *J. Appl. Electrochem.* **2003**, *33*, 885.
29. Cañizares, P.; Gadri, A.; Lobato, J.; Nasr, B.; Paz, R.; Rodrigo, M. A.; Saez, C.; *Ind. Eng. Chem. Res.* **2006**, *45*, 3468.
30. Andrade, L. S.; Rocha-Filho, R. C.; Bocchi, N.; Biaggio, S. R.; Iniesta, J.; Garcia-Garcia, V.; Montiel, V.; *J. Hazard. Mater.* **2008**, *153*, 252.
31. Perret, A.; Haenni, W.; Skinner, N.; Tang, X.-M.; Gandini, D.; Comninellis, C.; Correa, B.; Foti, G.; *Diamond Relat. Mater.* **1999**, *8*, 820.
32. Andrade, L. S.; Ruotolo, L. A. M.; Rocha-Filho, R. C.; Bocchi, N.; Biaggio, S. R.; Iniesta, J.; Garcia-Garcia, V.; Montiel, V.; *Chemosphere* **2007**, *66*, 2035.
33. Andrade, L. S.; Rocha-Filho, R. C.; Bocchi, N.; Biaggio, S. R.; *Electrochim. Acta* **2009**, *54*, 2024.
34. Iniesta, J.; Michaud, P. A.; Panizza, M.; Comninellis, C.; *Electrochem. Commun.* **2001**, *3*, 346.
35. Panizza, M.; Michaud, P. A.; Cerisola, G.; Comninellis, C.; *J. Electroanal. Chem.* **2001**, *507*, 206.
36. Rodrigo, M. A.; Michaud, P. A.; Duo I.; Panizza, M.; Cerisola, G.; Comninellis, C.; *J. Electrochem. Soc.* **2001**, *148*, 60.
37. Montilla, F.; Michaud, P. A.; Morallon, E.; Vazquez, J. L.; Comninellis, C.; *Electrochim. Acta* **2001**, *47*, 3509.
38. Brillas, E.; Boye, B.; Sirés, I.; Garrido, J. A.; Rodríguez, R. M.; Arias, C.; Cabot, P. L.; Comninellis, C.; *Electrochim. Acta* **2004**, *49*, 4487.
39. Boye, B.; Brillas, E.; Marselli, B.; Michaud, P. A.; Comninellis, C.; Farnia, G.; Sandonà, G.; *Electrochim. Acta* **2006**, *51*, 2872.
40. Cañizares, P.; Saez, C.; Lobato, J.; Rodrigo, M. A.; *Electrochim. Acta* **2004**, *49*, 4641.
41. Li, S.; Bejan, D.; McDowell, M. S.; Bunce, N. J.; *J. Appl. Electrochem.* **2008**, *38*, 151.
42. Rodrigo, M. A.; Cañizares, P.; Buitrón, C.; Sáez, C.; *Electrochim. Acta* **2010**, *55*, 8160.
43. Dirany, A.; Sirés, I.; Oturan, N.; Oturan, M. A.; *Chemosphere* **2010**, *81*, 594.
44. Boudreau, J.; Bejan, D.; Li, S. H.; Bunce, N. J.; *Ind. Eng. Chem. Res.* **2010**, *49*, 2537.
45. Hoffmann, Th.; Hoffmann, D.; Klumpp, S.; *Anal. Bioanal. Chem.* **2011**, *399*, 1859.
46. El-Ghenymy, A.; Cabot, P. L.; Centellas, F.; Garrido, J. A.; Rodríguez, R. M.; Arias, C.; Brillas, E.; *Electrochim. Acta* **2013**, *90*, 254.
47. El-Ghenymy, A.; Garrido, J. A.; Rodríguez, R. M.; Cabot, P. L.; Centellas, F.; Arias, C.; Brillas, E.; *J. Electroanal. Chem.* **2013**, *689*, 149.
48. de Amorim, K. P.; Romualdo, L. L.; Andrade, L. S.; *Sep. Purif. Technol.* **2013**, *120*, 319.
49. Andrade, L. S.; de Moraes, M. C.; Rocha-Filho, R. C.; Fatibello-Filho, O.; Cass, Q. B.; *Anal. Chim. Acta* **2009**, *654*, 127.
50. Wang, Y.; Liang, J. B.; Liao, X. D.; Wang, L.-S.; Loh, T. C.; Dai, J.; Ho, Y. W.; *Ind. Eng. Chem. Res.*, **2010**, *49*, 3527.
51. Neafsey, K.; Zeng, X.; Lemley, A. T.; *J. Agric. Food Chem.* **2010**, *58*, 1068.

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