Electro-Fenton and photoelectro-Fenton degradation of the antimicrobial sulfamethazine using a boron-doped diamond anode and an air-diffusion cathode

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Electrochemical incineration of the antimicrobial sulfamethazine at a boron-doped diamond anode

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ABSTRACT

The electrochemical incineration of the antimicrobial sulfamethazine in acidic medium by anodic oxidation (AO) has been studied using an undivided or divided cell with a boron-doped diamond (BDD) anode and a stainless steel cathode. The oxidation power of AO with BDD was greater in the divided than in the undivided cell, as a result of the higher efficiency of reactive hydroxyl radicals generated at the BDD anode from water oxidation. A similar degradation rate was found over the pH range 2.0–6.0. The treatment of a 193 mg dm^{-3} drug solution in 0.50 mol dm^{-3} Na_2SO_4 at controlled pH 3.0 in the anodic compartment of the divided cell yielded 98% mineralization for current densities $\geq$ 66.6 mA cm^{-2}. Analogous almost total mineralization was attained using the undivided cell with 0.05 mol dm^{-3} Na_2SO_4 at current densities $\geq$ 100 mA cm^{-2}, but with lower degradation rate and efficiency. Decreasing current density and increasing drug content enhanced the mineralization current efficiency. Reversed-phase HPLC allowed determining a pseudo-first-order kinetics for sulfamethazine decay, which was faster in the divided cell. 1,2-Benzenediol, 1,4-benzenediol, *p*-benzoquinone and 4,6-dimethyl-2-pyrimidinamine were identified as aromatic intermediates in the divided cell by gas chromatography-mass spectrometry. Generated carboxylic acids like maleic, fumaric, acetic, formic, oxalic and oxamic were quantified by ion-exclusion HPLC. Ionic chromatography revealed the conversion of the initial N of sulfamethazine into NH_4^+ ion, along with NO_3^- ion in much smaller proportion. From all detected intermediates, a reaction pathway for sulfamethazine mineralization in acidic medium by AO with BDD is proposed.

1. Introduction

Advanced oxidation processes (AOPs) are receiving increasing attention for the remediation of waters containing toxic and/or biorefractory organic pollutants [1–5]. These methods are powerful chemical, photochemical, photocatalytic and electrochemical processes based on the in situ generation of hydroxyl radical (•OH) as strong oxidizing agent of the organic matter. This radical has a high standard reduction potential (E°(•OH/H_2O) = 2.80 V/SHE) making feasible its non-selective reaction with most organics giving dehydrogenated or hydroxylated derivatives, which can be in turn mineralized, i.e. transformed into carbon dioxide, water and inorganic ions.

Over the last decade, a high number of electrochemical AOPs (EAOPs) have been developed for water remediation because of their environmental compatibility, versatility, high efficiency, amenability of automation and safety since they operate at mild conditions [5–9]. Among these EAOPs, the most popular treatment is electro-oxidation or anodic oxidation (AO), in which pollutants are oxidized by direct charge transfer at the anode M and at high current, much more rapidly removed with physisorbed M(•OH) formed from water oxidation to O_2 as follows [6,8,10]:

$$M + H_2O \rightarrow M(^\bullet OH) + H^+ + e^- \quad (1)$$

Boron-doped diamond (BDD) thin-film electrodes are the best anodic materials known for AO. While in active anodes like Pt, IrO_2 and RuO_2, the corresponding M(•OH) is oxidized to a chemisorbed "superoxide" species with less oxidizing power that only yields the electrochemical conversion of organics into carboxylic acids [11–13], in non-active anodes like BDD and PbO_2, the M(•OH) radical becomes stable giving rise to the electrochemical incineration of organics [14–17]. The BDD anode has technologically important properties like an inert surface with low adsorption, remarkable corrosion stability even in strongly acidic media and extremely high O_2-evolution overvoltage, enhancing the reaction of organics with BDD(•OH) [8,18]. BDD possesses much higher oxidation power than common anodes like Pt [12,19] and PbO_2 [15,20],

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being able to mineralize aromatics like pesticides [11,16,20–23], pharmaceuticals [13,14,17,24–26] and dyes [15,18,19,27,28] from waters and their generated carboxylic acids [29–31]. Most of these AO treatments were made in an undivided cell instead of a divided one since it avoids the additional potential penalty of the separator between the anodic and cathodic compartment making the process much more economic. However, less is known about the comparative oxidation power of AO with BDD in both kinds of cells.

Sulfonamides are the oldest chemotherapeutic agents used as antimicrobials in human therapy and animal husbandry, as well as veterinary growth promoters. Disposal of domestic and hospital waste, fields fertilized with animal manure and runoff and infiltration from treated animals in farms result in the entry of sulfonamides into the environment [32]. They weakly adsorb to soil particles, have the potential to leach into groundwater and have been detected at relatively large quantities of $\mu g\,dm^{-3}$ in lakes and rivers because they are not biodegradable and poorly removed in sewage treatment plants [33–35]. Their presence in the soil and aquatic environment at subtherapeutic concentrations is dangerous since it may promote the growth of antibiotic-resistant bacteria and may alter the ecosystem structure by reducing the numbers of bacteria in soils [36,37]. Several AOPs have been applied to destroy a large number of sulfonamides from waters, but the possible use of AO has not been previously reported. For this reason, we have undertaken a study to check the oxidation power of AO on sulfamethazine (4-amino-*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide), a sulfonamide widely used in veterinary and agriculture. Sulfamethazine has been detected up to $140\,\mu g\,dm^{-3}$ in wastewaters and soils of animal farms, sewage treatment plants, rivers, lagoons and suburban and agricultural waters [34,35,38–41]. This contamination may promote the growth of resistant organisms in the environment [33] and then, it is needed the development of powerful processes to remove it from waters. In this way, several authors have describe the destruction of this sulfa drug by photolysis [42], ozonization [43], persulfate oxidation [43], ferrate(VI) [44] and AOPs like UV/H_2O_2 [42], photocatalysis [45], radiolysis [46], Fenton [43,47,48], photo-Fenton [48] and anodic Fenton treatment [33]. It has been reported that sulfamethazine is oxidized, but not reduced, on rotating disk electrodes of Au and Pt [49] and that it depicts a well-resolved irreversible oxidation peak on BDD by cyclic voltammetry, with a higher current signal than that obtained on a glassy carbon electrode [50,51].

In this paper, we present a careful and exhaustive study on the AO treatment of sulfamethazine solutions in acidic medium using a BDD anode and a stainless steel (SS) cathode. Experiments were carried out with an undivided or divided cell under comparable conditions in order to test the oxidation ability of each electrolytic system. The influence of pH in the range 2.0–6.0, current density (j) from 33.3 to $150\,mA\,cm^{-2}$ and sulfamethazine concentration between 193 and $1930\,mg\,dm^{-3}$ on the degradation rate, mineralization degree and mineralization current efficiency (MCE) was examined. The kinetics of sulfamethazine decay was followed by reversed-phase high-performance liquid chromatography (HPLC). Aromatic intermediates were identified by gas chromatography–mass spectrometry (GC–MS) and the evolution of generated carboxylic acids and released inorganic nitrogen ions was followed by chromatographic techniques. From detected intermediates, a reaction sequence for sulfamethazine mineralization by AO with BDD is proposed.

2. Experimental

2.1. Chemicals

Reagent grade sulfamethazine with purity > 99% was purchased from Sigma–Aldrich and used as received. Maleic, fumaric, acetic, oxalic, oxamic and formic acids were of reagent grade supplied by Merck and Panreac. Anhydrous sodium sulfate, used as background electrolyte, and sulfuric acid and sodium hydroxide, used to regulate the solution pH, were of analytical grade supplied by Fluka and Merck. All the solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm at 25 °C). Organic solvents and other chemicals used were either of HPLC or analytical grade purchased from Merck, Fluka and Avocado.

2.2. Electrolytic systems

Comparative electrolyses were conducted in an undivided or divided cylindrical tank reactor of 150 cm^3 capacity. The cell was surrounded with a double jacket where external thermostated water recirculated to maintain the solution temperature at 35 °C using a Thermo Electron Corporation HAAKE DC 10 thermostat. This temperature was the maximum value that can be applied to the tank reactor without significant water evaporation of solution during prolonged electrolysis. In both cells a 3 cm^2 BDD thin-film electrode provided by Adamant Technologies was used as the anode. The cathode was a 3 cm^2 SS (AISI 304) sheet or a SS wire for the undivided or divided cell, respectively. In the undivided cell, the BDD anode and the SS cathode were directly immersed into 100 cm^3 of the treated solution, with an interelectrode gap of 1 cm. In the divided cell, the anodic half-cell contained 100 cm^3 of the treated solution and the BDD anode, whereas the cathodic half-cell contained the SS cathode immersed into 5 cm^3 of the same background electrolyte filling a glass tube with its bottom sealed with a glass filter separator (porosity number 2) in contact with the treated solution and placed in front of the anode at a distance of about 1 cm. All the electrolyses were made at constant j provided with an Amel 2049 potentiostat–galvanostat and the potential difference between electrodes was directly measured with a Demestres 6005 digital multimeter. To remove the surface impurities of the BDD anode, it was previously polarized in 100 cm^3 of 0.05 mol dm^{-3} Na_2SO_4 at $100\,mA\,cm^{-2}$ for 60 min in the undivided cell.

Solutions of 193–1930 $mg\,dm^{-3}$ sulfamethazine of pH 2.0–6.0, initially adjusted with H_2SO_4, at j values between 33.3 and $150\,mA\,cm^{-2}$ were comparatively treated in the undivided and divided cells. In most assays, the electrolyzed solution was acidified and then, its pH was regulated each 15 min to its initial value by adding small volumes of 0.10 mol dm^{-3} NaOH. The treated solution was always stirred with a magnetic bar at 700 rpm to ensure mixing and the transport of reactants toward/from the electrodes.

2.3. Instruments and analytical procedures

The solution pH was determined with a Crison GLP 22 pH-meter. Before analysis, the aliquots withdrawn from electrolyzed solutions were filtered with 0.45 μm PTFE filters from Whatman. The mineralization of sulfamethazine solutions was monitored from their dissolved organic carbon (DOC) decay, measured with a Shimadzu VCSN TOC analyzer. Reproducible DOC values with an accuracy of ±1% were found by injecting 50 μl samples to the analyzer.

The decay kinetics for sulfamethazine was followed by reversed-phase HPLC with a Waters 600 LC fitted with a Thermo Electron Corporation Hypersil ODS 5 μm, 150 mm × 3 mm (i.d.), column at 35 °C and coupled to a Waters 996 photodiode array detector selected at λ = 264 nm. The mobile phase was a 30:70 (v/v) acetonitrile/water (phosphate buffer of pH 3) mixture at $0.6\,cm^3\,min^{-1}$. Generated carboxylic acids were detected and quantified by ion-exclusion HPLC using the same LC system fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 °C and the photodiode array detector set at λ = 210 nm. In these measurements, the mobile phase was 4 mmol dm^{-3} H_2SO_4 at $0.6\,cm^3\,min^{-1}$.

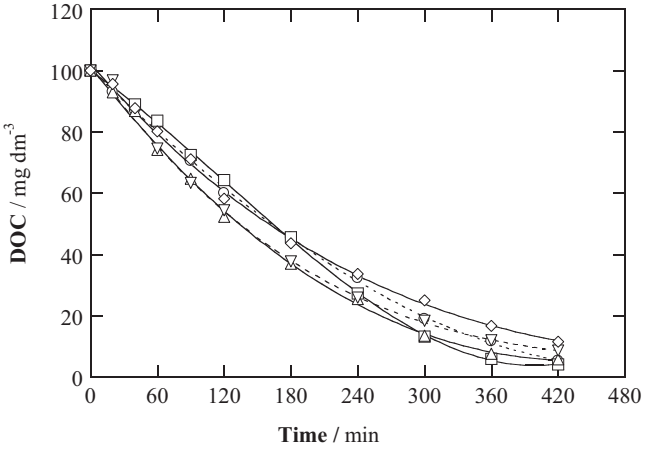


Fig. 1. Influence of pH on DOC decay with electrolysis time for 100 cm^3 of a 193 mg dm^{-3} sulfamethazine solution in 0.05 mol dm^{-3} Na_2SO_4 treated by anodic oxidation (AO) in an undivided BDD/SS cell at 100 mA cm^{-2} and 35 °C. Solution pH: (○) 2.0, (□) 3.0, (△) 4.0, (▽) 5.0 and (◊) 6.0.

NH_4^+ and NO_3^- ions were detected in electrolyzed solutions by ionic chromatography with a Shimadzu 10 Avp LC coupled to a Shimadzu CDD 10 Avp conductivity detector. The NH_4^+ content was measured with a Shodex IC YK-421, 125 mm × 4.6 mm (i.d.), cation column at 40 °C and a mobile phase of 5.0 mmol dm^{-3} tartaric acid, 2.0 mmol dm^{-3} dipicolinic acid, 24.2 mmol dm^{-3} boric acid and 15.0 mmol dm^{-3} crown ether solution at 1.0 cm^3 min^{-1}. To measure the NO_3^- concentration, a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.), anion column at 40 °C was used under circulation of a 2.4 mmol dm^{-3} tris(hydroxymethyl)aminomethane and 2.5 mmol dm^{-3} phthalic acid solution at 1.5 cm^3 min^{-1} as mobile phase.

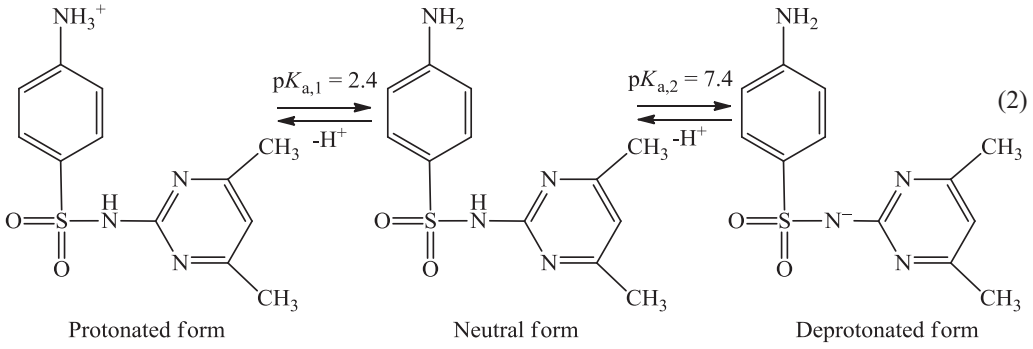
Aromatic intermediates formed after 40 min of AO treatment of 193 mg dm^{-3} sulfamethazine solutions in the undivided and divided cells at pH 3.0 and 66.6 mA cm^{-2} were identified by GC-MS. These analyses were performed with a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Hewlett-Packard 5989 A mass spectrophotometer operating in electron impact mode at 70 eV. The mass spectra were identified with a NIFT05 data library. The organic components of 15 cm^3 of each electrolyzed solution were extracted with 45 cm^3 of dichloromethane (in three times of 15 cm^3 each). The resulting organic solution was dried over about 2 g Na_2SO_4, filtered and rotavaporated to reduce its volume up to 1 cm^3. This sample was: (i) directly analyzed by GC–MS using a polar J&W Innowax 0.25 μm, 30 m × 0.25 mm (i.d.), column with a temperature ramp of 50 °C for 3 min, 5 °C min^{-1} up to 260 °C and hold time 20 min, and a temperature for the injector and detector of 240 and 260 °C, respectively, and (ii) treated with 1 cm^3 of acetic anhydride under stirring and heating at 50 °C for 30 min and the resulting acetate derivatives were identified by GC–MS using a non-polar J&W DB-5MS 0.25 μm, 30 m × 0.25 mm (i.d.), column with a temperature ramp of 50 °C for 3 min, 5 °C min^{-1} up to 300 °C and hold time 5 min, and a temperature for the injector and detector of 250 and 290 °C, respectively.

3. Results and discussion

3.1. Influence of pH on sulfamethazine mineralization in the undivided cell

A first series of experiments was performed to check the role of pH over the sulfamethazine mineralization in the undivided BDD/SS cell. These assays were carried out using 193 mg dm^{-3} substrate solutions with a common Na_2SO_4 concentration of 0.05 mol dm^{-3} in the pH range 2.0–6.0 at 100 mA cm^{-2} and 35 °C and their DOC abatement was measured for a time of 420 min. No apparent electrodeposition of reduction products at the SS cathode was observed in all these trials, indicating that sulfamethazine can undergo electrochemical incineration at the BDD anode. In the electrolyses starting from pH 2.0 and 3.0, the solution pH decreased very slightly with time and it was not controlled, but operating in the pH interval 4.0–6.0, a more rapid acidification of solutions was found, probably due to the formation of acidic intermediates [5,8,22,23], and solution pH was regulated to its initial value with 0.10 mol dm^{-3} NaOH.

Fig. 1 illustrates the DOC-time plots determined for the above AO treatments. As can be seen, DOC was removed at similar rate for all pH values and the solutions attained an almost total mineralization with 90–96% DOC decay in 420 min of electrolysis. These results indicate an analogous reactivity of sulfamethazine and its intermediates with a similar amount of BDD(•OH) formed at the anode regardless of the acidic medium used. This suggests that the substrate always presents the same electroactive species. Sulfamethazine is an ampholyte with both a basic (—NH_2) and an acidic (—SO_2—NH—R) group. In aqueous medium, its protonated, neutral and deprotonated forms are in acid–base equilibrium according to the following reactions [52]:



(2)

(2)

Although the neutral form of sulfamethazine predominates in solution from pH 2.4 to 7.4, the electroactive species throughout the pH range of our experiments is probably the protonated conjugate, due to the highly acidic medium near the BDD anode.

From the above considerations, a pH 3.0 was set for the solutions with 0.05 mol dm^{-3} Na_2SO_4 treated in the undivided cell to further examine the effect of current density and substrate content on the mineralization process of sulfamethazine, because no pH regulation was required. However, when comparative electrolyses were conducted in the anodic compartment of the divided BDD/SS cell, two problems were found. On one hand, the large potential penalty originated by the glass filter separator between its half-cells avoided the application of j values > 70 mA cm^{-2} from the available

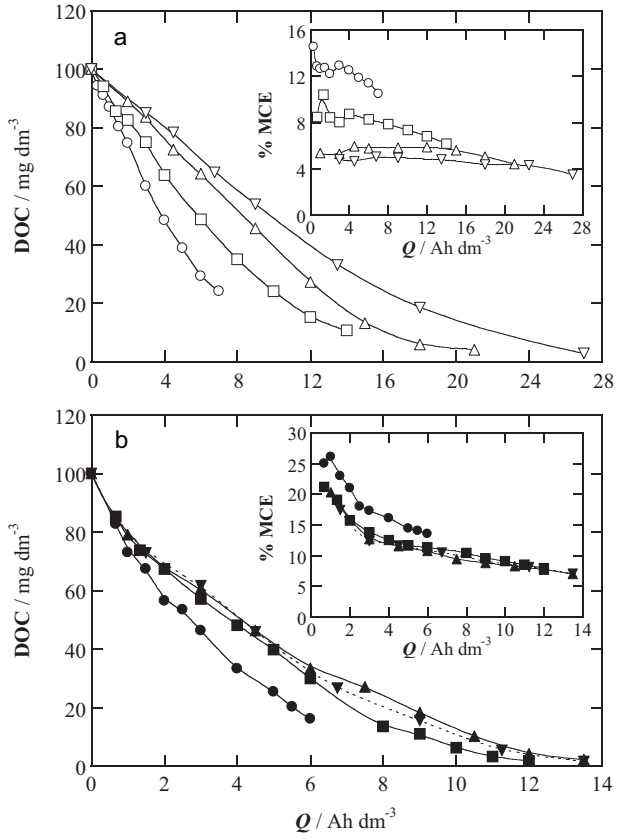


Fig. 2. Effect of current density on DOC removal with specific charge for the AO degradation of 100 cm^3 of a 193 mg dm^{-3} sulfamethazine solution in: (a) 0.05 mol dm^{-3} Na_2SO_4 using an undivided cell and (b) 0.50 mol dm^{-3} Na_2SO_4 in the anodic compartment of a divided cell, at pH 3.0 and 35 °C. Current density: (○,●) 33.3 mA cm^{-2}, (□,■) 66.6 mA cm^{-2}, (△,▲) 100 mA cm^{-2} and (▽,▼) 150 mA cm^{-2}. The inset panels present the corresponding mineralization current efficiency calculated from Eq. (9).

power source of 30 V. To solve this problem, the background electrolyte of solutions electrolyzed in the divided cell was increased to 0.50 mol dm^{-3} Na_2SO_4, thus raising their conductivity and allowing operating up to j values as high as 150 mA cm^{-2}. In previous work [53], it was shown that the rise in Na_2SO_4 concentration from 0.05 to 0.50 mol dm^{-3} did not vary significantly the oxidation power of BDD on the organic matter in AO, mainly causing greater conductivity and lower ohmic drop of the solution. On the other hand, the solutions of pH 3.0 degraded in the anodic compartment of the divided cell were rapidly acidified as a result of the release of protons during the water discharge to O_2 at BDD initiated by reaction (1) and followed by reaction (3) [8,19]:

$$2BDD(^{\bullet}OH) \rightarrow 2BDD + O_2(g) + 2H^+ + 2e^- \quad (3)$$

Since the anodically generated protons were not neutralized by their consumption (or OH^- production) at the cathode, the solution pH was continuously controlled to its initial value of pH 3.0 by adding 0.10 mol dm^{-3} NaOH.

3.2. Effect of current density on sulfamethazine mineralization in the undivided and divided cells

The applied j is a key variable in AO because it controls the amount of reactive BDD(•OH) generated at the anode. Its effect on sulfamethazine mineralization was checked by treating a 193 mg dm^{-3} substrate solution of pH 3.0 between 33.3 and 150 mA cm^{-2} at 35 °C. Fig. 2a and b depicts the change of DOC with specific charge Q (Ah dm^{-3}) obtained for the trials performed in the undivided and divided cells, respectively. A slower DOC abatement with Q as j rises can be observed in both cells. However, the DOC decay became faster with electrolysis time, reaching a greater mineralization degree at shorter time. For the undivided cell, Fig. 2a shows that an almost total mineralization with 96–97% DOC removal was only found for 100 mA cm^{-2} at 420 min of electrolysis (21 Ah dm^{-3}) and more quickly for 150 mA cm^{-2} in 360 min (27 Ah dm^{-3}). In contrast, Fig. 2b evidences that 98% DOC decay was obtained in the divided cell after 360 min at 66.6 mA cm^{-2} (12 Ah dm^{-3}), 270 min at 100 mA cm^{-2} (13.5 Ah dm^{-3}) and 180 min at 150 mA cm^{-2} (13.5 Ah dm^{-3}). The larger acceleration of DOC abatement with time when j rises is expected by the concomitant generation of more amounts of BDD(•OH) [8,17,22]. The opposite tendency related to the greater consumption in specific charge can be associated with a gradual loss in the relative quantity of BDD(•OH) formed owing to the enhancement of its waste reactions that causes the decrease in organic events inhibiting the mineralization process. These waste reactions involve, for example, oxidation to O_2 at the anode from reaction (3), dimerization to H_2O_2 from reaction (4) and reaction with H_2O_2 generating the weaker oxidizing agent hydroperoxyl radical (BDD($HO_2^{\bullet}$)) from reaction (5) [5,8,18]. In addition, a smaller relative proportion of BDD(•OH) can also be generated by the larger acceleration of reactions (6) and (7) at the BDD anode giving the weaker oxidants persulfate ion ($S_2O_8^{2-}$) and ozone, respectively [10,22,53].

$$2BDD(^{\bullet}OH) \rightarrow 2BDD + H_2O_2 \quad (4)$$

$$BDD(^{\bullet}OH) + H_2O_2 \rightarrow BDD(HO_2^{\bullet}) + H_2O \quad (5)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (6)$$

$$3H_2O \rightarrow O_3(g) + 6H^+ + 6e^- \quad (7)$$

The fact that a similar DOC decay is found for 100 and 150 mA cm^{-2} using the divided cell (see Fig. 2b) suggests the existence of a mass-transfer control of the mineralization process at high j values owing to the greatest oxidation power of this system.

The influence of j on the mineralization process of sulfamethazine in the undivided and divided cells can be better interpreted from MCE. Note that the incineration of sulfamethazine to carbon dioxide involves the loss of inorganic ions such as sulfate, ammonium and nitrate ions. The production of sulfate ion is expected from the oxidation behavior of sulfa compounds [18,54,55]. Moreover, a major conversion of its initial N into NH_4^+ than NO_3^- ion was found, as will be discussed below. Based on these considerations, the overall mineralization reaction for sulfamethazine can be written, as first approach, as follows:

$$C_{12}H_{14}N_4O_2S + 26H_2O \rightarrow 12CO_2 + 4NH_4^+ + SO_4^{2-} + 50H^+ + 52e^- \quad (8)$$

The mineralization current efficiency value for each assay at current I (A) and time t (h) was then estimated from Eq. (9) [19]:

$$MCE\ (\%) = \frac{nFV_s\Delta(DOC)_{exp}}{4.32 \times 10^7 mIt} \times 100 \quad (9)$$

where n is the number of electrons consumed per molecule (52 electrons from reaction (8)), F is the Faraday constant (96,487 C mol^{-1}), V_s is the solution volume (dm^3), $\Delta(DOC)_{exp}$ is the experimental DOC decay (mg dm^{-3}), 4.32×10^7 is an homogenization factor (3600 s h^{-1} × 12,000 mg mol^{-1}) and m is the number of carbon atoms of sulfamethazine (12 atoms).

The MCE values calculated from Eq. (9) for the trials of Fig. 2a and b are shown in the corresponding inset panels. For the undivided cell, the efficiency always dropped with raising j as expected by the larger acceleration of waste reactions (3)–(7). Greater MCE values can be observed at each j of the divided cell. However, these efficiencies also decreased rapidly from 33.3 to 66.6 mA cm^{-2}, whereupon similar values were found up to 150 mA cm^{-2}, indicating that organics were destroyed with a similar relative quantity of

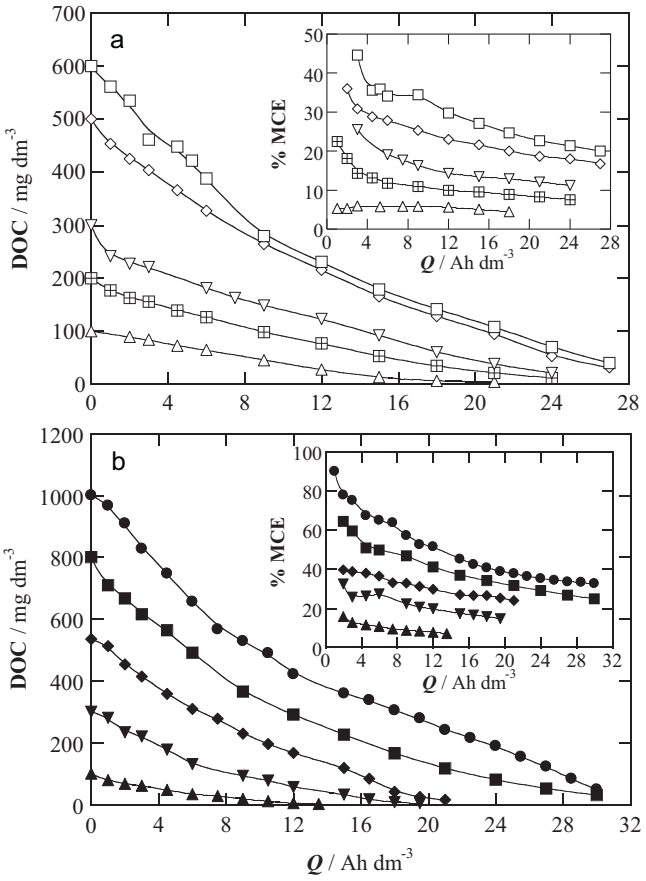


Fig. 3. Influence of sulfamethazine concentration on the variation of DOC with specific charge for the AO treatment of 100 cm^3 solutions at pH 3.0, 100 mA cm^{-2} and 35 °C. (a) Undivided and (b) divided cell. Substrate concentration: (△,▲) 193 mg dm^{-3}, (⊞) 386 mg dm^{-3}, (▽,▼) 579 mg dm^{-3}, (◇,◆) 965 mg dm^{-3}, (□) 1158 mg dm^{-3}, (■) 1544 mg dm^{-3} and (●) 1930 mg dm^{-3}. The corresponding mineralization current efficiency is depicted in the inset panels.

BDD(•OH). In most cases, the efficiency decreased slowly with Q and also electrolysis time, as a result of the progressive loss of organic matter and the formation of more recalcitrant intermediates like carboxylic acids [5,8].

Results of Fig. 2a and b evidence that the AO treatment of sulfamethazine is more powerful in the divided cell at all applied j. The quicker DOC removal with higher efficiency found for this cell is indicative of greater oxidation ability of the BDD anode in it than in the undivided one. This can seem surprising since intuitively one might expect a similar oxidation power in both cells at the same j because organics are mineralized under the action of BDD(•OH) formed at the anode. However, each electrode of the undivided cell comparatively acted over twice the volume of treated solution [33], causing a decrease of the oxidation ability of electrogenerated BDD(•OH) since it is more rapidly wasted by non-oxidizing reactions (3)–(5), which makes the mineralization process more inefficient. The cathodic reduction of some intermediates, as well as of weaker generated oxidants (H_2O_2, $S_2O_8^{2-}$ ion, etc.), could also explain the loss of performance of the undivided cell.

3.3. Effect of sulfamethazine concentration on the AO behavior

Fig. 3a and b illustrates the influence of sulfamethazine concentration between 193 and 1930 mg dm^{-3} on its mineralization process by AO using the undivided and divided cells at pH 3.0 and 100 mA cm^{-2}, respectively. An almost total mineralization of sulfamethazine can be observed in both cells for all drug concentrations. For the undivided cell (see Fig. 3a), the specific charge for attaining 93–97% DOC decay in the interval 193–1158 mg dm^{-3} varied between 21 and 27 Ah dm^{-3} with times between 420 and 540 min, whereas for the divided cell (see Fig. 3b), lower specific charge between 13.5 and 30 Ah dm^{-3} and shorter times between 270 and 600 min were required to reach 95–98% DOC removal for 193–1930 mg dm^{-3}. This behavior corroborates again that the divided cell is more powerful to mineralize sulfamethazine. Nevertheless, results of Fig. 3a and b show that at a given Q, higher amount of DOC was removed at greater substrate content, making the process more efficient. For example, after the consumption of 9 Ah dm^{-3} in the divided cell, a greater DOC reduction in 82, 270 and 470 mg dm^{-3} was found starting from 193, 965 and 1930 mg dm^{-3} of sulfamethazine. This tendency can be associated with the destruction of greater amounts of organics by a larger proportion of BDD(•OH) due to the decay in rate of its waste reactions (3)–(7).

The inset panels of Fig. 3a and b highlight the expected increase in MCE with raising sulfamethazine concentration in both cells. The high MCE values obtained for contents ≥ 965 mg dm^{-3} indicate the great oxidation power of AO with BDD to mineralize high concentrations of the drug. The highest efficiency was found for the treatment of a 1930 mg dm^{-3} substrate solution in the divided cell, which dramatically decayed from 90% at 1 Ah dm^{-3} to 33% at 30 Ah dm^{-3}. This loss in efficiency is due to the gradual removal of organic matter and the concomitant formation of large quantities of intermediates that are more difficultly oxidized with BDD(•OH). However, this phenomenon is less significant with decreasing initial substrate content, indicating that the oxidation ability of reactive BDD(•OH) over all organics becomes more uniform during AO treatment.

3.4. Influence of current density and substrate concentration on the decay kinetics of sulfamethazine

The removal rate of sulfamethazine in the undivided and divided cells under the above experimental conditions was followed by reversed-phase HPLC, where it exhibited a well-defined peak at retention time of 2.8 min. A reduction experiment was also made by treating 100 cm^3 of a 193 mg dm^{-3} sulfamethazine solution in 0.50 mol dm^{-3} Na_2SO_4 at regulated pH 3.0, 66.6 mA cm^{-2} and 35 °C in the cathodic compartment of a divided cell containing a 3 cm^2 SS cathode, but no drug decay was found. This indicates that the drug is only oxidized at the anode under the action of BDD(•OH), but not reduced in the cathode, in the trials performed with the undivided cell. Under these conditions, however, the cathodic reduction of some intermediates formed cannot be excluded.

Fig. 4a and b shows the complete removal of sulfamethazine from a 193 mg dm^{-3} substrate solution of pH 3.0 between 33.3 and 150 mA cm^{-2} and at 35 °C in both electrolytic systems. At each j, a much shorter time was needed for its overall disappearance in the divided cell, in agreement with the higher oxidation ability of the BDD anode in this cell than in the undivided one. Higher j always caused a much quicker decay of the drug, which can be explained by the production of greater amount of the oxidant BDD(•OH) from reaction (1). By comparing these results with those of Fig. 2a and b, one can conclude that sulfamethazine always disappears in much less time than that required for its almost total mineralization, as expected if intermediates that are more recalcitrant with BDD(•OH) are generated. The above concentration decays were analyzed by kinetic equations related to simple reaction orders and good linear correlations were found for a pseudo-first-order reaction, as illustrated in the inset panels of Fig. 4a and b. Table 1 collects the pseudo-first-order rate constant (k_1) obtained from this analysis. As expected, k_1 increases with increasing j and is comparatively greater for the divided cell. This behavior suggests that

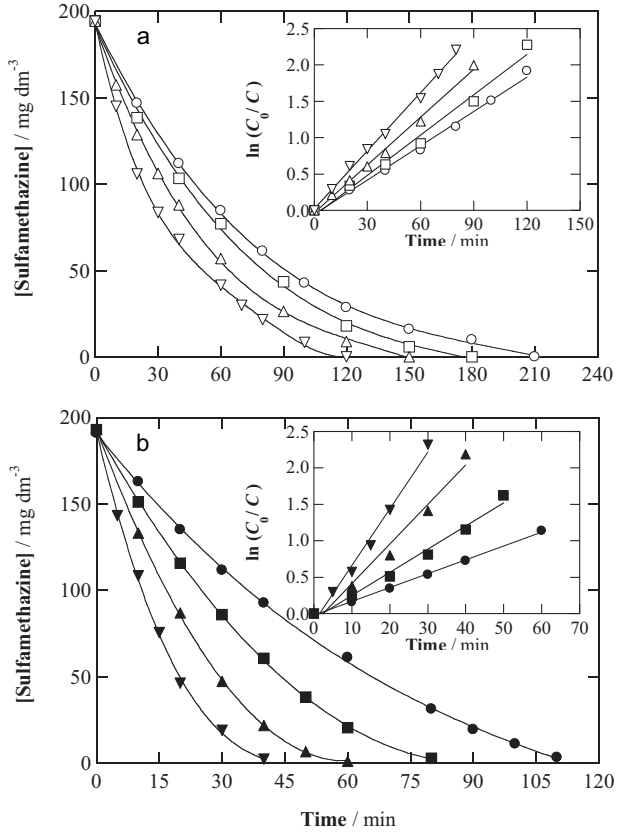


Fig. 4. Effect of current density on the decay of sulfamethazine concentration by AO for 100 cm^3 of a 193 mg dm^{-3} drug solution at pH 3.0 and 35 °C. (a) Undivided and (b) divided cell. Current density: (○,●) 33.3 mA cm^{-2}, (□,■) 66.6 mA cm^{-2}, (△,▲) 100 mA cm^{-2} and (▽,▼) 150 mA cm^{-2}. The inset panels present the kinetic analysis assuming that sulfamethazine follows a pseudo-first-order reaction.

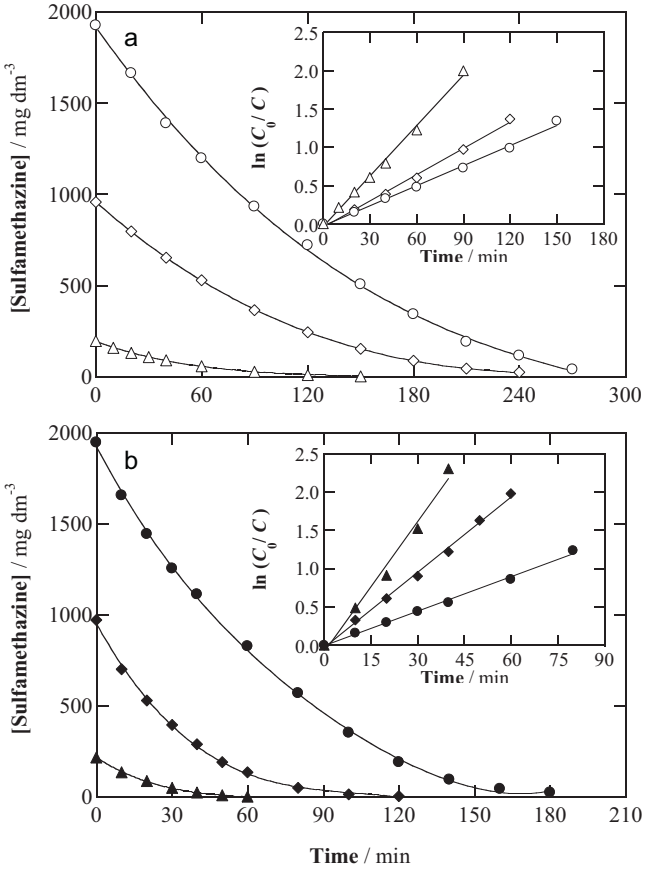


Fig. 5. Effect of sulfamethazine content on its decay for the AO treatment of 100 cm^3 of solutions at pH 3.0, 100 mA cm^{-2} and 35 °C. (a) Undivided and (b) divided cell. Sulfamethazine concentration: (△,▲) 193 mg dm^{-3}, (◊,♦) 965 mg dm^{-3} and (○,●) 1930 mg dm^{-3}. The kinetic analysis considering that the drug follows a pseudo-first-order reaction is shown in the inset panels.

sulfamethazine is oxidized with a constant amount of BDD(•OH) at the anode, which is more largely produced at higher *j*.

The influence of sulfamethazine concentration on its decay kinetics is highlighted in Fig. 5a and b for the undivided and divided cells, respectively. In these trials, 193, 965 and 1930 mg dm^{-3} of the drug were comparatively removed at pH 3.0 and 100 mA cm^{-2}. These results show that the BDD anode is potent enough to rapidly remove the highest concentration of 1930 mg dm^{-3} in both cells, needing 180 min in the divided one and a much longer time of about 270 min in the undivided one. The excellent linear correlations found from the kinetic analysis of these data assuming a pseudo-first-order reaction for sulfamethazine are presented in the inset panels of Fig. 5a and b. The k_1 values thus obtained, also collected in Table 1, dropped quickly with increasing drug content, suggesting that a larger proportion of generated BDD(•OH) is consumed to attack the intermediates formed, as expected from the concomitant increase in MCE of their AO processes shown in the inset panels of Fig. 3a and b.

Table 1
Pseudo-first-order rate constant determined for the sulfamethazine decay by means of AO using solutions with either 0.05 mol dm^{-3} or 0.50 mol dm^{-3} Na_2SO_4 in an undivided or divided BDD/SS cell, respectively, at pH 3.0 and 35 °C under different conditions.

Cell	[Sulfamethazine] (mg dm^{-3})	*j* (mA cm^{-2})	$k_1 \times 10^4$ (s^{-1})	R^2
Undivided	193	33.3	2.6	0.994
		66.6	3.2	0.989
		100	3.7	0.996
		150	4.5	0.997
	965	100	1.9	0.995
	1930		1.5	0.995
Divided	193	33.3	3.7	0.998
		66.6	5.3	0.989
		100	9.0	0.986
		150	12.9	0.990
	965	100	5.4	0.996
	1930		2.5	0.996

3.5. Identification and evolution of intermediates

Solutions of 193 mg dm^{-3} of sulfamethazine of pH 3.0 were degraded in the undivided and divided cells at 66.6 mA cm^{-2} for 40 min to detect its primary aromatic intermediates by GC–MS using either direct extraction with dichloromethane or esterification with acetic anhydride. Table 2 summarizes the products detected by this technique and their characteristics. As can be seen, of all the primary aromatics detected, only 4,6-dimethyl-2-pyrimidinamine was identified in the undivided cell, probably because other primary aromatics were oxidized while were generated during the slow sulfamethazine decay (see Fig. 4a). In contrast, apart from the above compound, 1,2-benzenediol (catechol), 1,4-benzenediol (hydroquinone) and *p*-benzoquinone were detected in the anodic compartment of the divided cell since they were more rapidly accumulated during the much faster decay of the drug under the stronger oxidation conditions of electrogenerated BDD(•OH) (see Fig. 4b). While 1,2-benzenediol and 1,4-benzenediol are two dihydroxylated derivatives of the drug, *p*-benzoquinone is the oxidation product of 1,4-benzenediol

Table 2
Oxidation products detected during the AO treatment of a 193 mg dm^{-3} sulfamethazine solution at pH 3.0, 66.6 mA cm^{-2} and 35 °C with an undivided or divided BDD/SS cell by GC–MS and ion-exclusion HPLC.

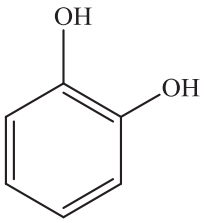
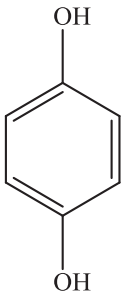
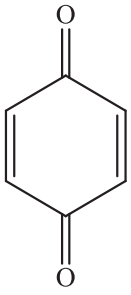
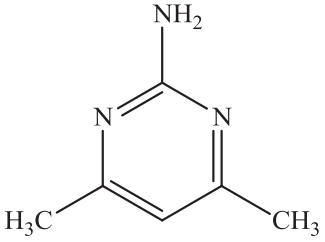
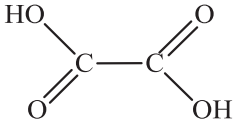
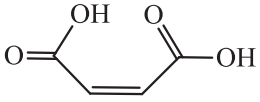
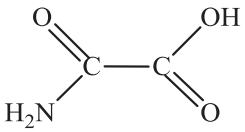
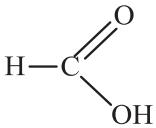
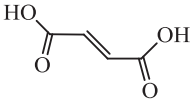
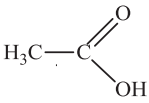
Compound	Molecular formula	Analytical technique	Retention time (min)	Molecular mass (g mol^{-1})
1,2-Benzenediol[a]		GC–MS with esterification	17.23	194[b]
1,4-Benzenediol[a]		GC–MS with extraction	43.98	110
p-Benzoquinone[a]		GC–MS with extraction	7.95	108
4,6-Dimethyl-2-pyrimidinamine[c]		GC–MS with extraction	26.36	123
Oxalic acid[c]		HPLC	6.9	90
Maleic acid[a]		HPLC	8.3	116
Oxamic acid[c]		HPLC	9.4	89
Formic acid[c]		HPLC	13.7	46

Table 2 (*Continued*)

Compound	Molecular formula	Analytical technique	Retention time (min)	Molecular mass ($g\,mol^{-1}$)
Fumaric acid[c]		HPLC	14.7	116
Acetic acid[d]		HPLC	15.2	60

[a] Only detected in a divided cell.
[b] Detected as ester by reaction with two acetic acid molecules (diacetate ester).
[c] Detected in both cells.
[d] Only detected in an undivided cell.

and 4,6-dimethyl-2-pyrimidinamine proceeds from the release of the lateral sulfonamide group of sulfamethazine with loss of the sulfonyl (SO_2) group.

Ion-exclusion chromatograms of the above treated solutions exhibited well-defined peaks related to fumaric, oxalic, oxamic and formic acid, whose characteristics are listed in Table 2. This table also depicts that maleic acid was only identified in the divided cell, whereas acetic acid was only detected in the undivided one. Maleic, its *trans*-isomer fumaric and acetic acids are expected to be formed from the cleavage of the benzenic ring of intermediates, being oxidized to oxalic and formic acids [10,53]. Oxamic acid could be produced from the breaking of aromatic moieties with a $-NH_2$ group and 4,6-dimethyl-2-pyrimidinamine degradation. Oxalic, oxamic and formic acids are ultimate acids that are directly converted into CO_2 [5,8,18,31].

Maleic, fumaric and acetic acids were poorly accumulated (<1.8 $mg\,dm^{-3}$) usually appearing between 40 and 180 min in the undivided and/or divided cell. In contrast, Fig. 6a highlights that oxalic, oxamic and formic acids remained in the solution after 420 min of AO treatment in the undivided cell with contents of 3.4, 0.3 and 14.9 $mg\,dm^{-3}$, respectively, corresponding to 4.9 $mg\,dm^{-3}$ DOC, a value much lower than 10.4 $mg\,dm^{-3}$ DOC found for the final electrolyzed solution (see Fig. 2a). This evidences the formation of higher amounts of other undetected recalcitrant organics during prolonged electrolysis. In contrast, Fig. 6a shows that in the divided cell, oxamic and oxalic acids disappeared in 270 and 300 min, respectively, whereas formic acid persisted up to 390 min, i.e. when the solution DOC was reduced by 98% (see Fig. 2b). That means that other final recalcitrant organics, which are persistent in the undivided cell, can also be efficiently removed in the divided one. The higher oxidation power of the divided cell can then be explained by the quicker decay of the drug (see Figs. 4 and 5), ultimate carboxylic acids (see Fig. 6a) and other undetected recalcitrant derivatives compared to those of the undivided one.

The mineralization of *N*-compounds by AO is expected to be accompanied by the release of nitrogen inorganic ions like NH_4^+ and NO_3^- [14,26,54]. The generation of both ions during the degradation of 193 $mg\,dm^{-3}$ sulfamethazine (38.9 $mg\,dm^{-3}$ of N) at pH 3.0 was confirmed by ionic chromatography, without detecting the presence of other inorganic nitrogen ions such as NO_2^-. Nevertheless, the trial in the divided cell was performed with 0.05 $mol\,dm^{-3}$ Na_2SO_4 at $j = 66.6\,mA\,cm^{-2}$ since greater contents of this salt caused the overlapping of the chromatographic peak of Na^+ or SO_4^{2-} ion with that of NH_4^+ or NO_3^- ion, respectively. Fig. 6b shows that the profiles of both NH_4^+ and NO_3^- ions are quite similar for the undivided and divided cells. All the NH_4^+ ion released is practically accumulated for the first 60–90 min of electrolysis in both cells, whereas the release of NO_3^- ion takes place gradually during both treatments. A similar but much larger accumulation of NH_4^+ than NO_3^- ion in both processes can be observed, as proposed in reaction (8). At 360 min of treatment in the divided cell, the final solution contained 40 $mg\,dm^{-3}$ of NH_4^+ ion (80% of initial N) and 18 $mg\,dm^{-3}$ of NO_3^- ion (10% of initial N), values very similar to 41 (82% of initial N) and 20 (11% of initial N) $mg\,dm^{-3}$ of such ions determined after 420 min of electrolysis in the undivided cell. This mean that a small proportion of initial N, between 7 and 10%, was not mineralized but loss as volatile *N*-compounds, probably N_xO_y species, in both cells.

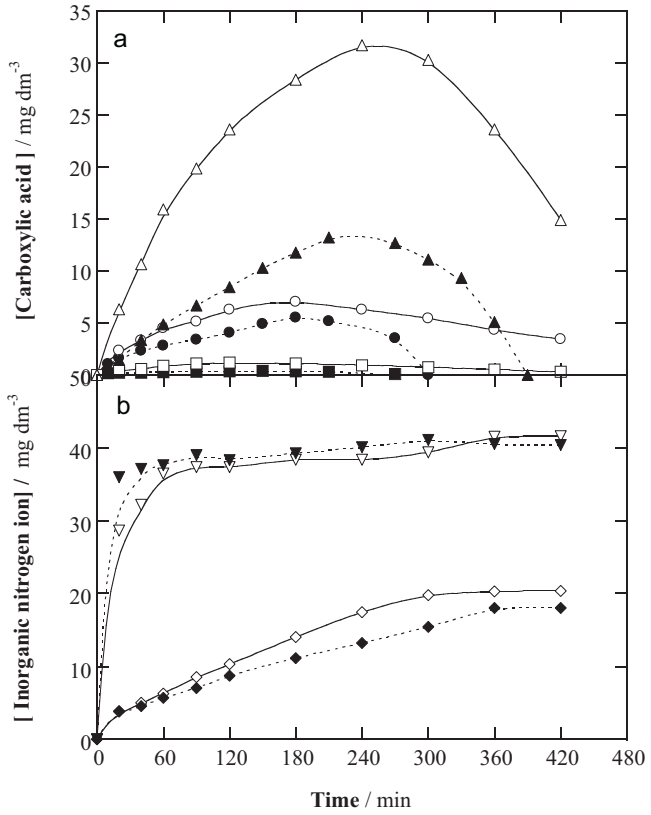


Fig. 6. Time course of the concentration of: (a) ultimate carboxylic acids and (b) inorganic nitrogen ions detected during the AO degradation of 100 cm^3 of a 193 $mg\,dm^{-3}$ sulfamethazine solution at pH 3.0, 66.6 $mA\,cm^{-2}$ and 35 °C. In (a) (○,●) oxalic, (□,■) oxamic and (△,▲) formic acids. In (b) (▽,▼) NH_4^+ and (◊,♦) NO_3^- ion. (○,□,△,▽,◊) Undivided cell. Divided cell with (●,■,▲) 0.50 or (▼,♦) 0.05 $mol\,dm^{-3}$ Na_2SO_4.

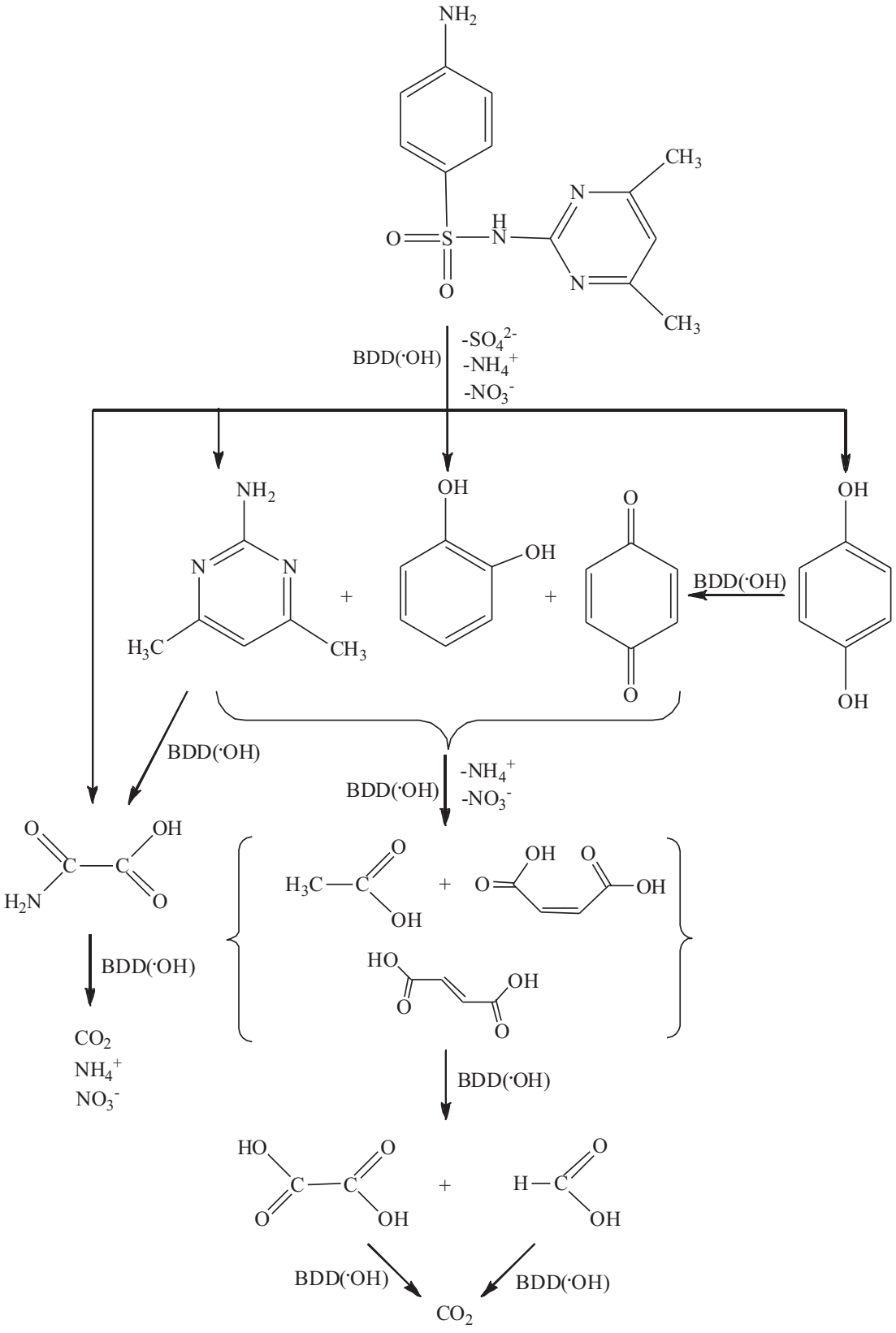


Fig. 7. Reaction sequence proposed for the electrochemical incineration of sulfamethazine in acidic medium by AO with a BDD anode.

3.6. Reaction sequence for sulfamethazine mineralization

On the basis of intermediates detected, the reaction pathway of Fig. 7 is proposed for the electrochemical incineration of sulfamethazine in acidic medium by AO with BDD, where it is considered that organics are oxidized by BDD(•OH) generated from reaction (1). The sequence is initiated by the attack of this radical on sulfamethazine giving rise to hydroxylation with loss

of its both lateral amino and sulfonamide groups. Dihydroxylated derivatives like 1,2-benzenediol and 1,4-benzenediol, which is subsequently oxidized to *p*-benzoquinone, are thus formed. The degradation of the released sulfonamide group leads to 4,6-dimethyl-2-pyrimidinamine with loss of the sulfonyl group, which is converted into SO_4^{2-} ion. The deamination reaction of sulfamethazine and the subsequent degradation of 4,6-dimethyl-2-pyrimidinamine yield NH_4^+ ion along with NO_3^- ion in minor proportion. The release of the lateral sulfonamide group alone from sulfamethazine produces *N*-derivatives that generate oxamic acid. This acid can also be formed from the oxidation of 4,6-dimethyl-2-pyrimidinamine and it is further converted into CO_2 and NH_4^+ and NO_3^- ions [31]. The cleavage of the benzenic ring of aromatic derivatives gives a mixture of carboxylic acids like maleic, fumaric and acetic, which are oxidized to the ultimate oxalic and formic acids that are finally converted into CO_2.

4. Conclusions

AO with BDD is a powerful EAOP for the degradation of acidic solutions of sulfamethazine. The oxidation ability of this anode is much greater using a divided than an undivided cell. A similar degradation rate was found in the pH interval 2.0–6.0, as expected if sulfamethazine and its intermediates are removed at analogous rate in all acidic media. The AO treatment of a 193 mg dm^{-3} drug solution in 0.50 mol dm^{-3} Na_2SO_4 at controlled pH 3.0 in the anodic half-cell of the divided BDD/SS cell yielded an almost total mineralization with 98% DOC reduction for $j \geq 66.6$ mA cm^{-2}. A similar mineralization degree was obtained using the undivided BDD/SS cell with 0.05 mol dm^{-3} Na_2SO_4 at $j \geq 100$ mA cm^{-2}, but with slower degradation and lower MCE due to the smaller oxidation ability of generated BDD(•OH). The increase in *j* accelerated the mineralization process in both cells, but their efficiency dropped by the larger enhancement of parasitic reactions of BDD(•OH). Greater sulfamethazine content decreased the percentage of DOC decay with a higher efficiency owing to the inhibition of non-oxidizing reactions of BDD(•OH). The decay of sulfamethazine concentration always verified a pseudo-first-order reaction, being faster in the divided cell by its higher oxidation power. The pseudo-first-order rate constant thus obtained rose with increasing *j* and decreasing drug content. GC–MS analysis of solutions electrolyzed in the most oxidant divided cell allowed the identification of aromatic intermediates such as 1,2-benzenediol, 1,4-benzenediol, *p*-benzoquinone and 4,6-dimethyl-2-pyrimidinamine. Generated carboxylic acids like maleic, fumaric, acetic, formic, oxalic and oxamic were detected and quantified by ion-exclusion HPLC. The initial N was mainly released as NH_4^+ ion and in much smaller proportion as NO_3^- ion, as confirmed by ionic chromatography. A reaction pathway for sulfamethazine mineralization in acidic medium by AO considering BDD(•OH) as main oxidant and involving all detected intermediates is proposed.

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