Advanced oxidation of real sulfamethoxazole + trimethoprim formulations using different anodes and electrolytes

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A commercial sulfamethoxazole + trimethoprim formulation has been degraded in 0.050 M Na₂SO₄ at pH 3.0 by electrochemical oxidation with electrogenerated H₂O₂ (EO-H₂O₂), electro-Fenton (EF), photoelectro-Fenton with a 6-W UVA lamp (PEF) and solar photoelectro-Fenton (SPEF). The tests were performed in an undivided cell with an IrO₂-based, Pt or boron-doped diamond (BDD) anode and an air-diffusion cathode for H₂O₂ electrogeneration. The anode material had little effect on the accumulated H₂O₂ concentration. Both drugs always obeyed a pseudo-first-order decay with low apparent rate constant in EO-H₂O₂. Much higher values were found in EF, PEF and SPEF, showing no difference because the main oxidant was always •OH formed from Fenton’s reaction between H₂O₂ and added Fe²⁺. The solution mineralization increased in the sequence EO-H₂O₂ < EF < PEF < SPEF regardless of the anode. The IrO₂-based and Pt anodes behaved similarly but BDD was always more powerful. In SPEF, similar mineralization profiles were found for all anodes because of the rapid removal of photoactive intermediates by sunlight. About 87% mineralization was obtained as maximum for the powerful SPEF with BDD anode. Addition of Cl⁻ enhanced the decay of both drugs due to their quicker reaction with generated active chlorine, but the formation of persistent chloroderivatives decelerated the mineralization process. Final carboxylic acids like oxalic and oxamic were detected, yielding Fe(III) complexes that remained stable in EF with BDD but were rapidly photolyzed in SPEF with BDD, explaining its superior mineralization ability.

**Keywords**: Electrochemical oxidation; Electro-Fenton; Photoelectro-Fenton; Sulfamethoxazole; Sunlight; Trimethoprim
1. Introduction

Over the last two decades, there has been an increasing concern about the presence of substances classified as emerging contaminants in water. Their long-term effects on humans or aquatic organisms are still unknown. Pharmaceuticals, which are defined as prescription, over the counter and veterinary drugs to prevent or treat human and animal diseases, are among these pollutants (Thiele-Bruhn and Beck, 2005; Ebele et al., 2017). In particular, the wide use of antibiotics favors their presence in the aquatic environment and, even at trace concentrations, they may induce the development of resistant bacteria or genes (Sirès and Brillas, 2012; Dias et al., 2014).

Sulfamethoxazole (C₁₀H₁₁N₃O₃S, 4-amino-N-(5-methyl-3-isoxazolyl)benzene-sulfonamide) and trimethoprim (C₁₄H₁₈N₄O₃, 2,4-diamino-5-(3,4,5-trimethoxybenzyl)-pyrimidine) (see molecular structures in Fig. 1) are two drugs prescribed for treating bacterial infections in humans, being commonly available as a unique commercial formulation (Dias et al., 2014). Approximately 15% and 60% of sulfamethoxazole and trimethoprim are excreted from the human body in their original form. As a result, metabolites and non-metabolized residues of both drugs have been detected in surface water at μg L⁻¹ levels (Hirsch et al., 1999).

Most drugs from a wide spectrum of therapeutic classes enter in natural aquatic environments mainly conveyed by the effluents of sewage treatment plants due to the inefficacy of conventional water treatment technologies. Sulfamethoxazole and trimethoprim have been degraded by biological treatments, but after relatively long residence times (3-20 days) (Pérez et al., 2005). The degradation of both drugs by photolysis has been reported as well (Ryan et al., 2011). The main drawback of these processes is the production of metabolites that could be more recalcitrant or toxic than parent molecules.
Electrochemical advanced oxidation processes (EAOPs) such as electrochemical oxidation (EO), EO with electrogenerated H₂O₂ (EO-H₂O₂), electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) have been successfully applied to the remediation of wastewater containing drugs (Sirés and Brillas, 2012; Feng et al., 2013; Moreira et al., 2017). Their oxidation power is based on their ability to generate hydroxyl radical (•OH) as strong oxidant to attack the organic pollutants, which depends on parameters like electrode material, applied current and electrolyte composition. Several authors degraded synthetic sulfamethoxazole solutions by EO with a boron-doped diamond anode (BDD) in 1 M Na₂SO₄ (Martín de Vidales et al., 2012) and in chloride + sulfate mixtures (Boudreau et al., 2010) and with a mixed oxide anode (Ti/Ru₀.₃Ti₀.₇O₂) in 0.1 M NaCl at pH 3.0 (Hussain et al., 2015). Fast decay of the drug and partial mineralization were found in all cases, with formation of chloroderivatives in the presence of Cl⁻. In contrast, Dirany et al. (2010, 2011) described the total mineralization of sulfamethoxazole solutions with 0.2 mM Fe²⁺ at pH 3.0 by EF using a BDD/carbon-felt cell. Wang et al. (2011) compared the degradation of up to 300 mg L⁻¹ sulfamethoxazole in sulfate medium by EO, EO-H₂O₂, EF and PEF with UVA light using a Ti/RuO₂ anode and a carbon fiber cathode, attaining a maximum mineralization of 80% after 360 min of PEF at 0.36 A. Under similar conditions, Zhang et al. (2016) reported the same mineralization for 200 mg L⁻¹ trimethoprim after 360 min of SPEF under optimum pH 3.0, 1.0 mM Fe²⁺ and current density (j) of 18 mA cm². For this drug, optimum conditions of pH 3, j = 207 mA cm⁻² and 0.49 M Na₂SO₄ were found for the EO treatment with BDD (González et al., 2011). Mansour et al. (2015) tried to optimize the EF process with a Pt/carbon-felt cell, but they only reached 12% mineralization. Moreira et al. (2014) reported partial mineralization of near 78% by PEF and SPEF for 20 mg L⁻¹ trimethoprim in 7.0 g L⁻¹ Na₂SO₄ with 2 mg L⁻¹ Fe²⁺ at pH 3.0 using a BDD/air-diffusion cell. However, only a reduced number of articles examined the EO treatment of mixtures of drugs,
like sulfamethoxazole with ciprofloxacin in sulfate and chloride media using a BDD anode (Lan et al., 2017), with diclofenac in phosphate and sulfate media using a Pt anode (Sifuna et al., 2016) and with trimethoprim using a BDD anode (Amorim et al., 2013). In the latter case, 1.0 L of 250 mg L\(^{-1}\) sulfamethoxazole + 50 mg L\(^{-1}\) trimethoprim in 0.1 M Na\(_2\)SO\(_4\) were treated in a flow cell at 5 L min\(^{-1}\) to achieve a partial mineralization of 90\% at pH 5.0 after 3 h at \(j = 36\) mA cm\(^{-2}\). More research efforts are then required to evaluate the oxidation ability and viability of more powerful EAOPs to destroy such mixtures upon use of different anode materials and electrolytes.

This work aims to study the degradation of sulfamethoxazole + trimethoprim mixtures by EO-H\(_2\)O\(_2\), EF, PEF and SPEF. The comparative oxidation power of all these treatments with three different anodes, namely a metal oxide (IrO\(_2\) based), Pt and BDD, and an air-diffusion cathode has been examined. The decay kinetics of each drug and the mineralization degree have been analyzed to establish the best anode and the most efficient EAOP. The effect of electrolyte composition including sulfate and/or chloride has been clarified. Final carboxylic acids have been detected to explain the oxidation ability of the Fenton-based processes.

2. Experimental

2.1. Reagents

Mixtures of sulfamethoxazole + trimetrophim were prepared from the commercial formulation Bactrim\(^{\circledast}\). Analytical standards of both drugs were purchased from Sigma-Aldrich. Sodium sulfate, sodium chloride, iron(II) sulfate heptahydrate and sulfuric acid (to adjust the pH to 3.0) were of analytical grade provided by Panreac and Fischer. Ultrapure Millipore Milli-Q water (resistivity > 18 M\(\Omega\) cm) was used to prepare all solutions. Other chemicals were of analytical or HPLC grade supplied by Panreac and Riedel de H\ä{}en.
The EO-H$_2$O$_2$, EF, PEF and SPEF trials were carried out in a conventional undivided tank reactor of 200 mL capacity, surrounded with a jacket to keep the solution temperature at 30 ºC through thermostated water recirculation. Solutions of 130 mL vigorously stirred with a magnetic bar, were degraded in the cell. Three anodes of 3 cm$^2$ area were alternately used for each EAOP: a BDD thin film on Si (NeoCoat), a Pt sheet (99.99% purity, SEMPSA) and an IrO$_2$-based plate (NMT Electrodes). The latter electrode was mainly composed of IrO$_2$ with a minor proportion of Ta$_2$O$_5$ as stabilizer. A 3 cm$^2$ carbon-PTFE air-diffusion electrode from Sainergy Fuel Cell was always used as the cathode. It was mounted as previously reported (Guinea et al., 2010) and fed with air pumped at 1 L min$^{-1}$ for continuous H$_2$O$_2$ generation. The interelectrode gap was about 1 cm. Trials were made at constant $j = 33.3$ mA cm$^{-2}$ supplied by an Amel 2049 potentiostat-galvanostat. This $j$ value was selected because it is high enough to achieve a large mineralization of organics in our electrolytic system, as previously reported (Coria et al., 2014; Steter et al., 2016). The cell voltage was monitored with a Demestres 601BR digital multimeter. The EF, PEF and SPEF assays were performed in the presence of 0.50 mM Fe$^{2+}$, since this is the optimum content found for such EAOPs in this kind of cell (Ruiz et al., 2011). The PEF trials were ran by illuminating the solution with a Philips TL/6W/08 fluorescent that supplied UVA light with $\lambda_{\text{max}} = 360$ nm and power density of 5 W m$^{-2}$, measured with a Kipp&Zonen CUV 5 UV radiometer. The SPEF assays were performed for 4 h upon direct sunlight irradiation in clear and sunny days of summer 2017 in our laboratory of Barcelona, starting at noon. The average solar irradiance in the UV range was 32.6 W m$^{-2}$.

The solution pH was determined with a Crison GLP 22 pH-meter. The H$_2$O$_2$ content was obtained from the light absorption of its Ti(IV) complex using an Unicam UV/Vis
spectrophotometer at $\lambda = 408$ nm (Welcher, 1975). Samples withdrawn from treated solutions were filtered with Whatman 0.45 µm PTFE filters before analysis.

The sulfamethoxazole and trimethoprim concentrations were determined by reversed-phase high-performance liquid chromatography (HPLC). In the EF, PEF and SPEF assays, samples were immediately diluted with 50% vol. acetonitrile to the sample to stop the degradation process. The analyses were carried out by injecting aliquots into a Waters 600 liquid chromatograph, fitted with a BDS Hypersil C18, 250 mm × 4.6 mm (i.d.), column at 25 ºC, and coupled to a Waters 996 photodiode array detector set at $\lambda = 270$ nm. A 70:30 (v/v) acetonitrile:water (KH$_2$PO$_4$ 10 mM, pH 3) mixture was eluted at 1.0 mL min$^{-1}$ as mobile phase. The chromatograms displayed well-defined peaks for sulfamethoxazole and trimethoprim at retention time ($t_r$) of 3.3 and 3.9 min, respectively. The above chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 ºC, and the photodiode array detector selected at $\lambda = 210$ nm were employed to quantify generated carboxylic acids. The mobile phase was 4 mM H$_2$SO$_4$, eluted at 0.6 mL min$^{-1}$. The chromatograms exhibited peaks for oxalic ($t_r = 6.7$ min), maleic ($t_r = 8.0$ min), oxamic ($t_r = 9.3$ min), formic ($t_r = 13.9$ min) and fumaric ($t_r = 15.5$ min) acids. NH$_4^+$ concentration was measured by the standard indophenol blue method using the previous spectrophotometer. NO$_3^-$ content was quantified by ion chromatography (Pipi et al., 2014).

Total organic carbon (TOC) was obtained by injecting fresh samples to a Shimadzu VCSN TOC analyzer. Total nitrogen (TN) was measured on a Shimadzu TNM-1 unit coupled to the above analyzer. Kinetic and mineralization assays were always replicated and average data are reported. Since the error of all the values obtained within 95% confidence interval was very small (< 2%), no error bars are depicted in figures.

2.4. Mineralization current efficiency
A tablet of the formulation Bactrim® (508 mg) was completely dissolved in 2 L of Milli-
Q water and the concentration of the two drugs was determined by reversed-phase HPLC
upon comparison with pure standards. From this analysis, it was found that the tablet
contained 360 mg of sulfamethoxazole and 80 mg of trimethoprim, with 68 mg of additives.
Hence, their respective molar fractions were 0.818 and 0.182. This composition agreed with
the expected molar ratio 0.80:0.20 from commercial Bactrim® tablets.

The TOC of a solution with 50.0 mg L\(^{-1}\) sulfamethoxazole + 11.1 mg L\(^{-1}\) trimethoprim
was 30.1 mg L\(^{-1}\), with a TN of 10.4 mg L\(^{-1}\), which means that both drugs were the only
organic components of the tablet. Neither NH\(_4^+\) nor NO\(_3^-\) were detected in the initial sample.
When 0.050 M Na\(_2\)SO\(_4\) and 0.50 mM Fe\(^{2+}\) were added to the above solution and EF and SPEF
were carried out with an IrO\(_2\)-based/air-diffusion cell at pH 3.0 and \(j = 33.3\) mA cm\(^{-2}\) for 240
min, the final solutions contained 8.6±0.2 mg L\(^{-1}\) of NH\(_4^+\) (64.3±0,1% of initial N) and no
NO\(_3^-\) ions. The final TN value was slightly superior to that accumulated as NH\(_4^+\), suggesting
that a small part of initial N was lost as volatile N-products, as reported for other N-containing
targets (Thiam et al. 2015a, 2015b). As a result, reactions (1) and (2) can be written for the
theoretical total mineralization of sulfamethoxazole and trimethoprim, respectively:

\[
\begin{align*}
\text{C}_{10}\text{H}_{11}\text{N}_{3}\text{O}_{3}\text{S} + 21\text{H}_2\text{O} & \rightarrow 10\text{CO}_2 + \text{SO}_4^{2-} + 3\text{NH}_4^+ + 41\text{H}^+ + 42\text{e}^- \quad (1) \\
\text{C}_{14}\text{H}_{18}\text{N}_{4}\text{O}_{3} + 25\text{H}_2\text{O} & \rightarrow 14\text{CO}_2 + 4\text{NH}_4^+ + 52\text{H}^+ + 56\text{e}^- \quad (2)
\end{align*}
\]

As a plausible approximation, the drug mixture was mineralized with a mean number of
electrons \(n_{\text{mean}} = (0.818\times42) + (0.182\times56) = 44.54\), which acted on a mean number of C atoms
\(m_{\text{mean}} = (0.818\times10) + (0.182\times14) = 10.73\). The mineralization current efficiency (MCE) for
each assay at current \(I\) (A) and electrolysis time \(t\) (h) was then estimated as (Ruiz et al., 2011):

\[
\% \text{MCE} = \frac{n_{\text{mean}} F V \triangle(\text{TOC})}{4.32\times10^7 m_{\text{mean}} I t} \times 100 \quad (3)
\]
where \( F \) is the Faraday constant \((96,485 \, \text{C mol}^{-1})\), \( V \) is the solution volume \((\text{L})\), \( \Delta(\text{TOC}) \) is the TOC decay \((\text{mg L}^{-1})\) and \(4.32 \times 10^7\) is a conversion factor \((3600 \, \text{s h}^{-1} \times 12000 \, \text{mg C mol}^{-1})\).

3. Results and discussion

3.1. Effect of anode on the degradation of sulfamethoxazole + trimethoprim by EAOPs

3.1.1. \(\text{H}_2\text{O}_2\) electrogeneration

Three anode materials, namely Pt, IrO\(_2\)-based and BDD, were selected to examine the degradation of the drug mixture by EAOPs using an air-diffusion cathode. It has been well-established that at high enough \( j \), all these anodes \((M)\) originate adsorbed hydroxyl radical \((M(\cdot\text{OH}))\) at their surface as follows (Boye et al., 2002; Marselli et al., 2003; Panizza and Cerisola, 2009):

\[
M + \text{H}_2\text{O} \rightarrow M(\cdot\text{OH}) + \text{H}^+ + \text{e}^- \quad (4)
\]

This electrogenerated hydroxyl radical is a strong oxidant that attacks most organic pollutants. However, the nature of the anode limits its oxidation ability. Pt and IrO\(_2\)-based anodes are active materials in which a large proportion of \(M(\cdot\text{OH})\) is transformed into a weaker superoxide \((\text{MO})\) that causes the conversion of organics (Scialdone et al., 2009; Coria et al., 2016; Ridruejo et al., 2017). In contrast, BDD is a non-active anode with much larger \(\text{O}_2\)-overvoltage, producing great amounts of physisorbed BDD(\(\cdot\text{OH}\)) leading to mineralization (Özcan et al., 2008; Brinzila et al., 2014; Olvera-Vargas et al., 2014; Steter et al., 2016).

When an air-diffusion cathode is utilized in an undivided cell, \(\text{H}_2\text{O}_2\) is efficiently produced from the reduction of injected \(\text{O}_2\) gas via reaction (5) (Sirés et al., 2014). The extent of \(\text{H}_2\text{O}_2\) accumulation depends on its decomposition rate at the anode to yield \(\text{O}_2\) gas with formation of the weaker oxidant hydroperoxyl radical \((M(\text{HO}_2\cdot))\) as intermediate via reactions (6) and (7) (Brillas et al., 2009).
Large \( \text{H}_2\text{O}_2 \) production is essential in EAOPs based on Fenton’s reaction chemistry like EF, PEF and SPEF. To clarify this behavior for the three anodes, 130 mL of 0.050 M \( \text{Na}_2\text{SO}_4 \) at pH 3.0 were electrolyzed under EO-\( \text{H}_2\text{O}_2 \) conditions at \( j = 33.3 \text{ mA cm}^{-2} \) for 360 min. In all cases, the \( \text{H}_2\text{O}_2 \) content in solution increased rapidly at the beginning of electrolysis due to efficient reaction (5), but the accumulation was progressively decelerated by the rise in rate of reaction (6), thus attaining a plateau once the rate of reactions (5) and (6) equated. High and similar steady \( \text{H}_2\text{O}_2 \) concentrations of 23.7, 33.8 and 26.0 mM for the Pt/air-diffusion, IrO\(_2\)-based/air-diffusion and BDD/air-diffusion cells, respectively, were obtained at the end of the trials. This means that little effect should be expected from the anode nature on the generation of \( \cdot \text{OH} \) in the EF, PEF and SPEF treatments of sulfamethoxazole + trimethoprim mixtures.

### 3.1.2. EO-\( \text{H}_2\text{O}_2 \) process

A first series of assays was performed by treating 130 mL of 50.0 mg L\(^{-1} \) sulfamethoxazole + 11.1 mg L\(^{-1} \) trimethoprim in 0.050 M \( \text{Na}_2\text{SO}_4 \) at pH 3.0 and \( j = 33.3 \text{ mA cm}^{-2} \) for 360 min. No significant change in pH was found, gradually dropping to final values of 2.6-2.7 by the formation of acidic by-products.

Fig. 2a and b depicts the decay of sulfamethoxazole and trimethoprim concentrations during these treatments. The degradation rate of both drugs was enhanced in the order: IrO\(_2\)-based \( << \) Pt \( < \) BDD. Removals of 52.8% for IrO\(_2\)-based, 87.2% for Pt and 96.1% for BDD were finally obtained for the former drug, whereas the latter one dropped by 92.1% for IrO\(_2\)-based and disappeared completely after 360 min with Pt and 150 min with BDD. Although weak reactive oxygen species (ROS) like \( \text{H}_2\text{O}_2 \) and \( \text{M(HO}_2^* \) are generated under EO-\( \text{H}_2\text{O}_2 \)
conditions, both drugs were pre-eminently destroyed by M(OH). Our results indicate the much larger oxidation ability of BDD(OH) compared to IrO₂(OH) and Pt(OH) (Panizza and Cerisola, 2009; Thiam et al., 2015a; Steter et al., 2016). All decays obeyed a pseudo-first-order kinetics, as shown in the inset panels of Fig. 2a and b, and the corresponding apparent rate constants (k_SMX and k_TMP) are summarized in Table 1. The k_SMX-value using BDD was about 5- and 2-fold higher than that with IrO₂-based and Pt, respectively, whereas the k_TMP-value using BDD was even relatively greater, near 8- and 4.5-fold compared to IrO₂-based and Pt. This corroborates the superiority of BDD over the two active anodes to destroy the drugs, and suggests that a constant and low M(OH) content attacks both substrates.

A different behavior can be observed in Fig. 2c for the TOC abatement in the three EO-H₂O₂ trials. A very low mineralization (< 5% TOC decay) was finally achieved with the two active anodes, whereas the alternative use of BDD yielded 58.1% mineralization. This was also reflected in the MCE values presented in Fig. 2d. The mineralization current efficiency was very small (< 0.28%) with IrO₂-based and Pt, and varied between 3.4% and 3.7% using BDD, informing about a constant mineralization rate during the treatment.

The aforementioned results demonstrate a clear superiority of BDD(OH) to destroy sulfamethoxazole and trimethoprim, as well as to mineralize the solutions.

3.1.3. EF process

The drug mixture in 0.050 M Na₂SO₄ at pH 3.0 was further treated under EF conditions with 0.50 mM Fe²⁺. Again, a slight decay in solution pH to 2.6-2.7 was determined during the 360 min of these assays at 33.3 mA cm⁻².

Fig. 3a and b reveals a similar and very fast abatement of both substrates by EF. Sulfamethoxazole disappeared between 12 min with Pt and 8 min with BDD, whereas overall removal of trimethoprim was achieved between 7 and 5 min, respectively. This trend differs largely from the behavior in EO-H₂O₂ (see Fig. 2a and b) and suggests the generation of some
stronger oxidant. This species is the homogeneous \( \cdot \text{OH} \) formed from Fenton’s reaction (8) between electrogenerated \( \text{H}_2\text{O}_2 \) and added \( \text{Fe}^{2+} \), with optimum pH 2.8 (Brillas et al., 2009; Dirany et al., 2010; Feng et al., 2014). This reaction is propagated by \( \text{Fe}^{2+} \) regeneration from cathodic \( \text{Fe}^{3+} \) reduction.

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad (8)
\]

The concentration decays of Fig. 3a and b also obeyed a pseudo-first-order reaction, as can be seen in their inset panels. Table 1 shows \( k_{\text{SMX}} \) values near 0.30 min\(^{-1}\) with the active anodes and slightly higher (0.37 min\(^{-1}\)) with BDD. The same tendency can be observed for \( k_{\text{TMP}} \), with values close to 0.43-0.50 min\(^{-1}\) using the former anodes and 0.55 min\(^{-1}\) using the latter one. This means that both drugs were competitively degraded by \( \cdot \text{OH} \) in the bulk and, to a much smaller extent, by \( \text{M}(\cdot \text{OH}) \) generated at each anode surface from reaction (4). The superior oxidation ability of BDD(\( \cdot \text{OH} \)) compared to \( \text{IrO}_2(\cdot \text{OH}) \) and \( \text{Pt}(\cdot \text{OH}) \) can then explain the slightly greater \( k_{\text{SMX}} \) and \( k_{\text{TMP}} \) values found using BDD.

Conversely, the TOC removal depended on the anode nature (see Fig. 3c). Slow and similar TOC abatements were obtained with the two active anodes, attaining a mineralization of 36.2\% and 40.2\% using Pt and \( \text{IrO}_2 \)-based. Much quicker TOC decay was found with BDD, yielding 66.8\% mineralization. In all cases, the MCE values dropped at long time (see Fig. 3d) as result of the loss of organic matter and the production of more recalcitrant by-products (Panizza and Cerisola, 2009; Thiam et al., 2015b). Final mineralization current efficiencies of 2.2\%, 2.4\% and 4.0\% with Pt, \( \text{IrO}_2 \)-based and BDD, respectively, were determined. These findings inform about the positive role of BDD(\( \cdot \text{OH} \)) to mineralize intermediates that are not removed by \( \cdot \text{OH} \), making this anode preferable for the EF treatment.

3.1.4. PEF and SPEF processes
The effect of UV radiation was finally examined using PEF and SPEF to treat the drug mixture in 0.050 M Na$_2$SO$_4$ with 0.50 mM Fe$^{2+}$ at pH 3.0 and $j = 33.3$ mA cm$^{-2}$. Under these conditions, the additional generation of •OH in the bulk is expected from the photolysis of Fe(OH)$_2^+$, which is the predominant Fe(III) species at pH near 3 (Flox et al., 2007; Ruiz et al., 2011; Sirés et al., 2014):

$$\text{Fe(OH)}_2^+ + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} \quad (9)$$

However, the concentration decay of both drugs in PEF and SPEF was quite similar to that mentioned in EF, suggesting a minor contribution of •OH induced by reaction (9). This fact can be easily deduced by comparing the analogous $k_{\text{SMX}}$ and $k_{\text{TMP}}$ values given in Table 1 for each anode in these three EAOPs. In contrast, the TOC removal was very different in each system, as shown in Fig. 4a. In PEF, TOC was continuously abated for 300 min, giving rise to 66.1%, 68.1% and 84.7% mineralization using IrO$_2$-based, Pt and BDD, respectively. In SPEF, the same anodes led to 78.5%, 81.3% and 87.4% TOC reduction after 240 min, with no significant mineralization increase from 180 min. For all these trials, the MCE values dropped along electrolysis, being higher in SPEF (see Fig. 4b).

It is noticeable that the use of the two active anodes yielded analogous mineralization in PEF, which was greater using BDD. The same behavior was found in SPEF. From the TOC and MCE values listed in Table 1 after 240 min, one can infer for each anode a higher oxidation ability in the sequence: EO-H$_2$O$_2$ < EF < PEF < SPEF, always being superior with BDD. The higher mineralization attained by PEF and SPEF compared to EF can be accounted for by the photolysis of photoactive intermediates by UV radiation, such as the photodecomposition of Fe(III) complexes with generated carboxylic acids (Brillas et al., 2009; Pérez et al., 2016; Moreira et al., 2017):

$$\text{Fe(OOCR)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{R}^* \quad (10)$$
The fact that organics are more quickly destroyed by SPEF can be related to the high UV intensity provided by sunlight ($\lambda > 300$ nm). This causes a much rapid photodecomposition of intermediates with the consequent rise in mineralization rate. Although the SPEF process with BDD is the most powerful EAOP for the remediation of water containing sulfamethoxazole + trimethoprim, overall mineralization was not achieved because of the accumulation of highly recalcitrant by-products than are quite stable against BDD(•OH), •OH and sunlight.

3.2. Influence of electrolyte composition on SPEF degradation

Cl$^-$ ion is a common species in real wastewater. It can be easily oxidized at the anode of an electrolytic cell to produce the strong oxidant active chlorine (Cl$_2$/HClO) in acidic medium from reactions (11) and (12) (Sirès et al., 2014; Thiam et al., 2015a; Steter et al., 2016):

\[
\begin{align*}
2\text{Cl}^- & \rightarrow \text{Cl}_2(\text{aq}) + 2\text{e}^- \\
\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} & \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ 
\end{align*}
\]

To clarify the effect of this ion on the effectiveness of the most powerful process, i.e., SPEF with BDD, the drug mixture was treated in either 0.035 M NaCl + 0.020 M Na$_2$SO$_4$ or 0.070 M NaCl, both having a conductivity ~ 10 mS cm$^{-1}$ as that of 0.050 M Na$_2$SO$_4$. Fig. 5a and b shows a faster decay of both drugs with increasing Cl$^-$ concentration, meaning that their destruction with active chlorine prevailed over that with BDD(•OH) and •OH produced from reactions (4) and (8), respectively. For example, sulfamethoxazole disappeared in about 10 min using 0.050 M Na$_2$SO$_4$, but in only 4 min in 0.070 M NaCl. The inset panel of Fig. 5a highlights the good pseudo-first-order kinetics obtained in all cases, suggesting a reaction with a constant quantity of all oxidants (Cl$_2$/HClO, BDD(•OH) and •OH). This behavior can also be observed for trimethoprim in the inset panel of Fig. 5b except in 0.070 M NaCl, where bad linear fitting was found. Thus, active chlorine, the most powerful oxidant in this medium, destroyed the major part of the drug very quickly, even before reaching a steady content. Note
that the $k_{\text{SMX}}$-value was 1.12- and 2.65-fold higher in the chloride + sulfate mixture and 0.070 M NaCl, respectively, compared to that in 0.050 M Na$_2$SO$_4$ (see Table 1), as result of the increasing generation of active chlorine. This enhancement was even larger for $k_{\text{TMP}}$, which rose 1.30-fold in the chloride + sulfate mixture, evidencing a quicker attack of active chlorine over this molecule. This explains its complex kinetics in 0.070 M NaCl, where much larger content of such oxidant was produced.

For the above assays, Fig. 5c shows a progressive loss of TOC abatement at higher Cl$^-$ concentration, confirmed with the concomitant decay in MCE, as depicted in Fig. 5d. The final TOC and current efficiency dropped from 87.4% and 7.9% in 0.050 M Na$_2$SO$_4$ to 65.8% and 6.0% in 0.070 M NaCl (see Table 1). This behavior can be associated to the gradual formation of persistent chloroderivatives that are more hardly oxidized under SPEF conditions (Sirés et al., 2014; Hussain et al., 2015; Thiam et al., 2015a; Steter et al., 2016).

The above findings demonstrate the complex influence of Cl$^-$ on the performance of SPEF with BDD. Although it was beneficial to remove more quickly the parent drugs, the chloroderivatives formed inhibited the mineralization process and hence, low Cl$^-$ contents are preferable to achieve the best mineralization by this EAOP.

**3.3. Detection of final carboxylic acids**

To corroborate the formation of final carboxylic acids during the mineralization of the sulfamethoxazole + trimethoprim mixtures, solutions with 0.050 M Na$_2$SO$_4$ treated by EF and SPEF with BDD at $j = 33.3$ mA cm$^{-2}$ were analyzed by ion-exclusion HPLC. The chromatograms exhibited peaks corresponding to maleic, fumaric, formic, oxalic and oxamic acids. The two former acids came from the cleavage of the benzene rings and were oxidized to oxalic acid (Brillas et al., 2009; Sirés et al, 2014). Oxamic acid should came from the degradation of $N$-derivatives. Formic, oxalic and oxamic acids were the final by-products,
being directly mineralized to CO₂ (Sirés et al., 2014; Thiam et al., 2015a, 2015b). All these acids were mainly in the form of Fe(III) complexes.

Maleic, fumaric and formic acids were detected as traces (< 0.1 mg L⁻¹), disappearing after 120-180 min. This means that Fe(III)-maleate, Fe(III)-fumarate and Fe(III)-formate complexes were easily oxidized by generated hydroxyl radicals. In contrast, oxalic and oxamic acids were largely produced and persisted for 240 min, as can be seen in Fig. 6a and b, respectively. These acids were accumulated up to 33.1 and 7.50 mg L⁻¹ in EF, which accounts for a total TOC of 10.85 mg L⁻¹, corresponding to 60.3% of the solution TOC (18.0 mg L⁻¹, see Fig. 3c). Conversely, only 1.09 mg L⁻¹ of oxalic acid and 0.13 mg L⁻¹ of oxamic acid were found at the end of SPEF, corresponding to 0.3 mg L⁻¹ TOC, i.e., 7.9% of the final solution TOC (see Fig. 4c). Oxalic and oxamic acids were largely accumulated in EF because Fe(III)-oxalate and Fe(III)-oxamate complexes are quite stable against BDD(•OH) and •OH, whereas such species were rapidly photodecomposed via reaction (10) in SPEF. This positive action of UV radiation provided by sunlight on final Fe(III)-carboxylate complexes explains the superior oxidation ability of SPEF, although other undetected recalcitrant products (about 12% of initial TOC) remained in the final solution, thus impeding overall mineralization.

4. Conclusions

The decay of sulfamethoxazole and trimethoprim in 0.050 M Na₂SO₄ always agreed with a pseudo-first-order reaction. Their apparent rate constants were very low in EO-H₂O₂, being much higher in EF, PEF and SPEF with small influence of the anode used because they were mainly destroyed by •OH in the bulk. The mineralization process was enhanced in the order: EO-H₂O₂ < EF < PEF < SPEF, regardless of the anode. All methods were more powerful with BDD due to the higher oxidation ability of BDD(•OH) compared to IrO₂(•OH) and Pt(•OH). The difference in TOC abatement using the different anodes was not substantial in SPEF due to the very positive action of natural UV radiation to remove photoactive intermediates. The
most powerful process was SPEF with BDD, although it yielded 87.4% mineralization as maximal owing to the accumulation of very recalcitrant by-products. The presence of Cl\(^-\) in the medium accelerated the decay of both drugs by the quicker attack of generated active chlorine, but lower mineralization was reached due to the formation of persistent chloroderivatives. Oxalic and oxamic acids were detected as final carboxylic acids. Their Fe(III) complexes were slowly destroyed by BDD(•OH) and •OH in EF, whereas they were rapidly photolyzed in SPEF, thus explaining the superiority of the latter method.

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