Mineralization of the recalcitrant oxalic and oxamic acids by electrochemical advanced oxidation processes using a boron-doped diamond anode

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Abstract

Oxalic and oxamic acids are the ultimate and more persistent by-products of the degradation of $N$-heteroaromatics by electrochemical advanced oxidation processes (EAOPs). In this paper, the kinetics and oxidative paths of these acids have been studied for several EAOPs using a boron-doped diamond (BDD) anode and a stainless steel or an air-diffusion cathode. Anodic oxidation (AO-BDD) in the presence of Fe$^{2+}$ (AO-BDD-Fe$^{2+}$) and under UVA irradiation (AO-BDD-Fe$^{2+}$-UVA), along with electro-Fenton (EF-BDD), were tested. The oxidation of both acids and their iron complexes on BDD was clarified by cyclic voltammetry. AO-BDD allowed the overall mineralization of oxalic acid, but oxamic acid was removed much more slowly. Each acid underwent a similar decay in AO-BDD-Fe$^{2+}$ and EF-BDD, as expected if its iron complexes were not attacked by hydroxyl radicals in the bulk. The faster and total mineralization of both acids was achieved in AO-BDD-Fe$^{2+}$-UVA due to the high photoactivity of their Fe(III) complexes that were continuously regenerated by oxidation of their Fe(II) complexes. Oxamic acid always released a larger proportion of NH$_4^+$ than NO$_3^-$ ion, as well as volatile NO$_x$ species. Both acids were independently oxidized at the anode in AO-BDD, but in AO-BDD-Fe$^{2+}$-UVA oxamic acid was more slowly degraded as its content decreased, without significant effect on oxalic acid decay. The increase in current density enhanced the oxidation power of the latter method, with loss of efficiency. High Fe$^{2+}$ contents inhibited the oxidation of Fe(II) complexes by the competitive oxidation of Fe$^{2+}$ to Fe$^{3+}$. Low current densities and Fe$^{2+}$ contents are preferable to remove more efficiently these acids by the most potent AO-BDD-Fe$^{2+}$-UVA method.

Keywords: Carboxylic acids; Iron complexes; Anodic oxidation; Electro-Fenton; UVA light; Removal kinetics
1. Introduction

Recently, a large variety of advanced oxidation processes (AOPs) has been proposed for the remediation of wastewaters containing low contents of toxic and/or biorefractory organic pollutants (Andreozzi et al., 1999; Pera-Titus et al., 2004; Cañizares et al., 2008). These powerful oxidation methods include chemical, photochemical and electrochemical treatments based on the in situ generation of hydroxyl radical (\(\cdot\)OH). This radical is the second most strong oxidizing specie known after fluorine with a high standard reduction potential \(E^\circ(\cdot\)OH/H\(_2\)O) = 2.80 V vs. SHE) that allows its non-selectively reaction with most organics leading to their overall mineralization to CO\(_2\), water and inorganic ions. However, the effectiveness of AOPs is limited by the formation of recalcitrant carboxylic acids (Cañizares et al., 2003; Oturan et al., 2008; Serra et al., 2009). The most common ultimate by-product from aromatics is oxalic acid, which is hardly destroyed with \(\cdot\)OH largely prolonging the mineralization time with the consequent efficiency loss and/or greater operation cost of the treatment (Brillas et al., 2004; Pera-Titus et al., 2004; Diagne et al., 2007; Özcan et al., 2008). In the degradation of wastewaters with N-aromatics, a mixture of oxalic and oxamic acids is finally formed (Sirés et al., 2006; Hammami et al., 2008; Hamza et al., 2009; Brillas et al., 2010). Oxamic acid is even more recalcitrant than oxalic acid (Faria et al., 2008). While the removal rate of oxalic acid is strongly enhanced in photoassisted AOPs with iron ions (Zuo and Hoigné, 1992; Faust and Zepp, 1993; Zuo and Hoigné, 1994; Šima and Makáňová, 1997), less is known about the mineralization of oxamic acid by photochemical treatments.

The most typical electrochemical AOP (EAOP) is anodic oxidation (AO) in which organic pollutants contained in an electrolytic cell can be oxidized at the anode surface either by direct charge transfer and/or with \(\cdot\)OH generated from water oxidation at high current. For a boron-doped diamond (BDD) electrode, the formation of hydroxyl radical can be written as reaction (1) (Marselli et al., 2003; Sirés et al., 2008; Panizza and Cerisola, 2009; Brillas et al., 2010):
\[ \text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}^{(\cdot}\text{OH}) + \text{H}^+ + \text{e}^- \]  
(1)

The BDD electrode has a much higher oxidation power than other conventional anodes and it is able to effectively mineralize oxalic acid (Gandini et al., 2000; Martínez-Huitle et al., 2004; Vandini et al., 2006; Weiss et al., 2007; Scialdone et al., 2008), but no information is available on the AO treatment of oxamic acid. The high oxidation power of BDD also allows generating reactive oxygen species (ROS) like \( \text{H}_2\text{O}_2 \) and ozone, as well as peroxo-derivatives coming from the oxidation of the anion of the background electrolyte (Cañizares et al., 2003; Panizza and Cerisola, 2009). In previous work (Guinea et al., 2009), we found that the presence of \( \text{H}_2\text{O}_2 \) in AO accelerates the mineralization process of carboxylic acids, although Fe(III)-oxalate complexes are quickly photolyzed by UVA light.

EAOPs based on Fenton’s reaction chemistry have been recently developed (Brillas et al., 2009). In electro-Fenton (EF), \( \text{H}_2\text{O}_2 \) is continuously supplied to an acidic contaminated solution from the two-electron reduction of injected \( \text{O}_2 \) at a carbonaceous cathode, mainly carbon felt (Oturan et al., 2008; Balci et al., 2009) and carbon-PTFE gas-diffusion electrodes (Sirés et al., 2007, Ruiz et al., 2011), by reaction (2):

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]  
(2)

Fe\(^{2+}\) ion is then added to the solution to react with \( \text{H}_2\text{O}_2 \) producing \( \cdot\text{OH} \) in the bulk and \( \text{Fe}^{3+} \) by Fenton’s reaction (3) (Sun and Pignatello, 1993):

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

An advantage of EF is that \( \text{Fe}^{2+} \) can be regenerated from \( \text{Fe}^{3+} \) reduction at the cathode, thus accelerating Fenton’s reaction (3) and the oxidation of organics with \( \cdot\text{OH} \) (Brillas et al., 2009). When a one-compartment cell with a BDD anode is used, the degradation of organic pollutants is additionally enhanced by the attack of BDD(\( \cdot\text{OH} \)) formed from reaction (1) (Serra et al., 2009; Ruiz et al. 2011). The mineralization of aromatics can also be accelerated...
by exposing the contaminated solution to UVA light while is treated by EF (Brillas et al., 2004; Sirés et al., 2006; Ruiz et al., 2011). The main action of UVA irradiation is the photodecarboxylation of Fe(III)-carboxylate complexes.

The degradation of $N$-aromatics by EAOPs involves a high number of by-products that are simultaneously formed and destroyed by the different oxidizing species. Oxalic and oxamic acids are accumulated from the beginning of the process and their slow destruction limits the oxidation power of these methods. However, the influence of oxidants and/or UVA light on their removal, particularly of their iron species, is not well known yet.

To gain a better insight on the mineralization processes of oxalic and oxamic acids to better understand the degradation of $N$-aromatics, we report a study on the kinetics and oxidative paths of both acids by EAOPs with a BDD anode under typical treatment conditions of synthetic wastewaters with organics in sulfate medium. Special attention was taken on the action of Fe$^{2+}$ and UVA light to clarify the destruction of their iron complexes. The oxidation of these compounds on BDD was analyzed by cyclic voltammetry (CV). The change in degradation rate of each acid when mixed in different proportions was examined. The effect of current density and Fe$^{2+}$ content on oxamic acid removal was assessed. NH$_4^+$ and NO$_3^−$ ions lost during the mineralization of oxamic acid were followed by ionic chromatography.

2. Materials and methods

2.1. Chemicals

Oxalic and oxamic acids were of analytical grade from Avocado. Anhydrous sodium sulfate, ferrous sulfate heptahydrate and ferric sulfate hydrate were of analytical grade from Fluka and Sigma. Solutions were prepared with high-purity water obtained from a Millipore Milli-Q system with resistivity $> 18$ MΩ cm at 25 °C. Organic solvents and other chemicals used were of HPLC or analytical grade from Aldrich, Lancaster, Merck and Panreac.
2.2. Apparatus

The solution pH was measured with a Crison GLP 22 pH-meter. CV was conducted with an Ecochemie Autolab PGSTAT100 potentiostat-galvanostat controlled by an Autolab Nova 1.5 software. Electrolyses were performed with an Amel 2053 potentiostat-galvanostat. The concentration of dissolved O$_2$ was determined with a Thermo Electron Corporation Orion 4 Star pH-DO portable with a Sensor Orion 083005MD DO probe. Total organic carbon (TOC) of solutions was measured with a Shimadzu VCSN TOC analyzer. Total nitrogen (TN) was determined with a Shimadzu TNM-1 unit coupled with the TOC analyzer. The concentration of oxalic and oxamic acids was quantified by ion-exclusion HPLC using a Waters 600 liquid chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 ºC, coupled with a Waters 996 photodiode array detector at $\lambda = 210$ nm. Inorganic ions lost during oxamic acid degradation were detected by ionic chromatography using a Shimadzu 10 Avp HPLC coupled with a Shimadzu CDD 10 Avp conductivity detector. NH$_4^+$ concentration was obtained with a Shodex IC YK-421, 125 mm × 4.6 mm (i.d.), cation column at 40 ºC, whereas NO$_3^-$ content was determined with a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.), anion column at 40 ºC.

2.3. Electrochemical systems

All electrolytic experiments were conducted in an open, undivided and thermostated cylindrical cell, so that all gases formed were directly released to the atmosphere. The anode was a BDD thin film provided by Adamant Technologies (La-Chaux-de-Fonds, Switzerland), while the cathode was either a stainless steel (AISI 304 grade) sheet (SS) or a carbon-PTFE air-diffusion electrode (ADE) from E-TEK (Somerset, NJ, USA). The preparation of the ADE cathode were described elsewhere (Brillas et al., 2004). It was fed with air pumped at 300 mL min$^{-1}$ to generate H$_2$O$_2$ by reaction (2). The area of all electrodes was 3 cm$^2$ and the interelectrode gap was ca. 1 cm. To remove the impurities of the BDD surface and activate...
the ADE cathode, they were previously polarized in 0.05 M Na$_2$SO$_4$ at 300 mA for 60 min. The same cell without electrodes was used for the photochemical assays under UVA light.

Comparative photochemical and electrochemical degradations of 100 mL of 2.08 mM (50 mg L$^{-1}$ of TOC) of oxalic (188 mg L$^{-1}$) or oxamic (185 mg L$^{-1}$) acid in 0.05 M Na$_2$SO$_4$ at pH 3.0 were performed. The photochemical assays with direct UVA exposition were made after addition of 0.5 mM Fe$^{2+}$ (UVA-Fe$^{2+}$) or 0.5 mM Fe$^{3+}$ (UVA-Fe$^{3+}$). The electrolytic methods were anodic oxidation with a BDD/SS cell (AO-BDD), the same treatment after addition of 0.5 mM Fe$^{2+}$ (AO-BDD-Fe$^{2+}$) and under UVA illumination (AO-BDD-Fe$^{2+}$-UVA), and electro-Fenton with a BDD/ADE cell and 0.5 mM Fe$^{2+}$ (EF-BDD). For the trials with UVA irradiation, a Philips TL/6W/08 fluorescent black light blue tube placed at 7 cm above the solution was employed. The tube emitted UVA light in the wavelength region 320-420 nm with $\lambda_{\text{max}} = 360$ nm, supplying a photoionization energy of 5 W m$^{-2}$ as detected with a Kipp & Zonen CUV 5 radiometer. In all experiments, the solution was kept at 35.0 ºC under vigorous stirring with a magnetic bar at 800 rpm to ensure its homogenization, as well as the transport of reactants towards/from the electrodes in the electrolytic assays.

CV measurements were carried out with a three-electrode one-compartment cell thermostated at 25 ºC. The working electrode was a 0.40 cm$^2$ BDD, the counter reference was a Pt wire and the reference electrode was a Ag|AgCl|KCl (saturated) electrode (E$^\circ = 0.197$ V/SHE). Cyclic voltammograms were recorded at a scan rate of 100 mV s$^{-1}$ under an Ar atmosphere after previous bubbling of this gas through the solution for 30 min.

2.4. Analytical procedures

Before analysis, aliquots withdrawn from treated solutions were filtered with 0.45 µm PTFE filters from Whatman. Reproducible TOC values with an accuracy of ±1% were found by injecting 50 µL aliquots to the TOC analyzer. The mineralization current efficiency (MCE) for electrolyzed solutions at time $t$ (h) was then calculated by Eq. (4) (Hamza et al., 2009):
\[
\text{MCE (\%) } = \frac{nF \cdot V_s \cdot \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \cdot m \cdot I \cdot t} \times 100
\]  
(4)

where \(F\) is the Faraday constant (96487 C mol\(^{-1}\)), \(V_s\) is the solution volume (L), \(\Delta(\text{TOC})_{\text{exp}}\) is the experimental TOC removal (mg L\(^{-1}\)), \(4.32 \times 10^7\) is a conversion factor (3600 s h\(^{-1}\) x 12000 mg mol\(^{-1}\)), \(m\) is the number of carbon atoms of each acid (2 C atoms) and \(I\) is the current (A).

The number of electrons \((n)\) consumed was taken as 2 for oxalic acid and 10 for oxamic acid, assuming that their overall mineralization corresponds to reactions (5) and (6), respectively:

\[
\begin{align*}
\text{C}_2\text{H}_2\text{O}_4 & \rightarrow 2 \text{CO}_2 + 2 \text{H}^+ + 2 e^- \quad (5) \\
\text{C}_2\text{H}_3\text{NO}_3 + 4 \text{H}_2\text{O} & \rightarrow 2 \text{CO}_2 + \text{NO}_3^- + 11 \text{H}^+ + 10 e^- \quad (6)
\end{align*}
\]

The ion-exclusion HPLC measurements were made after injection of 20 µL aliquots into the liquid chromatograph and circulation of 4 mM H\(_2\)SO\(_4\) at 0.6 mL min\(^{-1}\) as mobile phase. Ionic chromatography was performed with 25 µL aliquots using a mobile phase composed of 5.0 mM tartaric acid, 1.0 mM dipicolinic acid, 24.2 mM boric acid and 1.5 mM corona ether at 1.0 mL min\(^{-1}\) for NH\(_4^+\) and 2.4 mM tris(hydroxymethyl)aminomethane and 2.5 mM phthalic acid of pH 4.0 at 1.5 mL min\(^{-1}\) for NO\(_3^-\).

### 3. Results and discussion

#### 3.1. CV behavior of oxalic and oxamic acids and their iron complexes

Fig. 1a shows the cyclic voltammograms obtained for the oxidation of 2.08 mM oxalic and oxamic acids in 0.05 M Na\(_2\)SO\(_4\) on a BDD electrode at pH 3.0 and 100 mV s\(^{-1}\). Both compounds display an irreversible peak, with an anodic peak potential \((E_p^a)\) of 2.10 and 2.14 V for oxalic and oxamic acids, respectively, which partially overlap with that of water discharge to O\(_2\) beginning at 2.2 V. The CV behaviour found for oxalic acid agrees with that reported by other authors (Martínez-Huitle et al., 2004; Weiss et al., 2007; Scialdone et al., 2008), who suggested the direct anodic oxidation of the acid at the BDD anode surface rather
than its mediated reaction with BDD(•OH) produced from reaction (1) to be converted into CO₂. This behavior can also be extended to the case of oxamic acid, which is oxidized at slightly higher potentials than oxalic acid and with a greater peak current due to the additional transformation of its -NH₂ group into inorganic ions.

The comparative cyclic voltammograms recorded for the above acids in the presence of 0.5 mM Fe²⁺ or 0.5 mM Fe³⁺ are depicted in Fig. 1b. Fe(II)- or Fe(III)-carboxylate complexes formed are oxidized at much more positive potentials than pure acids, clearly overlapping with the water discharge region. The irreversible peak for Fe(II)-oxalate complexes with \( E_{p}^{a} = 2.31 \) V has much higher height than that of oxalic acid (see Fig. 1a), as a result of the more complex oxidation of their electroactive species, predominantly Fe\(^{II}\)(C₂O₄)₂⁻ (Lan et al. 2010). In contrast, the dominant Fe\(^{III}\)(C₂O₄)₃⁻ and Fe\(^{III}\)(C₂O₄)₂⁻ ions in the solution of Fe(III)-oxalate complexes (Balmer and Sulzberger, 1999; Kwan and Chu, 2007; Lan et al., 2010) are oxidized at so high potentials that any peak is displayed in CV. Fe(II)- and Fe(III)-oxamate complexes exhibit a similar irreversible peak, with high \( E_{p}^{a} \) of 2.54 and 2.72 V, respectively, suggesting that their ionic structures (not reported in literature) are analogous to those of iron-oxalate complexes, although the Fe(III)-oxamate species are more easily oxidizable. This is not surprising since oxamic like oxalic acid behaves as a bidentate ligand, coordinated with the amidic N, after ionization of one amidic H, and with the carboxylate O (Pardo et al., 2004). The fact that the iron complexes of oxalic and oxamic acids are destroyed in the water discharge zone indicates that they react predominantly with BDD(•OH) at the anode surface.

### 3.2. Photochemical degradation of oxalic and oxamic acids and their iron complexes

A series of trials was made to assess the degradation effect of the 6 W UVA light on 100 mL of the 2.08 mM acid solutions in the absence and presence of 0.5 mM Fe²⁺ or 0.5 mM Fe³⁺. The evolution of each compound was monitored by ion-exclusion chromatography, which displayed a well-defined adsorption peak at retention time of 6.8 min for oxalic acid
and 9.4 min for oxamic acid. Fig. 2a and 2b show that both acids are very stable under UVA irradiation, as expected if they are not directly photolyzed. In contrast, their iron complexes are photodegraded at different rate depending on the acid and iron ion tested. The fastest removal was found for the UVA-Fe$^{3+}$ treatment of oxalic acid, which disappears in about 150 min. Overall destruction of this acid is also feasible using UVA-Fe$^{2+}$, although a longer time close to 360 min is required. The kinetic analysis of these experiments showed good linear correlations for a pseudo first-order reaction. The pseudo first-order rate constant ($k_{\text{oxalic}}$) thus determined, along the corresponding square of regression coefficient, are collected in Table 1.

The quick photodegradation of Fe(III)-oxalate complexes can be accounted for by the high photoactivity of their dominant ionic species by reactions (7) and (8) (Faust and Zepp, 1993; Balmer and Sulzberger, 1999; Jeong and Yoon, 2005):

$\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^{3-} + h\nu \rightarrow \text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_2^{2-} + \text{C}_2\text{O}_4^{-}$ (7)

$\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^{2-} + h\nu \rightarrow \text{Fe}^{\text{II}}(\text{C}_2\text{O}_4) + \text{C}_2\text{O}_4^{-}$ (8)

These reactions are photoredox processes with a ligand-to-metal charge transfer leading to the homolytic break of a Fe(III)-O coordination bond of the bidentate oxalate ligand (Šima and Makáňová, 1997). The anion radical C$_2$O$_4^{-}$ released yields CO$_2$ and the anion radical CO$_2^{-}$ by reaction (9), which then reacts with dissolved O$_2$ to produce the ion superoxide (O$_2^{-}$) from reaction (10). This specie originates a cascade of other ROS like hydroperoxide radical (HO$_2^-$) from reaction (11) and H$_2$O$_2$ from reaction (12). H$_2$O$_2$ can further oxidize the Fe(II) to Fe(III) complexes, as exemplified for Fe$^{\text{II}}(\text{C}_2\text{O}_4)_2^{2-}$ in reaction (13), at a rate about 1000 times higher than that of Fenton’s reaction (3) (Faust and Zepp, 1993), thus closing the Fe(III)/Fe(II) catalytic loop. The large production of *OH from the reaction (13), which does not attack the iron-oxalate complexes, has been well proven in photoassisted ferrioxalate systems (Jeong and Yoon, 2005; Rodríguez et al., 2007; Monteagudo et al., 2008).
\begin{align*}
C_2O_4^{2-} & \rightarrow CO_2 + CO_2^{2-} \\
CO_2^{2-} + O_2 & \rightarrow CO_2 + O_2^{2-} \\
O_2^{2-} + H^+ & \rightarrow HO_2^* \\
O_2^{2-} + HO_2^* + H^+ & \rightarrow H_2O_2 + O_2 \\
Fe^{II}(C_2O_4)_2^{2-} + H_2O_2 & \rightarrow Fe^{III}(C_2O_4)_2^{2-} + \cdot OH + OH^- \\
\end{align*}

The slow decay of oxalic acid in the UVA-Fe^{2+} system can then be related to the much lower photoactivity of Fe(II) complexes to be converted into Fe(III) ones, as exemplified by reaction (14) (Faust and Zepp, 1993; Kwan and Chu, 2007):

\begin{align*}
Fe^{II}(C_2O_4)_2^{2-} + h\nu & \rightarrow Fe^{III}(C_2O_4)_2^{2-} \\
\end{align*}

Once the Fe(III)-oxalate complexes are formed, a photodegradation path similar to that described above for the UVA-Fe^{3+} treatment takes place, although the large preponderance of Fe(II)-oxalate complexes at the beginning of the process makes it slower.

The aforementioned experiments for oxalic acid were performed with 7.6 mg L\(^{-1}\) of dissolved O\(_2\). To clarify the generation of ROS via reactions (10)-(12), the same trials were repeated with 28.0 mg O\(_2\) L\(^{-1}\) in solution under O\(_2\) bubbling at 0.5 L min\(^{-1}\). Results of Table 1 confirm the increase in \(k_{\text{oxalic}}\) in both systems, much more for UVA-Fe\(^{2+}\) (1.77-fold) than for UVA-Fe\(^{3+}\) (1.06-fold). The excess of H\(_2\)O\(_2\) formed under O\(_2\) bubbling strongly accelerates the oxidation of Fe\(^{II}(C_2O_4)_2^{2-}\) by reaction (13) in UVA-Fe\(^{2+}\), while this reaction is only slightly enhanced in UVA-Fe\(^{3+}\) due to the much lower concentration of Fe(II) species.

Fig. 2b evidences that the very low photoactivity of Fe(II)- and Fe(III)-oxamate complexes only allows a 57% and 77% destruction of the acid after 360 min of UVA-Fe\(^{2+}\) and UVA-Fe\(^{3+}\) treatments, respectively. This is also reflected in the low pseudo first-order rate constant (\(k_{\text{oxamic}}\)) values obtained (see Table 1). As can be seen in Fig. 3, a larger percentage of its initial N is lost as NH\(_4^+\) (43% for UVA-Fe\(^{2+}\) and 65% for UVA-Fe\(^{3+}\)) at the end of these
trials, although the oxidation to NO$_3^-$ is significant in both cases (9% of initial N for UVA-Fe$^{2+}$ and 12% of initial N for UVA-Fe$^{3+}$). Note that for the UVA-Fe$^{2+}$ system, about 5% of initial N is released as volatile compounds, probably NO$_x$ species.

3.3. Mineralization of oxalic acid by EAOPs

Comparative degradations of 100 mL of 2.08 mM oxalic acid by different EAOPs were made at 33.3 mA cm$^{-2}$. Fig. 2a shows that this acid is completely removed at 300 min of the AO-BDD treatment, since it is transformed into CO$_2$ by direct oxidation at the anode, as stated above. When 0.5 mM Fe$^{2+}$ is added to the solution, a strong inhibition of oxalic acid decay occurs during the AO-BDD-Fe$^{2+}$ process, only being reduced by 72% after 360 min of electrolysis. A similar tendency can be observed in Fig. 2a for the EF-BDD system, where the large generation of H$_2$O$_2$ from the ADE cathode favors the rapid conversion of Fe(II)- into Fe(III)-oxalate complexes, e.g. via reaction (13). This suggests that in AO-BDD-Fe$^{2+}$, the initial Fe(II)-oxalate complexes are quickly oxidized to Fe(III)-oxalate species by BDD($^\cdot$OH) at the anode surface. This oxidation is also feasible with H$_2$O$_2$ since it is produced in low amounts from dimerization of BDD($^\cdot$OH) by reaction (15) (Guinea et al., 2009):

$$2 \text{BDD}(^\cdot\text{OH}) \rightarrow 2 \text{BDD} + \text{H}_2\text{O}_2 \quad (15)$$

The slow destruction of Fe(III)-oxalate complexes with BDD($^\cdot$OH), as confirmed by CV (see Fig. 1b), then explains the similar and slow abatement of the acid in AO-BDD-Fe$^{2+}$ and EF-BDD, without oxidation by $^\cdot$OH formed from Fenton’s reaction (3). From these results, the effect of UVA illumination was studied for the AO-BDD-Fe$^{2+}$-UVA treatment. Fig. 2a shows that this EAOP leads to total destruction of the acid in only 90 min, as expected from the rapid photolysis of Fe(III)-oxalate complexes. Since a steady concentration of 13 mg O$_2$ L$^{-1}$ was reached in this trial, significant amounts of H$_2$O$_2$ are formed from reaction (12), which contribute to the oxidation of Fe(II)- to Fe(III)-oxalate complexes.
The $k_{\text{oxalic}}$ value obtained for the above EAOPs is listed in Table 1. It increased 1.40-fold for the most potent AO-BDD-Fe$^{2+}$-UVA system compared with UV-Fe$^{3+}$, as expected if the photoactive Fe(III)-oxalate species are more quickly regenerated, involving its oxidation with H$_2$O$_2$ from reaction (13) and with BDD(•OH) at the anode surface.

TOC was always removed in a similar way to oxalic acid due to the insignificant formation of by-products. For example, after 360 min of AO-BDD-Fe$^{2+}$ and EF-BDD, TOC was reduced to 13 mg L$^{-1}$, corresponding to 49 mg L$^{-1}$ oxalic acid in good agreement with 52 mg L$^{-1}$ found for the final electrolyzed solutions (see Fig. 2a). Total mineralization was achieved after about 300 min of AO-BDD and close to 90 min of AO-BDD-Fe$^{2+}$-UVA, times similar to those required for the total removal of oxalic acid, as shown in Fig. 2a. The efficiency calculated from Eq. (4) decreased with electrolysis time by the gradual drop in oxalic acid content. For example, the MCE value decayed from 7.2% or 12.5% at 10 min to 1.6% or 6.7% at the end of the AO-BDD or AO-BDD-Fe$^{2+}$-UVA treatment.

From the above results, the reaction sequence of Fig. 4 is proposed for oxalic acid mineralization by AO-BDD-Fe$^{2+}$-UVA. It is initiated by the oxidation of Fe$^{II}$($C_2O_4$)$_2^{2-}$ with BDD(•OH) to yield Fe$^{III}$($C_2O_4$)$_2^{2-}$, in equilibrium with Fe$^{III}$($C_2O_4$)$_3^{3-}$. These ionic species are quickly photolyzed regenerating Fe$^{II}$($C_2O_4$) and Fe$^{II}$($C_2O_4$)$_2^{2-}$, respectively, with the loss of CO$_2$ and CO$_2$•$. Further reaction of CO$_2$• with O$_2$ originates CO$_2$ and ROS. The catalytic loop between Fe(II)- and Fe(III)-oxalate complexes is then propagated by the continuous oxidation of Fe$^{II}$($C_2O_4$)$_2^{2-}$ with BDD(•OH) and ROS (primordially H$_2$O$_2$). All ionic species can also be oxidized to CO$_2$ at the BDD anode, although reactions with BDD(•OH) are much slower than the photodegradation of Fe(III) species with UVA light. A slow oxidation of oxalic acid, in equilibrium with the above complexes, at the anode is also feasible.

3.4. Mineralization of oxamic acid by EAOPs
The degradation of 2.08 mM oxamic acid solutions by the same EAOPs always followed a pseudo first-order abatement. Fig. 2b evidences that AO-BDD-Fe$^{2+}$ and EF-BDD processes yield the same decay rate for this acid, as expected if its Fe(II) complexes are oxidized by BDD($\cdot$OH) with insignificant participation of $\cdot$OH in the bulk. Both treatments are more potent than AO-BDD because of the most effective destruction of Fe(III)-oxamate complexes by BDD($\cdot$OH) than that of oxamic acid by direct charge transfer. Comparison of Fig. 2a and 2b evidences that AO-BDD-Fe$^{2+}$ and EF-BDD methods are more effective for the abatement of oxamic than oxalic acid, in agreement with the higher oxidation ability of Fe(III)-oxamate species at BDD (see Fig. 1b). Fig. 2b also shows that oxamic acid disappears in 270 min for AO-BDD-Fe$^{2+}$-UVA. Since $k_{\text{oxamic}}$ for this method is 2.56 times higher than for UV-Fe$^{3+}$ (see Table 1), one can infer that Fe(III)-oxamate species are rapidly formed from the oxidation of Fe(II)-oxamate ones with BDD($\cdot$OH) and generated H$_2$O$_2$ to be photolyzed by UVA light regenerating the Fe(II) species with loss of CO$_2$ and inorganic N products. Results of Table 1 indicate that $k_{\text{oxalic}} > k_{\text{oxamic}}$ for AO-BDD and AO-BDD-Fe$^{2+}$-UVA, while $k_{\text{oxalic}} < k_{\text{oxamic}}$ for AO-BDD-Fe$^{2+}$ and EF-BDD. That means that oxamic acid is more recalcitrant than oxalic acid only in the two former methods, but not in the two latter. For the EAOPs tested, TOC was removed similarly to oxamic acid, indicating the formation of insignificant amounts of organic by-products during all mineralization processes. In addition, the progressive loss in oxidizable organic matter caused a continuous fall in MCE.

Fig. 3 illustrates the predominance of N lost as NH$_4^+$ ion at the end of all EAOPs tested to mineralize the 2.08 mM oxalic acid solution at 33.3 mA cm$^{-2}$. The larger proportion of N lost as NO$_3^-$ ion is found for AO-BDD, indicating that NH$_4^+$ ion is preferentially formed during the oxidation of Fe(III)-oxamate species than oxamic acid. TN analysis of final electrolyzed solutions confirmed the release of N as NO$_x$ species. For AO-BDD-Fe$^{2+}$-UVA, for example, the initial 29.6 mg L$^{-1}$ of N were reduced to 23.1 mg L$^{-1}$ in 270 min, i.e. when all oxamic acid
is mineralized, corresponding to a loss of 21.9% of N as NO\(_x\) species, a value close to 21.8% determined from the N obtained for NH\(_4^+\) (64%) and NO\(_3^-\) (14.2%), as depicted in Fig. 3.

3.5. Mineralization of mixtures of oxalic and oxamic acid by EAOPs

Since a mixture of oxalic and oxamic acid is obtained as ultimate by-product of the degradation of N-aromatics by EAOPs (Sirés et al., 2006; Hammami et al., 2008; Hamza et al., 2009), the possible influence of the relative proportion of both acids on their removal rate was investigated. To do this, 8%, 25% and 43% of oxamic acid was added to the 2.08 mM oxalic acid solution to be treated by AO-BDD, AO-BDD-Fe\(^{2+}\) and AO-BDD-Fe\(^{2+}\)-UVA at 33.3 mA cm\(^{-2}\), after adding 0.5 mM Fe\(^{2+}\) in the two latter methods. The \(k_{\text{oxamic}}\) and \(k_{\text{oxalic}}\) values determined simultaneously for these experiments are summarized in Table 2.

For AO-BDD, similar \(k_{\text{oxamic}} \sim 1.1 \times 10^{-4}\) s\(^{-1}\) and \(k_{\text{oxalic}} \sim 1.5 \times 10^{-4}\) s\(^{-1}\) to that of pure solutions (see Table 1) are found, evidencing that both acids are independently oxidized at the BDD anode via direct charge transfer. In contrast, the competition between Fe(III)-oxamate and Fe(III)-oxalate complexes causes a change in the removal rate of acids in the EAOPs with Fe\(^{2+}\). Thus, for AO-BDD-Fe\(^{2+}\), \(k_{\text{oxalic}}\) gradually decays with decreasing the percentage of oxamic acid, while \(k_{\text{oxamic}} \sim 1.3 \times 10^{-4}\) s\(^{-1}\) is similar to \(1.2 \times 10^{-4}\) s\(^{-1}\) for pure iron-oxamate complexes (see Table 1). This deceleration of oxalic acid removal is due to the progressive formation of a larger proportion of Fe(III)-oxalate complexes that are more difficultly oxidized with BDD(\(^{•}\)OH). The much faster destruction of Fe(III)-oxamate species with this radical explains the slight change in \(k_{\text{oxamic}}\) in all mixtures. The smaller amount of Fe(III)-oxamate species formed and the rise in Fe(III)-oxalate ones with decreasing the percentage of oxamic acid are also reflected in AO-BDD-Fe\(^{2+}\)-UVA, where the low photoactivity of the former accounts for the drop in \(k_{\text{oxamic}}\), whereas the much greater photoactivity of the latter justifies the slight increase in \(k_{\text{oxalic}}\). A slower removal of oxamic acid is then expected as its content decreases, without significant effect on oxalic acid decay.
3.6. Effect of current density and Fe$^{2+}$ content on the mineralization of oxamic acid by AO-BDD-Fe$^{2+}$-UVA

The abatement of TOC and oxamic acid content between 16.6 and 100 mA cm$^{-2}$ for the most potent AO-BDD-Fe$^{2+}$-UVA process is presented in Fig. 5a and 5b, respectively. The rise in current density accelerates the decay of both parameters, enhancing the oxidation power of the process. The time required for overall mineralization (see Fig. 5a) is slightly longer than that needed for total destruction of the acid (see Fig. 5b), as expected if very low amounts of more recalcitrant by-products are formed. A progressive loss in MCE as current density increases can be observed in the inset panel of Fig. 5a, whereas the opposite trend is found for $k_{\text{oxamic}}$ in the inset panel of Fig. 5b, which gradually increases from $1.48 \times 10^{-4}$ s$^{-1}$ ($R^2 = 0.999$) for 16.6 mA cm$^{-2}$ to $3.15 \times 10^{-4}$ s$^{-1}$ ($R^2 = 0.996$) for 100 mA cm$^{-2}$. This behavior agrees with the expected production of more amounts of oxidant BDD$(\cdot \text{OH})$ from reaction (1) at greater current density (Brillas et al., 2009; Panizza and Cerisola, 2009), accelerating the oxidation of Fe(II) into Fe(III) complexes to be more quickly photolyzed by UVA light. The loss in efficiency evidences that the excess of generated BDD$(\cdot \text{OH})$ is mainly wasted by oxidation to O$_2$ via reaction (16) (Marselli et al., 2003; Panizza and Cerisola, 2009):

$$2 \text{BDD}(\cdot \text{OH}) \rightarrow 2 \text{BDD} + \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \quad (16)$$

The evolution of NH$_4^+$ and NO$_3^-$ ions detected during 360 min in the above experiments is shown in Fig. 6a and 6b, respectively. NH$_4^+$ ion is continuously accumulated up to 33.3 mA cm$^{-2}$, but it undergoes a gradual drop as electrolysis time is prolonged at current densities ≥ 66.6 mA cm$^{-2}$. The fast removal of NH$_4^+$ ion at 100 mA cm$^{-2}$ is accompanied by a large NO$_3^-$ accumulation, while much lower contents of this ion are found at lower current densities. Increasing percentages of N lost as NO$_x$ species of 15.3%, 21.8%, 44.0% and 55.5% were thus determined for 16.6, 33.3, 66.6 and 100 mA cm$^{-2}$, also confirmed from TN analysis of...
final electrolyzed solutions. These findings suggest that high current densities accelerate the 
parasite oxidation of $\text{NH}_4^+$ to $\text{NO}_3^-$ ion with the greater amounts of BDD(\textsuperscript{\bullet}OH) produced, 
increasing the loss of NO\textsubscript{x} species. This suggestion was corroborated by electrolyzing a 
($\text{NH}_4$)$_2$SO\textsubscript{4} solution with 20 mg L\textsuperscript{-1} of N under similar conditions. For 100 mA cm\textsuperscript{-2}, $\text{NH}_4^+$ ion 
was totally removed in 270 min generating 4.6 mg L\textsuperscript{-1} of N as $\text{NO}_3^-$ ion and releasing 78\% of 
N as NO\textsubscript{x} species. In contrast, after 360 min of electrolysis at 33.3 mA cm\textsuperscript{-2}, 11.3 mg L\textsuperscript{-1} of N 
as $\text{NH}_4^+$ ion and 1.2 mg L\textsuperscript{-1} of N as $\text{NO}_3^-$ ion were found, with loss of 37\% of N as NO\textsubscript{x} 
species. Note that $\text{NH}_4^+$ is converted into $\text{NO}_3^-$ in larger extent in the treatment of ($\text{NH}_4$)$_2$SO\textsubscript{4} 
that oxamic acid, probably because $\text{NH}_4^+$ ion is gradually released to the medium in the latter 
case and its oxidation at the BDD anode competes with that of iron-oxamate complexes.

Fig. 7a evidences that oxamic acid removal is inhibited with increasing Fe\textsuperscript{2+} content. This 
trend can be related to a gradual decay in rate of the reaction between Fe(II)-oxamate species 
and BDD(\textsuperscript{\bullet}OH), decelerating its conversion into photoactive Fe(III) complexes, due to the 
competition of the oxidation of larger amounts of free Fe\textsuperscript{2+} to Fe\textsuperscript{3+} ion at the anode (Sirés et 
al., 2007). The reduction of Fe\textsuperscript{3+} ion at the SS cathode regenerates the Fe\textsuperscript{2+} ion and maintains 
the equilibrium between both ions in solution (Brillas et al., 2009). The loss of oxidation 
ability of the system is also reflected in Fig. 7b, where higher Fe\textsuperscript{2+} content causes a gradual 
decay in the percentage of N lost as $\text{NO}_3^-$ ion and a larger proportion of N lost as $\text{NH}_4^+$ ion, 
with a similar percentage of N lost as NO\textsubscript{x} species. The presence of small amounts of Fe\textsuperscript{2+} in 
solution then minimizes the undesired oxidation of Fe\textsuperscript{2+} at the anode, favouring the rapid 
conversion of Fe(II)-oxamate complexes into photoactive Fe(III)-oxamate species.

4. Conclusions

Oxalic and oxamic acids were efficiently mineralized by AO-BDD-Fe\textsuperscript{2+}-UVA, as a result 
of the high photoactivity of their Fe(III) complexes that are continuously regenerated by
oxidation of their Fe(II) complexes with BDD(•OH) formed at the anode surface and H₂O₂ generated from O₂ reduction or BDD(•OH) dimerization. In this method, oxamic acid was more recalcitrant by the lower photoactivity of its Fe(III) complexes, releasing a larger proportion of NH₄⁺ than NO₃⁻ ion. The loss of volatile NOₓ species was confirmed from TN analysis of the final electrolyzed solutions. Each acid underwent a similar decay in AO-BDD-Fe²⁺ and EF-BDD since its iron complexes were not attacked with •OH in the bulk. AO-BDD also allowed the total conversion of oxalic acid into CO₂ by direct charge transfer at the anode. This process explained the slower destruction of oxamic acid by this method. In contrast, oxamic acid was less recalcitrant in AO-BDD-Fe²⁺ and EF-BDD, since Fe(III)-oxamate complexes were oxidized more quickly with BDD(•OH) than Fe(III)-oxalate ones. TOC always decayed similarly to the corresponding acid, indicating a insignificant formation of by-products. While both acids when mixed were independently oxidized at the anode in AO-BDD, the proportion of their Fe(III) complexes and their ability to be oxidized and/or photolyzed affected their degradation rate in the EAOPs with Fe²⁺. For the most potent AO-BDD-Fe²⁺-UVA, a lower oxamic acid content decelerated its degradation, without significant effect on oxalic acid decay. Greater current density enhanced the oxidation power of this method since oxamic acid removal was accelerated, but losing efficiency. High Fe²⁺ contents inhibited the oxidation of Fe(II)-oxamate complexes by the competitive oxidation of free Fe²⁺ to Fe³⁺. Low current densities and Fe²⁺ contents are then preferable for the more efficient removal of these acids in AO-BDD-Fe²⁺-UVA.

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References


Figure Captions

**Fig. 1.** Cyclic voltammograms recorded for the oxidation of (a) 2.08 mM oxalic and oxamic acids and (b) their solutions with 0.5 mM Fe$^{2+}$ or 0.5 mM Fe$^{3+}$ in 0.05 M Na$_2$SO$_4$ of pH 3.0 on a 0.40 cm$^2$ boron-doped diamond (BDD) anode. Initial and final potentials 1.0 V, reversal potential: (a) 2.3 V and (b) 3.3 V. Scan rate 100 mV s$^{-1}$. Temperature 25 ºC.

**Fig. 2.** Decay of the concentration of (a) oxalic and (b) oxamic acids from 100 mL of 2.08 mM of each carboxylic acid in 0.05 M Na$_2$SO$_4$ at pH 3.0 and 35 ºC. Method: (●) 6 W UVA irradiation (UVA), (■) 0.5 mM Fe$^{2+}$ solution and UVA light (UVA-Fe$^{2+}$), (♦) 0.5 mM Fe$^{3+}$ solution and UVA light (UVA-Fe$^{3+}$), (□) AO in BDD/stainless steel (SS) cell (AO-BDD), (△) AO-BDD with 0.5 mM Fe$^{2+}$ (AO-BDD-Fe$^{2+}$), (▲) electro-Fenton (EF) in BDD/air-diffusion electrode (ADE) cell with 0.5 mM Fe$^{2+}$ (EF-BDD) and (▽) AO-BDD with 0.5 mM Fe$^{2+}$ under UVA irradiation (AO-BDD-Fe$^{2+}$-UVA). Current density of 33.3 mA cm$^{-2}$ in all EAOPs.

**Fig. 3.** Percentage of nitrogen released as (■) NH$_4^+$ ion, (□□) NO$_3^-$ ion and (◮) NO$_x$ species at the end of the trials of Fig. 2b for oxamic acid.

**Fig. 4.** Proposed reaction sequence for the mineralization of Fe(III)-oxalate complexes in acidic aqueous medium by EAOPs with Fe$^{2+}$ as catalyst under UVA irradiation using a BDD anode.

**Fig. 5.** Effect of current density on (a) TOC removal and (b) concentration decay for the AO-BDD-Fe$^{2+}$-UVA treatment of 100 mL of 2.08 mM oxamic acid in 0.05 M Na$_2$SO$_4$ with 0.5 mM Fe$^{2+}$ at pH 3.0 and 35 ºC. Current density: (○) 16.6 mA cm$^2$, (□) 33.3 mA cm$^2$, (◇) 66.6 mA cm$^2$ and (△) 100 mA cm$^2$. The inset panels show: (a) the mineralization current efficiency calculated from Eq. (4) and (b) the kinetic analysis assuming a pseudo first-order reaction for oxamic acid.
Fig. 6. Evolution of the concentration of (a) ammonium and (b) nitrate ions released during the experiments of Fig. 5.

Fig. 7. (a) Effect of Fe$^{2+}$ content on the decay of oxamic acid concentration for the AO-BDD-Fe$^{2+}$-UVA degradation of 100 mL of 2.08 mM of the carboxylic acid in 0.05 M Na$_2$SO$_4$ at pH 3.0, 33.3 mA cm$^{-2}$ and 35 ºC. [Oxamic acid]/[Fe$^{2+}$] ratio: (○) 4:1, (□) 2:1, (△) 1:1, (△) 1:2 and (▽) 1:4. (b) Percentage of nitrogen lost as (■) NH$_4^+$ ion, (□□) NO$_3^-$ ion and (□□□) NO$_x$ species vs [oxamic acid]/[Fe$^{2+}$] ratio at the end of these experiments.
Fig. 1
Fig. 2

[Graph showing the decay of oxalic acid and oxamic acid over time.]

(a) Oxalic acid decay

(b) Oxamic acid decay

[Axes: Oxalic acid concentration (mg L$^{-1}$) vs. time (min)]
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Table 1. Pseudo first-order rate constant and square regression coefficient (in parenthesis) for the decay of oxalic and oxamic acids during the degradation of 2.08 mM of each compound in 0.05 M Na$_2$SO$_4$ with 0.5 mM Fe$^{2+}$ or 0.5 mM Fe$^{3+}$ of pH 3.0 at 35 °C. The solution was irradiated with a 6 W UVA light and a current density of 33.3 mA cm$^{-2}$ was applied in all EAOPs.

<table>
<thead>
<tr>
<th>Method</th>
<th>$k_{\text{oxalic}} \times 10^4$ (s$^{-1}$)</th>
<th>$k_{\text{oxamic}} \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVA-Fe$^{2+}$</td>
<td>0.75 (0.995)</td>
<td>0.40 (0.978)</td>
</tr>
<tr>
<td>UVA-Fe$^{2+}$ (O$_2$ sat.)</td>
<td>1.33 (0.988)</td>
<td>---$^a$</td>
</tr>
<tr>
<td>UVA-Fe$^{3+}$</td>
<td>6.43 (0.985)</td>
<td>1.10 (0.996)</td>
</tr>
<tr>
<td>UVA-Fe$^{3+}$ (O$_2$ sat.)</td>
<td>6.83 (0.984)</td>
<td>---$^a$</td>
</tr>
<tr>
<td>AO-BDD</td>
<td>1.49 (0.999)</td>
<td>1.01 (0.993)</td>
</tr>
<tr>
<td>AO-BDD-Fe$^{2+}$</td>
<td>0.61 (0.986)</td>
<td>1.20 (0.998)</td>
</tr>
<tr>
<td>EF-BDD-Fe$^{2+}$</td>
<td>0.61 (0.989)</td>
<td>1.15 (0.998)</td>
</tr>
<tr>
<td>AO-BDD-Fe$^{2+}$-UVA</td>
<td>9.01 (0.983)</td>
<td>2.82 (0.995)</td>
</tr>
</tbody>
</table>

$^a$Not determined
Table 2. Pseudo first-order rate constant and square regression coefficient (in parenthesis) determined for the decay of oxamic and oxalic acids during the degradation of 100 mL solutions of different percentages of oxamic acid with a total acid concentration of 2.08 mM by several EAOPs at 33.3 mA cm$^{-2}$.

<table>
<thead>
<tr>
<th>% Oxamic acid</th>
<th>AO-BDD $k_{\text{oxamic}} \times 10^4$ (s$^{-1}$)</th>
<th>$k_{\text{oxalic}} \times 10^4$ (s$^{-1}$)</th>
<th>AO-BDD-Fe$^{2+}$ $k_{\text{oxamic}} \times 10^4$ (s$^{-1}$)</th>
<th>$k_{\text{oxalic}} \times 10^4$ (s$^{-1}$)</th>
<th>AO-BDD-Fe$^{2+}$-UVA $k_{\text{oxamic}} \times 10^4$ (s$^{-1}$)</th>
<th>$k_{\text{oxalic}} \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1.05 (0.989)</td>
<td>1.53 (0.998)</td>
<td>1.33 (0.987)</td>
<td>1.03 (0.995)</td>
<td>2.27 (0.992)</td>
<td>7.65 (0.990)</td>
</tr>
<tr>
<td>25</td>
<td>1.12 (0.997)</td>
<td>1.54 (0.996)</td>
<td>1.27 (0.989)</td>
<td>0.97 (0.980)</td>
<td>2.00 (0.999)</td>
<td>7.62 (0.993)</td>
</tr>
<tr>
<td>8</td>
<td>1.12 (0.993)</td>
<td>1.50 (0.998)</td>
<td>1.36 (0.991)</td>
<td>0.72 (0.988)</td>
<td>1.61 (0.993)</td>
<td>7.90 (0.981)</td>
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