1 # Mineralization of the recalcitrant oxalic and oxamic

2 # acids by electrochemical advanced oxidation processes

3 # using a boron-doped diamond anode

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11 **Abstract**

12 Oxalic and oxamic acids are the ultimate and more persistent by-products of the degradation of

13 *N*-heteroaromatics by electrochemical advanced oxidation processes (EAOPs). In this paper,

14 the kinetics and oxidative paths of these acids have been studied for several EAOPs using a

15 boron-doped diamond (BDD) anode and a stainless steel or an air-diffusion cathode. Anodic

16 oxidation (AO-BDD) in the presence of Fe^{2+} (AO-BDD-Fe^{2+}) and under UVA irradiation (AO-

17 BDD-Fe^{2+}-UVA), along with electro-Fenton (EF-BDD), were tested. The oxidation of both

18 acids and their iron complexes on BDD was clarified by cyclic voltammetry. AO-BDD

19 allowed the overall mineralization of oxalic acid, but oxamic acid was removed much more

20 slowly. Each acid underwent a similar decay in AO-BDD-Fe^{2+} and EF-BDD, as expected if its

21 iron complexes were not attacked by hydroxyl radicals in the bulk. The faster and total

22 mineralization of both acids was achieved in AO-BDD-Fe^{2+}-UVA due to the high

23 photoactivity of their Fe(III) complexes that were continuously regenerated by oxidation of

24 their Fe(II) complexes. Oxamic acid always released a larger proportion of NH_4^+ than NO_3^-

25 ion, as well as volatile NO_x species. Both acids were independently oxidized at the anode in

26 AO-BDD, but in AO-BDD-Fe^{2+}-UVA oxamic acid was more slowly degraded as its content

27 decreased, without significant effect on oxalic acid decay. The increase in current density

28 enhanced the oxidation power of the latter method, with loss of efficiency. High Fe^{2+} contents

29 inhibited the oxidation of Fe(II) complexes by the competitive oxidation of Fe^{2+} to Fe^{3+}. Low

30 current densities and Fe^{2+} contents are preferable to remove more efficiently these acids by the

31 most potent AO-BDD-Fe^{2+}-UVA method.

32 *Keywords*: Carboxylic acids; Iron complexes; Anodic oxidation; Electro-Fenton; UVA light;

33 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 ($^{\bullet}$OH). This radical is the second most strong oxidizing specie known after fluorine with a high standard reduction potential ($E°(^{\bullet}OH/H_2O) = 2.80$ 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 $^{\bullet}$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 $^{\bullet}$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):

3

59    $BDD + H_2O \rightarrow BDD(^\bullet OH) + H^+ + e^-$ (1)
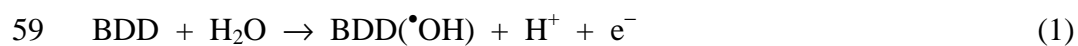
60   The BDD electrode has a much higher oxidation power than other conventional anodes and it

61   is able to effectively mineralize oxalic acid (Gandini et al., 2000; Martínez-Huitle et al., 2004;

62   Vandini et al., 2006; Weiss et al., 2007; Scialdone et al., 2008), but no information is

63   available on the AO treatment of oxamic acid. The high oxidation power of BDD also allows

64   generating reactive oxygen species (ROS) like H_2O_2 and ozone, as well as peroxo-derivatives

65   coming from the oxidation of the anion of the background electrolyte (Cañizares et al., 2003;

66   Panizza and Cerisola, 2009). In previous work (Guinea et al., 2009), we found that the

67   presence of H_2O_2 in AO accelerates the mineralization process of carboxylic acids, although

68   Fe(III)-oxalate complexes are quickly photolyzed by UVA light.

69   EAOPs based on Fenton's reaction chemistry have been recently developed (Brillas et al.,

70   2009). In electro-Fenton (EF), H_2O_2 is continuously supplied to an acidic contaminated

71   solution from the two-electron reduction of injected O_2 at a carbonaceous cathode, mainly

72   carbon felt (Oturan et al., 2008; Balci et al., 2009) and carbon-PTFE gas-diffusion electrodes

73   (Sirés et al., 2007, Ruiz et al., 2011), by reaction (2):

74    $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (2)

75   Fe^{2+} ion is then added to the solution to react with H_2O_2 producing $^\bullet OH$ in the bulk and Fe^{3+}

76   by Fenton's reaction (3) (Sun and Pignatello, 1993):

77    $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^-$ (3)

78   An advantage of EF is that Fe^{2+} can be regenerated from Fe^{3+} reduction at the cathode,

79   thus accelerating Fenton's reaction (3) and the oxidation of organics with $^\bullet OH$ (Brillas et al.,

80   2009). When a one-compartment cell with a BDD anode is used, the degradation of organic

81   pollutants is additionally enhanced by the attack of $BDD(^\bullet OH)$ formed from reaction (1)

82   (Serra et al., 2009; Ruiz et al. 2011). The mineralization of aromatics can also be accelerated

83 by exposing the contaminated solution to UVA light while is treated by EF (Brillas et al.,

84 2004; Sirés et al., 2006; Ruiz et al., 2011). The main action of UVA irradiation is the

85 photodecarboxylation of Fe(III)-carboxylate complexes.

86   The degradation of *N*-aromatics by EAOPs involves a high number of by-products that

87 are simultaneously formed and destroyed by the different oxidizing species. Oxalic and

88 oxamic acids are accumulated from the beginning of the process and their slow destruction

89 limits the oxidation power of these methods. However, the influence of oxidants and/or UVA

90 light on their removal, particularly of their iron species, is not well known yet.

91   To gain a better insight on the mineralization processes of oxalic and oxamic acids to

92 better understand the degradation of *N*-aromatics, we report a study on the kinetics and

93 oxidative paths of both acids by EAOPs with a BDD anode under typical treatment conditions

94 of synthetic wastewaters with organics in sulfate medium. Special attention was taken on the

95 action of Fe^{2+} and UVA light to clarify the destruction of their iron complexes. The oxidation

96 of these compounds on BDD was analyzed by cyclic voltammetry (CV). The change in

97 degradation rate of each acid when mixed in different proportions was examined. The effect

98 of current density and Fe^{2+} content on oxamic acid removal was assessed. NH_4^+ and NO_3^-

99 ions lost during the mineralization of oxamic acid were followed by ionic chromatography.

100 **2. Materials and methods**

101 *2.1. Chemicals*

102   Oxalic and oxamic acids were of analytical grade from Avocado. Anhydrous sodium

103 sulfate, ferrous sulfate heptahydrate and ferric sulfate hydrate were of analytical grade from

104 Fluka and Sigma. Solutions were prepared with high-purity water obtained from a Millipore

105 Milli-Q system with resistivity > 18 MΩ cm at 25 ºC. Organic solvents and other chemicals

106 used were of HPLC or analytical grade from Aldrich, Lancaster, Merck and Panreac.

2.2. Apparatus

108   The solution pH was measured with a Crison GLP 22 pH-meter. CV was conducted with

109   an Ecochemie Autolab PGSTAT100 potentiostat-galvanostat controlled by an Autolab Nova

110   1.5 software. Electrolyses were performed with an Amel 2053 potentiostat-galvanostat. The

111   concentration of dissolved O_2 was determined with a Thermo Electron Corporation Orion 4

112   Star pH-DO portable with a Sensor Orion 083005MD DO probe. Total organic carbon (TOC)

113   of solutions was measured with a Shimadzu V$_{CSN}$ TOC analyzer. Total nitrogen (TN) was

114   determined with a Shimadzu TNM-1 unit coupled with the TOC analyzer. The concentration

115   of oxalic and oxamic acids was quantified by ion-exclusion HPLC using a Waters 600 liquid

116   chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at

117   35 ºC, coupled with a Waters 996 photodiode array detector at $\lambda = 210$ nm. Inorganic ions lost

118   during oxamic acid degradation were detected by ionic chromatography using a Shimadzu 10

119   Avp HPLC coupled with a Shimadzu CDD 10 Avp conductivity detector. NH_4^+ concentration

120   was obtained with a Shodex IC YK-421, 125 mm × 4.6 mm (i.d.), cation column at 40 ºC,

121   whereas NO_3^- content was determined with a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.),

122   anion column at 40 ºC.

123   *2.3. Electrochemical systems*

124   All electrolytic experiments were conducted in an open, undivided and thermostated

125   cylindrical cell, so that all gases formed were directly released to the atmosphere. The anode

126   was a BDD thin film provided by Adamant Technologies (La-Chaux-de-Fonds, Switzerland),

127   while the cathode was either a stainless steel (AISI 304 grade) sheet (SS) or a carbon-PTFE

128   air-diffusion electrode (ADE) from E-TEK (Somerset, NJ, USA). The preparation of the ADE

129   cathode were described elsewhere (Brillas et al., 2004). It was fed with air pumped at 300 mL

130   min^{-1} to generate H_2O_2 by reaction (2). The area of all electrodes was 3 cm^2 and the

131   interelectrode gap was ca. 1 cm. To remove the impurities of the BDD surface and activate

132   the ADE cathode, they were previously polarized in 0.05 M Na_2SO_4 at 300 mA for 60 min.

133   The same cell without electrodes was used for the photochemical assays under UVA light.

134   Comparative photochemical and electrochemical degradations of 100 mL of 2.08 mM (50

135   mg L^{-1} of TOC) of oxalic (188 mg L^{-1}) or oxamic (185 mg L^{-1}) acid in 0.05 M Na_2SO_4 at pH

136   3.0 were performed. The photochemical assays with direct UVA exposition were made after

137   addition of 0.5 mM Fe^{2+} (UVA-Fe^{2+}) or 0.5 mM Fe^{3+} (UVA-Fe^{3+}). The electrolytic methods

138   were anodic oxidation with a BDD/SS cell (AO-BDD), the same treatment after addition of

139   0.5 mM Fe^{2+} (AO-BDD-Fe^{2+}) and under UVA illumination (AO-BDD-Fe^{2+}-UVA), and

140   electro-Fenton with a BDD/ADE cell and 0.5 mM Fe^{2+} (EF-BDD). For the trials with UVA

141   irradiation, a Philips TL/6W/08 fluorescent black light blue tube placed at 7 cm above the

142   solution was employed. The tube emitted UVA light in the wavelength region 320-420 nm

143   with λ_{max} = 360 nm, supplying a photoionization energy of 5 W m^{-2} as detected with a Kipp &

144   Zonen CUV 5 radiometer. In all experiments, the solution was kept at 35.0 ºC under vigorous

145   stirring with a magnetic bar at 800 rpm to ensure its homogenization, as well as the transport

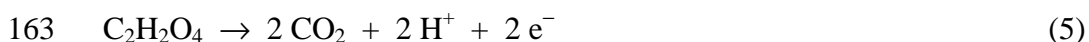146   of reactants towards/from the electrodes in the electrolytic assays.

147   CV measurements were carried out with a three-electrode one-compartment cell

148   thermostated at 25 ºC. The working electrode was a 0.40 cm^2 BDD, the counter reference was

149   a Pt wire and the reference electrode was a Ag|AgCl|KCl (saturated) electrode (E^o = 0.197

150   V/SHE). Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} under an Ar

151   atmosphere after previous bubbling of this gas through the solution for 30 min.

152   *2.4. Analytical procedures*

153   Before analysis, aliquots withdrawn from treated solutions were filtered with 0.45 µm

154   PTFE filters from Whatman. Reproducible TOC values with an accuracy of ±1% were found

155   by injecting 50 µL aliquots to the TOC analyzer. The mineralization current efficiency (MCE)

156   for electrolyzed solutions at time *t* (h) was then calculated by Eq. (4) (Hamza et al., 2009):

157 $$\text{MCE (\%)} = \frac{n\,F\,V_s\,\triangle(\text{TOC})_{\text{exp}}}{4.32\times10^7\,m\,I\,t} \times 100 \qquad\qquad (4)$$

158 where F is the Faraday constant (96487 C mol^{-1}), V_s is the solution volume (L), $\triangle(\text{TOC})_{\text{exp}}$ is

159 the experimental TOC removal (mg L^{-1}), 4.32×10^7 is a conversion factor (3600 s h^{-1} x 12000

160 mg mol^{-1}), m is the number of carbon atoms of each acid (2 C atoms) and I is the current (A).

161 The number of electrons (n) consumed was taken as 2 for oxalic acid and 10 for oxamic acid,

162 assuming that their overall mineralization corresponds to reactions (5) and (6), respectively:

163 $C_2H_2O_4 \rightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-$ $\qquad\qquad\qquad$ (5)

164 $C_2H_3NO_3 + 4\,H_2O \rightarrow 2\,CO_2 + NO_3^- + 11\,H^+ + 10\,e^-$ $\qquad\quad$ (6)

165 The ion-exclusion HPLC measurements were made after injection of 20 µL aliquots into

166 the liquid chromatograph and circulation of 4 mM H_2SO_4 at 0.6 mL min^{-1} as mobile phase.

167 Ionic chromatography was performed with 25 µL aliquots using a mobile phase composed of

168 5.0 mM tartaric acid, 1.0 mM dipicolinic acid, 24.2 mM boric acid and 1.5 mM corona ether

169 at 1.0 mL min^{-1} for NH_4^+ and 2.4 mM tris(hydroxymethyl)aminomethane and 2.5 mM

170 phthalic acid of pH 4.0 at 1.5 mL min^{-1} for NO_3^-.

171 **3. Results and discussion**

172 *3.1. CV behavior of oxalic and oxamic acids and their iron complexes*

173 Fig. 1a shows the cyclic voltammograms obtained for the oxidation of 2.08 mM oxalic

174 and oxamic acids in 0.05 M Na_2SO_4 on a BDD electrode at pH 3.0 and 100 mV s^{-1}. Both

175 compounds display an irreversible peak, with an anodic peak potential (E_p^a) of 2.10 and 2.14

176 V for oxalic and oxamic acids, respectively, which partially overlap with that of water

177 discharge to O_2 beginning at 2.2 V. The CV behaviour found for oxalic acid agrees with that

178 reported by other authors (Martínez-Huitle et al., 2004; Weiss et al., 2007; Scialdone et al.,

179 2008), who suggested the direct anodic oxidation of the acid at the BDD anode surface rather
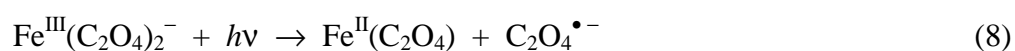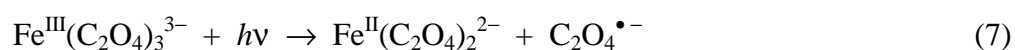
180   than its mediated reaction with BDD($^\bullet$OH) produced from reaction (1) to be converted into

181   CO_2. This behavior can also be extended to the case of oxamic acid, which is oxidized at

182   slightly higher potentials than oxalic acid and with a greater peak current due to the additional

183   transformation of its -NH_2 group into inorganic ions.

184   The comparative cyclic voltammograms recorded for the above acids in the presence of

185   0.5 mM Fe^{2+} or 0.5 mM Fe^{3+} are depicted in Fig. 1b. Fe(II)- or Fe(III)-carboxylate complexes

186   formed are oxidized at much more positive potentials than pure acids, clearly overlapping

187   with the water discharge region. The irreversible peak for Fe(II)-oxalate complexes with $E_p^a =$

188   2.31 V has much higher height than that of oxalic acid (see Fig. 1a), as a result of the more

189   complex oxidation of their electroactive species, predominantly $Fe^{II}(C_2O_4)_2^{2-}$ (Lan et al.

190   2010). In contrast, the dominant $Fe^{III}(C_2O_4)_3^{3-}$ and $Fe^{III}(C_2O_4)_2^{-}$ ions in the solution of Fe(III)-

191   oxalate complexes (Balmer and Sulzberger, 1999; Kwan and Chu, 2007; Lan et al., 2010) are

192   oxidized at so high potentials that any peak is displayed in CV. Fe(II)- and Fe(III)-oxamate

193   complexes exhibit a similar irreversible peak, with high E_p^a of 2.54 and 2.72 V, respectively,

194   suggesting that their ionic structures (not reported in literature) are analogous to those of iron-

195   oxalate complexes, although the Fe(III)-oxamate species are more easily oxidizable. This is

196   not surprising since oxamic like oxalic acid behaves as a bidentate ligand, coordinated with

197   the amidic N, after ionization of one amidic H, and with the carboxylate O (Pardo et al.,

198   2004). The fact that the iron complexes of oxalic and oxamic acids are destroyed in the water

199   discharge zone indicates that they react predominantly with BDD($^\bullet$OH) at the anode surface.

200   *3.2. Photochemical degradation of oxalic and oxamic acids and their iron complexes*

201   A series of trials was made to assess the degradation effect of the 6 W UVA light on 100

202   mL of the 2.08 mM acid solutions in the absence and presence of 0.5 mM Fe^{2+} or 0.5 mM

203   Fe^{3+}. The evolution of each compound was monitored by ion-exclusion chromatography,

204   which displayed a well-defined adsorption peak at retention time of 6.8 min for oxalic acid

205 and 9.4 min for oxamic acid. Fig. 2a and 2b show that both acids are very stable under UVA

206 irradiation, as expected if they are not directly photolyzed. In contrast, their iron complexes

207 are photodegraded at different rate depending on the acid and iron ion tested. The fastest

208 removal was found for the UVA-Fe^{3+} treatment of oxalic acid, which disappears in about 150

209 min. Overall destruction of this acid is also feasible using UVA-Fe^{2+}, although a longer time

210 close to 360 min is required. The kinetic analysis of these experiments showed good linear

211 correlations for a pseudo first-order reaction. The pseudo first-order rate constant (k_{oxalic}) thus

212 determined, along the corresponding square of regression coefficient, are collected in Table 1.

213 The quick photodegradation of Fe(III)-oxalate complexes can be accounted for by the high

214 photoactivity of their dominant ionic species by reactions (7) and (8) (Faust and Zepp, 1993;

215 Balmer and Sulzberger, 1999; Jeong and Yoon, 2005):

216 $\quad Fe^{III}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{II}(C_2O_4)_2^{2-} + C_2O_4^{\bullet-}$ $\qquad\qquad$ (7)

217 $\quad Fe^{III}(C_2O_4)_2^{-} + h\nu \rightarrow Fe^{II}(C_2O_4) + C_2O_4^{\bullet-}$ $\qquad\qquad\quad$ (8)

218 These reactions are photoredox processes with a ligand-to-metal charge transfer leading to the

219 homolytic break of a Fe(III)-O coordination bond of the bidentate oxalate ligand (Šima and

220 Makáňová, 1997). The anion radical $C_2O_4^{\bullet-}$ released yields CO_2 and the anion radical $CO_2^{\bullet-}$

221 by reaction (9), which then reacts with dissolved O_2 to produce the ion superoxide ($O_2^{\bullet-}$) from

222 reaction (10). This specie originates a cascade of other ROS like hydroperoxide radical

223 ($HO_2^{\bullet}$) from reaction (11) and H_2O_2 from reaction (12). H_2O_2 can further oxidize the Fe(II) to

224 Fe(III) complexes, as exemplified for $Fe^{II}(C_2O_4)_2^{2-}$ in reaction (13), at a rate about 1000 times

225 higher than that of Fenton's reaction (3) (Faust and Zepp, 1993), thus closing the

226 Fe(III)/Fe(II) catalytic loop. The large production of $^{\bullet}OH$ from the reaction (13), which does

227 not attack the iron-oxalate complexes, has been well proven in photoassisted ferrioxalate

228 systems (Jeong and Yoon, 2005; Rodríguez et al., 2007; Monteagudo et al., 2008).

229    $$C_2O_4^{\bullet -} \rightarrow CO_2 + CO_2^{\bullet -}$$ (9)

230    $$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -}$$ (10)

231    $$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$$ (11)

232    $$O_2^{\bullet -} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2$$ (12)

233    $$Fe^{II}(C_2O_4)_2^{2-} + H_2O_2 \rightarrow Fe^{III}(C_2O_4)_2^- + {}^{\bullet}OH + OH^-$$ (13)
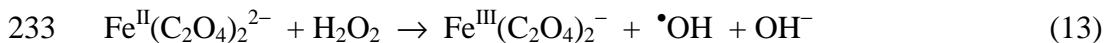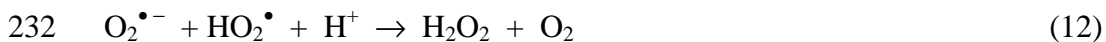
234   The slow decay of oxalic acid in the UVA-Fe^{2+} system can then be related to the much

235   lower photoactivity of Fe(II) complexes to be converted into Fe(III) ones, as exemplified by

236   reaction (14) (Faust and Zepp, 1993; Kwan and Chu, 2007):

237    $$Fe^{II}(C_2O_4)_2^{2-} + h\nu \rightarrow Fe^{III}(C_2O_4)_2^-$$ (14)
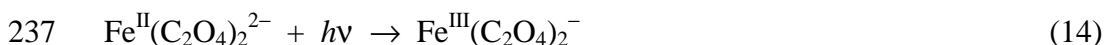
238   Once the Fe(III)-oxalate complexes are formed, a photodegradation path similar to that

239   described above for the UVA-Fe^{3+} treatment takes place, although the large preponderance of

240   Fe(II)-oxalate complexes at the beginning of the process makes it slower.

241   The aforementioned experiments for oxalic acid were performed with 7.6 mg L^{-1} of

242   dissolved O_2. To clarify the generation of ROS via reactions (10)-(12), the same trials were

243   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

244   confirm the increase in k_{oxalic} in both systems, much more for UVA-Fe^{2+} (1.77-fold) than for

245   UVA-Fe^{3+} (1.06-fold). The excess of H_2O_2 formed under O_2 bubbling strongly accelerates the

246   oxidation of $Fe^{II}(C_2O_4)_2^{2-}$ by reaction (13) in UVA-Fe^{2+}, while this reaction is only slightly

247   enhanced in UVA-Fe^{3+} due to the much lower concentration of Fe(II) species.

248   Fig. 2b evidences that the very low photoactivity of Fe(II)- and Fe(III)-oxamate

249   complexes only allows a 57% and 77% destruction of the acid after 360 min of UVA-Fe^{2+} and

250   UVA-Fe^{3+} treatments, respectively. This is also reflected in the low pseudo first-order rate

251   constant (k_{oxamic}) values obtained (see Table 1). As can be seen in Fig. 3, a larger percentage

252   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_2O_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($^\bullet$OH) at the anode surface. This oxidation is also feasible with H_2O_2 since it is produced in low amounts from dimerization of BDD($^\bullet$OH) by reaction (15) (Guinea et al., 2009):

$$2 \, BDD(^\bullet OH) \; \rightarrow \; 2 \, BDD \; + \; H_2O_2 \qquad\qquad (15)$$

The slow destruction of Fe(III)-oxalate complexes with BDD($^\bullet$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 $^\bullet$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_2O_2 are formed from reaction (12), which contribute to the oxidation of Fe(II)- to Fe(III)-oxalate complexes.

277   The k_{oxalic} value obtained for the above EAOPs is listed in Table 1. It increased 1.40-fold

278   for the most potent AO-BDD-Fe^{2+}-UVA system compared with UV-Fe^{3+}, as expected if the

279   photoactive Fe(III)-oxalate species are more quickly regenerated, involving its oxidation with

280   H_2O_2 from reaction (13) and with BDD($^\bullet$OH) at the anode surface.

281   TOC was always removed in a similar way to oxalic acid due to the insignificant

282   formation of by-products. For example, after 360 min of AO-BDD-Fe^{2+} and EF-BDD, TOC

283   was reduced to 13 mg L^{-1}, corresponding to 49 mg L^{-1} oxalic acid in good agreement with 52

284   mg L^{-1} found for the final electrolyzed solutions (see Fig. 2a). Total mineralization was

285   achieved after about 300 min of AO-BDD and close to 90 min of AO-BDD-Fe^{2+}-UVA, times

286   similar to those required for the total removal of oxalic acid, as shown in Fig. 2a. The

287   efficiency calculated from Eq. (4) decreased with electrolysis time by the gradual drop in

288   oxalic acid content. For example, the MCE value decayed from 7.2% or 12.5% at 10 min to

289   1.6% or 6.7% at the end of the AO-BDD or AO-BDD-Fe^{2+}-UVA treatment.

290   From the above results, the reaction sequence of Fig. 4 is proposed for oxalic acid

291   mineralization by AO-BDD-Fe^{2+}-UVA. It is initiated by the oxidation of $Fe^{II}(C_2O_4)_2^{2-}$ with

292   BDD($^\bullet$OH) to yield $Fe^{III}(C_2O_4)_2^{-}$, in equilibrium with $Fe^{III}(C_2O_4)_3^{3-}$. These ionic species are

293   quickly photolyzed regenerating $Fe^{II}(C_2O_4)$ and $Fe^{II}(C_2O_4)_2^{2-}$, respectively, with the loss of

294   CO_2 and $CO_2^{\bullet-}$. Further reaction of $CO_2^{\bullet-}$ with O_2 originates CO_2 and ROS. The catalytic

295   loop between Fe(II)- and Fe(III)-oxalate complexes is then propagated by the continuous

296   oxidation of $Fe^{II}(C_2O_4)_2^{2-}$ with BDD($^\bullet$OH) and ROS (primordially H_2O_2). All ionic species

297   can also be oxidized to CO_2 at the BDD anode, although reactions with BDD($^\bullet$OH) are much

298   slower than the photodegradation of Fe(III) species with UVA light. A slow oxidation of

299   oxalic acid, in equilibrium with the above complexes, at the anode is also feasible.

300   *3.4. Mineralization of oxamic acid by EAOPs*

301   The degradation of 2.08 mM oxamic acid solutions by the same EAOPs always followed

302   a pseudo first-order abatement. Fig. 2b evidences that AO-BDD-Fe^{2+} and EF-BDD processes

303   yield the same decay rate for this acid, as expected if its Fe(II) complexes are oxidized by

304   BDD($^{\bullet}$OH) with insignificant participation of $^{\bullet}$OH in the bulk. Both treatments are more

305   potent than AO-BDD because of the most effective destruction of Fe(III)-oxamate complexes

306   by BDD($^{\bullet}$OH) than that of oxamic acid by direct charge transfer. Comparison of Fig. 2a and

307   2b evidences that AO-BDD-Fe^{2+} and EF-BDD methods are more effective for the abatement

308   of oxamic than oxalic acid, in agreement with the higher oxidation ability of Fe(III)-oxamate

309   species at BDD (see Fig. 1b). Fig. 2b also shows that oxamic acid disappears in 270 min for

310   AO-BDD-Fe^{2+}-UVA. Since k_{oxamic} for this method is 2.56 times higher than for UV-Fe^{3+} (see

311   Table 1), one can infer that Fe(III)-oxamate species are rapidly formed from the oxidation of

312   Fe(II)-oxamate ones with BDD($^{\bullet}$OH) and generated H_2O_2 to be photolyzed by UVA light

313   regenerating the Fe(II) species with loss of CO_2 and inorganic N products. Results of Table 1

314   indicate that $k_{oxalic} > k_{oxamic}$ for AO-BDD and AO-BDD-Fe^{2+}-UVA, while $k_{oxalic} < k_{oxamic}$ for

315   AO-BDD-Fe^{2+} and EF-BDD. That means that oxamic acid is more recalcitrant than oxalic

316   acid only in the two former methods, but not in the two latter. For the EAOPs tested, TOC

317   was removed similarly to oxamic acid, indicating the formation of insignificant amounts of

318   organic by-products during all mineralization processes. In addition, the progressive loss in

319   oxidizable organic matter caused a continuous fall in MCE.

320   Fig. 3 illustrates the predominance of N lost as NH_4^+ ion at the end of all EAOPs tested to

321   mineralize the 2.08 mM oxalic acid solution at 33.3 mA cm^{-2}. The larger proportion of N lost

322   as NO_3^- ion is found for AO-BDD, indicating that NH_4^+ ion is preferentially formed during

323   the oxidation of Fe(III)-oxamate species than oxamic acid. TN analysis of final electrolyzed

324   solutions confirmed the release of N as NO_x species. For AO-BDD-Fe^{2+}-UVA, for example,

325   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

326   is mineralized, corresponding to a loss of 21.9% of N as NO_x species, a value close to 21.8%

327   determined from the N obtained for NH_4^+ (64%) and NO_3^- (14.2%), as depicted in Fig. 3.

328   *3.5. Mineralization of mixtures of oxalic and oxamic acid by EAOPs*

329   Since a mixture of oxalic and oxamic acid is obtained as ultimate by-product of the

330   degradation of *N*-aromatics by EAOPs (Sirés et al., 2006; Hammami et al., 2008; Hamza et

331   al., 2009), the possible influence of the relative proportion of both acids on their removal rate

332   was investigated. To do this, 8%, 25% and 43% of oxamic acid was added to the 2.08 mM

333   oxalic acid solution to be treated by AO-BDD, AO-BDD-Fe^{2+} and AO-BDD-Fe^{2+}-UVA at

334   33.3 mA cm^{-2}, after adding 0.5 mM Fe^{2+} in the two latter methods. The k_{oxamic} and k_{oxalic}

335   values determined simultaneously for these experiments are summarized in Table 2.

336   For AO-BDD, similar $k_{oxamic} \sim 1.1\times10^{-4}$ s^{-1} and $k_{oxalic} \sim 1.5\times10^{-4}$ s^{-1} to that of pure

337   solutions (see Table 1) are found, evidencing that both acids are independently oxidized at the

338   BDD anode via direct charge transfer. In contrast, the competition between Fe(III)-oxamate

339   and Fe(III)-oxalate complexes causes a change in the removal rate of acids in the EAOPs with

340   Fe^{2+}. Thus, for AO-BDD-Fe^{2+}, k_{oxalic} gradually decays with decreasing the percentage of

341   oxamic acid, while $k_{oxamic} \sim 1.3\times10^{-4}$ s^{-1} is similar to 1.2×10^{-4} s^{-1} for pure iron-oxamate

342   complexes (see Table 1). This deceleration of oxalic acid removal is due to the progressive

343   formation of a larger proportion of Fe(III)-oxalate complexes that are more difficultly

344   oxidized with BDD($^\bullet$OH). The much faster destruction of Fe(III)-oxamate species with this

345   radical explains the slight change in k_{oxamic} in all mixtures. The smaller amount of Fe(III)-

346   oxamate species formed and the rise in Fe(III)-oxalate ones with decreasing the percentage of

347   oxamic acid are also reflected in AO-BDD-Fe^{2+}-UVA, where the low photoactivity of the

348   former accounts for the drop in k_{oxamic}, whereas the much greater photoactivity of the latter

349   justifies the slight increase in k_{oxalic}. A slower removal of oxamic acid is then expected as its

350   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_{oxamic} in the inset panel of Fig. 5b, which gradually increases from 1.48×10^{-4} s^{-1} ($R^2 = 0.999$) for 16.6 mA cm^{-2} to 3.15×10^{-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($^{\bullet}$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($^{\bullet}$OH) is mainly wasted by oxidation to O$_2$ via reaction (16) (Marselli et al., 2003; Panizza and Cerisola, 2009):

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

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

375 final electrolyzed solutions. These findings suggests that high current densities accelerate the

376 parasite oxidation of NH_4^+ to NO_3^- ion with the greater amounts of BDD($^\bullet$OH) produced,

377 increasing the loss of NO_x species. This suggestion was corroborated by electrolyzing a

378 $(NH_4)_2SO_4$ solution with 20 mg L^{-1} of N under similar conditions. For 100 mA cm^{-2}, NH_4^+ ion

379 was totally removed in 270 min generating 4.6 mg L^{-1} of N as NO_3^- ion and releasing 78% of

380 N as NO_x species. In contrast, after 360 min of electrolysis at 33.3 mA cm^{-2}, 11.3 mg L^{-1} of N

381 as NH_4^+ ion and 1.2 mg L^{-1} of N as NO_3^- ion were found, with loss of 37% of N as NO_x

382 species. Note that NH_4^+ is converted into NO_3^- in larger extent in the treatment of $(NH_4)_2SO_4$

383 than oxamic acid, probably because NH_4^+ ion is gradually released to the medium in the latter

384 case and its oxidation at the BDD anode competes with that of iron-oxamate complexes.

385   Fig. 7a evidences that oxamic acid removal is inhibited with increasing Fe^{2+} content. This

386 trend can be related to a gradual decay in rate of the reaction between Fe(II)-oxamate species

387 and BDD($^\bullet$OH), decelerating its conversion into photoactive Fe(III) complexes, due to the

388 competition of the oxidation of larger amounts of free Fe^{2+} to Fe^{3+} ion at the anode (Sirés et

389 al., 2007). The reduction of Fe^{3+} ion at the SS cathode regenerates the Fe^{2+} ion and maintains

390 the equilibrium between both ions in solution (Brillas et al., 2009). The loss of oxidation

391 ability of the system is also reflected in Fig. 7b, where higher Fe^{2+} content causes a gradual

392 decay in the percentage of N lost as NO_3^- ion and a larger proportion of N lost as NH_4^+ ion,

393 with a similar percentage of N lost as NO_x species. The presence of small amounts of Fe^{2+} in

394 solution then minimizes the undesired oxidation of Fe^{2+} at the anode, favouring the rapid

395 conversion of Fe(II)-oxamate complexes into photoactive Fe(III)-oxamate species.

396 **4. Conclusions**

397   Oxalic and oxamic acids were efficiently mineralized by AO-BDD-Fe^{2+}-UVA, as a result

398 of the high photoactivity of their Fe(III) complexes that are continuously regenerated by

399 oxidation of their Fe(II) complexes with BDD($^{\bullet}$OH) formed at the anode surface and H_2O_2

400 generated from O_2 reduction or BDD($^{\bullet}$OH) dimerization. In this method, oxamic acid was

401 more recalcitrant by the lower photoactivity of its Fe(III) complexes, releasing a larger

402 proportion of NH_4^+ than NO_3^- ion. The loss of volatile NO_x species was confirmed from TN

403 analysis of the final electrolyzed solutions. Each acid underwent a similar decay in AO-BDD-

404 Fe^{2+} and EF-BDD since its iron complexes were not attacked with $^{\bullet}$OH in the bulk. AO-BDD

405 also allowed the total conversion of oxalic acid into CO_2 by direct charge transfer at the

406 anode. This process explained the slower destruction of oxamic acid by this method. In

407 contrast, oxamic acid was less recalcitrant in AO-BDD-Fe^{2+} and EF-BDD, since Fe(III)-

408 oxamate complexes were oxidized more quickly with BDD($^{\bullet}$OH) than Fe(III)-oxalate ones.

409 TOC always decayed similarly to the corresponding acid, indicating a insignificant formation

410 of by-products. While both acids when mixed were independently oxidized at the anode in

411 AO-BDD, the proportion of their Fe(III) complexes and their ability to be oxidized and/or

412 photolyzed affected their degradation rate in the EAOPs with Fe^{2+}. For the most potent AO-

413 BDD-Fe^{2+}-UVA, a lower oxamic acid content decelerated its degradation, without significant

414 effect on oxalic acid decay. Greater current density enhanced the oxidation power of this

415 method since oxamic acid removal was accelerated, but losing efficiency. High Fe^{2+} contents

416 inhibited the oxidation of Fe(II)-oxamate complexes by the competitive oxidation of free Fe^{2+}

417 to Fe^{3+}. Low current densities and Fe^{2+} contents are then preferable for the more efficient

418 removal of these acids in AO-BDD-Fe^{2+}-UVA.

419 **Acknowledgement**

423 **References**

424 Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999. Advanced oxidation processes

425   (AOP) for water purification and recovery. Catal. Today 53 (1), 51-59.

426 Balci, B., Oturan, N., Cherrier, R., Oturan, M.A. 2009. Degradation of atrazine in aqueous

427   medium by electrocatalytically generated hydroxyl radicals. A kinetic and mechanistic

428   study. Water Res. 43 (7), 1924-1934.

429 Balmer, M.E., Sulzberger, B., 1999. Atrazine degradation in irradiated iron/oxalate systems:

430   Effects of pH and oxalate. Environ. Sci. Technol. 33 (14), 2418-2424.

431 Brillas, E., Baños, M.A., Camps, S., Arias, C., Cabot, P.L., Garrido, J.A., Rodríguez, R.M.,

432   2004. Catalytic effect of Fe^{2+}, Cu^{2+} and UVA light on the electrochemical degradation of

433   nitrobenzene using an oxygen-diffusion cathode. New J. Chem. 28 (2), 314-322.

434 Brillas, E., Sirés, I., Oturan, M.A., 2009. Electro-Fenton process and related electrochemical

435   technologies based on Fenton's reaction chemistry. Chem. Rev. 109 (12), 6570-6631.

436 Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., 2010. Electrochemical incineration of

437   diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped

438   diamond anodes. Chemosphere 79 (6), 605–612.

439 Cañizares, P., García-Gómez, J., Lobato, J., Rodrigo, M.A., 2003. Electrochemical oxidation

440   of aqueous carboxylic acid wastes using diamond thin-film electrodes. Ind. Eng. Chem.

441   Res. 42 (5), 956-962.

442 Cañizares, P., Beteta, A., Saez, C., Rodríguez, L., Rodrigo, M.A., 2008. Use of

443   electrochemical technology to increase the quality of the effluents of bio-oxidation

444   processes. A case studied. Chemosphere 72 (7), 1080-1085.

445 Diagne, M., Oturan, N., Mehmet A.Oturan, M.A., 2007. Removal of methyl parathion from

446   water by electrochemically generated Fenton's reagent. Chemosphere 66 (5), 841-848.

447 Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R., 2008. Activated carbon catalytic ozonation of

448   oxamic and oxalic acids. Appl. Catal. B: Environ. 79 (3), 237–243.

449 Faust, B.C., Zepp, R.G., 1993. Photochemistry of aqueous iron(III)-polycarboxylate

450   complexes: roles in the chemistry of atmospheric and surface waters. Env. Sci. Technol.

451   27 (12), 2517-2522.

452 Gandini, D., Mahé, E., Michaud, P.A., Haenni, W., Perret, A., Comninellis, Ch., 2000.

453   Oxidation of carboxylic acids at boron-doped diamond electrodes for wastewater

454   treatment. J. Appl. Electrochem. 30 (12), 1345-1350.

455 Guinea E., Centellas, F., Garrido, J.A., Rodríguez, R.M., Arias, C., Cabot, P.L., Brillas, E.,

456   2009. Solar photoassisted anodic oxidation of carboxylic acids in presence of Fe^{3+} using a

457   boron-doped diamond electrode. Appl. Catal. B: Environ. 89 (3-4), 459-468.

458 Hammami, S., Bellakhal, N., Oturan, N., Oturan, M.A., Dachraoui, M., 2008. Degradation of

459   Acid Orange 7 by electrochemically generated $^\bullet$OH radicals in acidic aqueous medium

460   using a boron-doped diamond or platinum anode. A mechanistic study. Chemosphere 73

461   (5), 678-684.

462 Hamza, M., Abdelhedi, R., Brillas, E., Sirés, I., 2009. Comparative electrochemical

463   degradation of the triphenylmethane dye metil violet with boron-doped diamond and Pt

464   anodes. J. Electroanal. Chem. 627 (1-2), 41-50.

465 Jeong, J., Yoon, J., 2005. pH effect on OH radical production in photo/ferrioxalate system.

466   Water Res. 39 (13), 2893-2900.

467 Kwan, C.Y., Chu, W., 2007. The role of organic ligands in ferrous-induced photochemical

468   degradation of 2,4-dichlorophenoxyacetic acid. Chemosphere 67 (8), 1601-1611.

469 Lan, Q., Li, F.B., Sun, C.X., Liu, C.S., Li, X.Z., 2010. Heterogeneous photodegradation of

470   pentachlorophenol and iron cycling with goethite, hematite and oxalate under UVA

471   illumination. J. Hazard. Mater. 174 (1-3), 64-70.

472   Martínez-Huitle, C.A., Ferro, S., De Battisti, A., 2004. Electrochemical incineration of oxalic

473   acid: Role of electrode material. Electrochim. Acta 49 (22-23), 4027-4034.

474   Marselli, B., García-Gómez, J., Michaud, P.A., Rodrigo, M.A., Comninellis, Ch., 2003.

475   Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. J.

476   Electrochem. Soc. 150 (3), D79-D83.

477   Monteagudo, J.M., Durán, A., López-Almodóvar, C., 2008. Homogeneus ferrioxalate-assisted

478   solar photo-Fenton degradation of Orange II aqueous solutions. Appl. Catal. B: Environ.

479   83 (1-2), 46-55.

480   Oturan, M.A., Pimentel, M., Oturan, N., Sirés, I., 2008. Reaction sequence for the

481   mineralization of the short-chain carboxylic acids usually formed upon cleavage of

482   aromatics during electrochemical Fenton treatment. Electrochim. Acta 54(2), 173-182.

483   Özcan, A., Şahin, Y., Koparal, A.S., Oturan, M.A., 2008. Propham mineralization in aqueous

484   medium by anodic oxidation using boron-doped diamond anode. Experimental

485   parameters' influence on degradation kinetics and mineralization efficiency. Water Res.

486   42 (12), 2889-2898.

487   Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic pollutants.

488   Chem. Rev. 109 (12), 6541-6569.

489   Pardo, E., Lloret, F., Carrasco, R., M. Muñoz , C.,Temporal-Sánchez , T., Ruiz-García R.,

490   2004. Chemistry and reactivity of dinuclear iron oxamate complexes: alkane oxidation

491   with hydrogen peroxide catalysed by an oxo-bridged diiron(III) complex with amide and

492   carboxylate ligation. Inorg. Chim. Acta 357 (9), 2713-2720.

493   Pera-Titus, M., García-Molina, V., Baños, M.A., Giménez, J., Esplugas, S., 2004.

494   Degradation of chlorophenols by means of advanced oxidation processes: a general

495   review. Appl. Catal. B: Environ. 47 (4), 219-256.

496   Rodríguez, E., Mimbrero, M., Masa, F.J., Beltrán, F.J., 2007. Homogeneous iron-catalyzed

497   photochemical degradation of muconic acid in water. Water Res. 41 (6), 1325-1333.

498   Ruiz, E.J., Arias, C., Brillas, E., Hernández-Ramírez, A., Peralta-Hernández. J.M., 2011.

499   Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-

500   Fenton processes with a boron-doped diamond anode. Chemosphere 82 (4), 495-501.

501   Scialdone, O., Galia, A., Guarisco, C., Randazzo, S., Filardo, G., 2008. Electrochemical

502   incineration of oxalic acid at boron doped diamond anodes: Role of operative parameters.

503   Electrochim. Acta 53 (5), 2095-2108.

504   Serra, A., Domènech, X., Arias, C., Brillas, E., Peral, J., 2009. Oxidation of α-

505   methylphenylglycine under Fenton and electro-Fenton conditions in the dark and in the

506   presence of solar light. Appl. Catal. B: Environ. 89 (1-2), 12-21.

507   Šima, J., Makáňová, J., 1997. Photochemistry of iron(III) complexes. Coord. Chem. Rev. 160,

508   161-189.

509   Sirés, I., Garrido, J.A., Rodríguez, R.M., Cabot, P.L., Centellas, F., Arias, C., Brillas, E.,

510   2006. Electrochemical degradation of paracetamol from water by catalytic action of Fe^{2+},

511   Cu^{2+}, and UVA light on electrogenerated hydrogen peroxide. J. Electrochem. Soc. 153

512   (1), D1-D9.

513   Sirés, I., Centellas, F., Garrido, J.A., Rodríguez, R.M., Arias, C., Cabot, P.L., Brillas, E.,

514   2007. Mineralization of clofibric acid by electrochemical advanced oxidation processes

515   using a boron-doped diamond anode and Fe^{2+} and UVA light as catalysts. Appl. Catal. B:

516   Environ. 72 (3-4), 373-381.

517   Sirés, I., Brillas, E., Cerisola, G., Panizza, M., 2008. Comparative depollution of mecoprop

518   aqueous solutions by electrochemical incineration using BDD and PbO_2 as high oxidation

519   power anodes. J. Electroanal. Chem. 613 (2), 151-159.

520   Sun, Y., Pignatello, J.J., 1993. Photochemical-reactions involved in the total mineralization of

521   2,4-D by Fe^{3+}/H_2O_2/UV. Environ. Sci. Technol. 27 (2), 304-310.

522   Vandini, T.A., Rao, T.N., Fujishima, A., Einaga, Y., 2006. Electrochemical oxidation of

523   oxalic acid at highly boron-doped diamond electrodes. Anal. Chem. 78 (10), 3467-3471.

524   Weiss, E., Groenen-Serrano, K., Savall, A. Comninellis, Ch., 2007. A kinetic study of the

525   electrochemical oxidation of maleic acid on boron doped diamond. J. Electroanal. Chem.

526   37 (1), 41-47.

527   Zuo, Y., Hoigné, J., 1992. Formation of hydrogen peroxide and depletion of oxalic acid in

528   atmospheric water by photolysis of iron(III)-oxalato complexes. Environ. Sci. Technol.

529   26 (5), 1014-1022.

530   Zuo, Y., Hoigné, J., 1994. Photochemical decomposition of oxalic, glyoxalic and pyruvic acid

531   catalysed by iron in atmospheric waters. Atmos. Environ. 28 (7), 1231-1239.

532

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_2SO_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 ℃.

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_2SO_4 at pH 3.0 and 35 ℃. 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_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 and 35 ℃. 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.

556   **Fig. 6.** Evolution of the concentration of (a) ammonium and (b) nitrate ions released during

557   the experiments of Fig. 5.

558   **Fig. 7.** (a) Effect of Fe^{2+} content on the decay of oxamic acid concentration for the AO-BDD-

559   Fe^{2+}-UVA degradation of 100 mL of 2.08 mM of the carboxylic acid in 0.05 M Na_2SO_4 at pH

560   3.0, 33.3 mA cm^{-2} and 35 ℃. [Oxamic acid]/[Fe^{2+}] ratio: (○) 4:1, (□) 2:1, (◇) 1:1, (△) 1:2

561   and (▽) 1:4. (b) Percentage of nitrogen lost as (■) NH_4^+ ion, (▨) NO_3^- ion and (□) NO_x

562   species vs [oxamic acid]/[Fe^{2+}] ratio at the end of these experiments.

563

564

565

566

(a)

0.1

0.0

-0.1

-0.2

I / mA

-0.3

-0.4

-0.5

-0.6

.... Electrolyte
———— Oxalic acid
– – – Oxamic acid

2.40   2.20   2.00   1.80   1.60   1.40   1.20   1.00   0.80

E / V vs. SCE

567

568

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570

571

572

573

574

575

576

(b)

1

0

-1

-2

I / mA

-3

-4

-5

-6

-7

———— Oxalic acid + Fe^{2+}
.... Oxalic acid + Fe^{3+}
············ Electrolyte
– – – Oxamic acid + Fe^{2+}
– · – Oxamic acid + Fe^{3+}

3.5   3.0   2.5   2.0   1.5   1.0   0.5

E / V vs. SCE

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Fig. 1

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612 **Fig. 2**

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Fig. 3

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CO_2

BDD($^\bullet$OH)   BDD($^\bullet$OH)

$[\,\text{Fe}^{III}\,]^{3-}$ $\xrightarrow[\text{2 H}_2\text{O}]{h\nu}$ $[\,\text{Fe}^{II}\,(\text{OH}_2)(\text{OH}_2)\,]^{2-}$ $+\ CO_2\ +\ CO_2^{\bullet-}$

$\downarrow O_2$

CO_2
ROS

$-\ C_2O_4^{2-}$
$2\ H_2O$

BDD($^\bullet$OH)
ROS

$-\ C_2O_4^{2-}$
$2\ H_2O$

$[\,\text{Fe}^{III}(\text{OH}_2)(\text{OH}_2)\,]^{4-}$ $\xrightarrow[\text{2 H}_2\text{O}]{h\nu}$ $[\,\text{Fe}^{II}(\text{OH}_2)(\text{OH}_2)(\text{OH}_2)(\text{OH}_2)\,]$ $+\ CO_2\ +\ CO_2^{\bullet-}$

$\downarrow O_2$

CO_2
ROS

BDD($^\bullet$OH)   BDD($^\bullet$OH)

CO_2

Fig. 4

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Fig. 5

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Fig. 6

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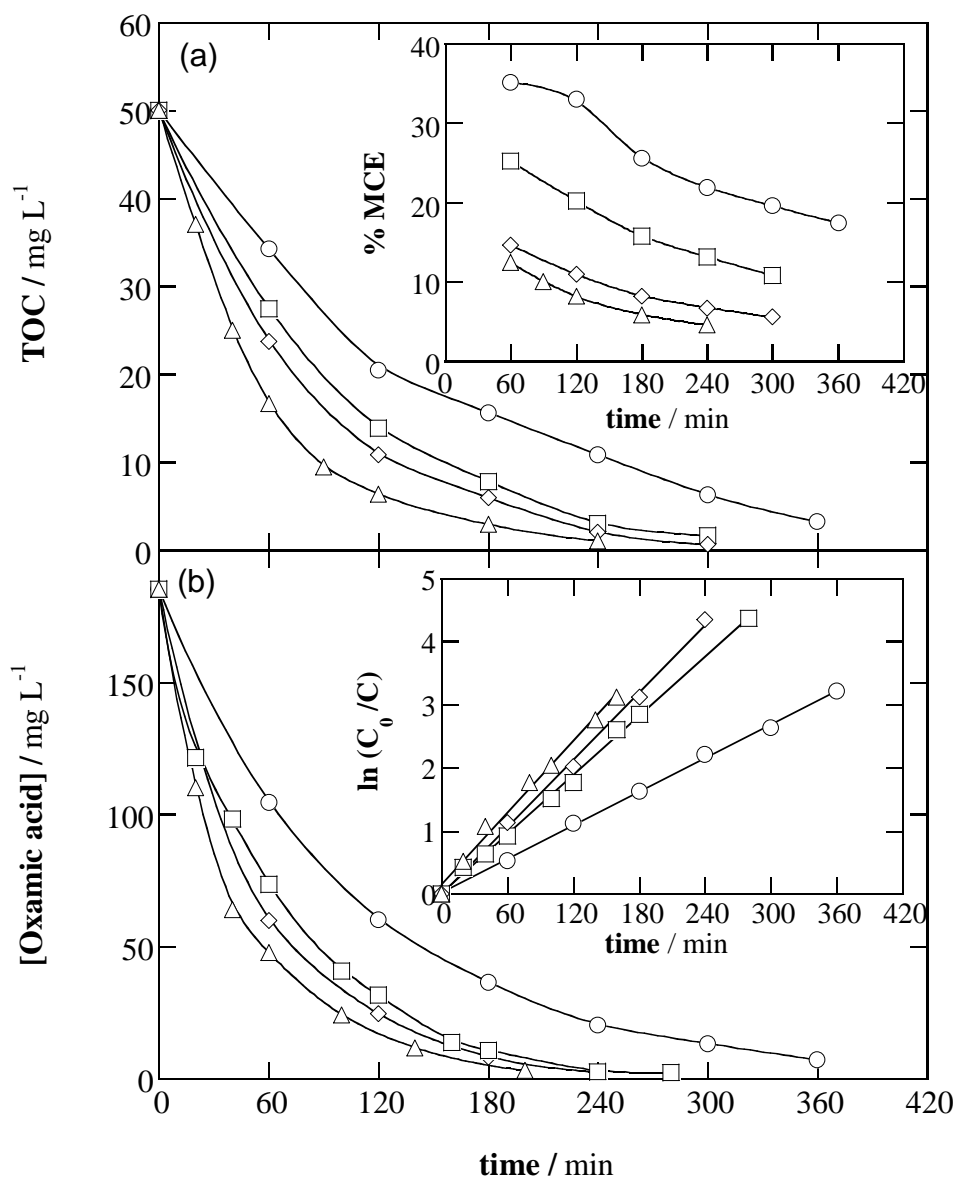777
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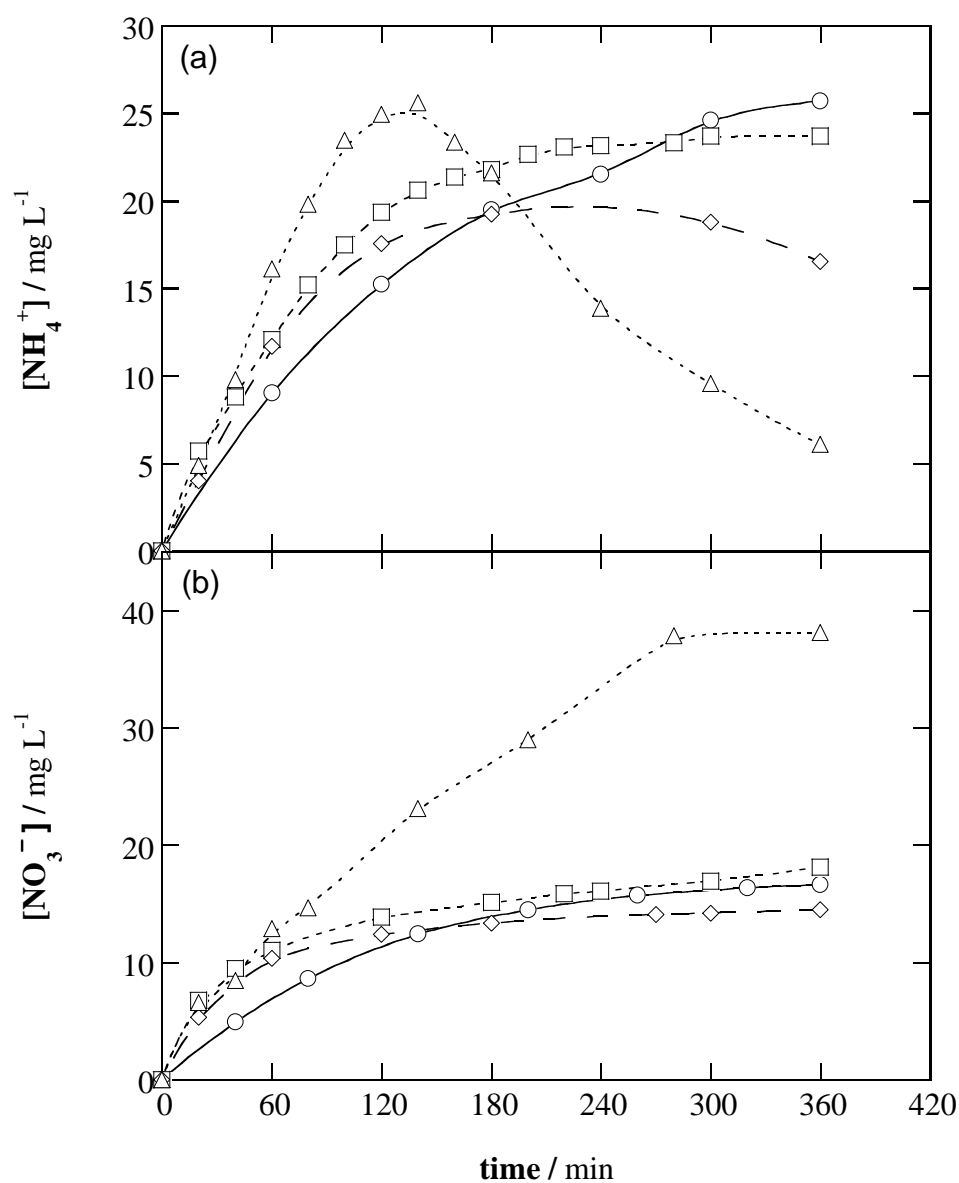779
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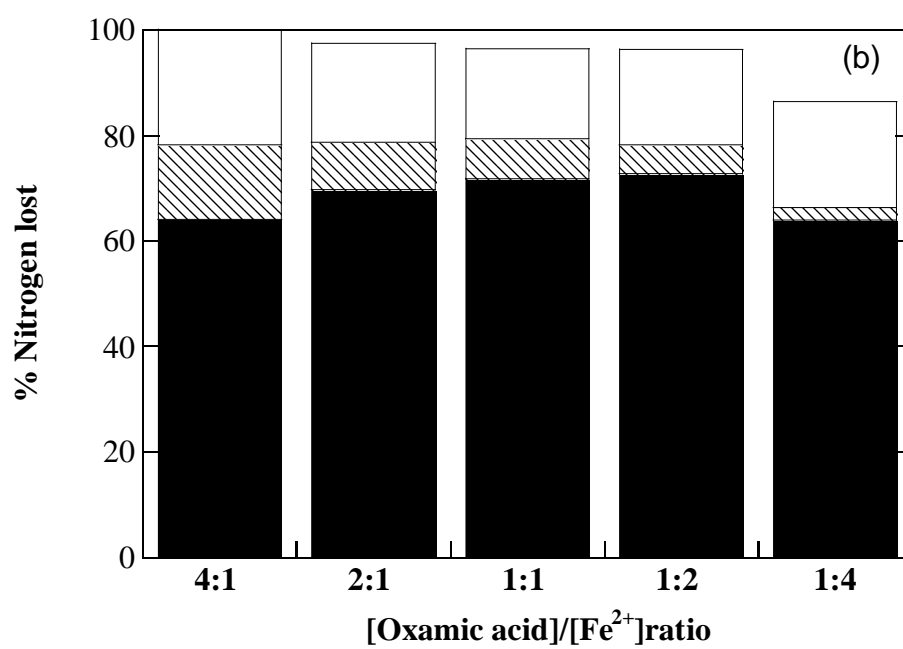781
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(a)

Fig. 7

789   Table 1. Pseudo first-order rate constant and square regression coefficient (in parenthesis) for

790   the decay of oxalic and oxamic acids during the degradation of 2.08 mM of each compound in

791   0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} or 0.5 mM Fe^{3+} of pH 3.0 at 35 ℃. The solution was

792   irradiated with a 6 W UVA light and a current density of 33.3 mA cm^{-2} was applied in all

793   EAOPs.

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Method	$k_{oxalic} \times 10^4$ (s^{-1})	$k_{oxamic} \times 10^4$ (s^{-1})
UVA-Fe^{2+}	0.75 (0.995)	0.40 (0.978)
UVA-Fe^{2+} (O_2 sat.)	1.33 (0.988)	---[a]
UVA-Fe^{3+}	6.43 (0.985)	1.10 (0.996)
UVA-Fe^{3+} (O_2 sat.)	6.83 (0.984)	---[a]
AO-BDD	1.49 (0.999)	1.01 (0.993)
AO-BDD-Fe^{2+}	0.61 (0.986)	1.20 (0.998)
EF-BDD-Fe^{2+}	0.61 (0.989)	1.15 (0.998)
AO-BDD-Fe^{2+}-UVA	9.01 (0.983)	2.82 (0.995)

795   [a] Not determined

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805   Table 2. Pseudo first-order rate constant and square regression coefficient (in parenthesis)

806   determined for the decay of oxamic and oxalic acids during the degradation of 100 mL

807   solutions of different percentages of oxamic acid with a total acid concentration of 2.08 mM

808   by several EAOPs at 33.3 mA cm^{-2}.

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

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