

# **Influence of the supporting electrolyte on the removal of ionic liquids by electrolysis with diamond anodes**

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## **Abstract**

In this work, it is studied the electrolysis with diamond anodes of three different ionic liquids (ILs): 1-butyl-3-methylimidazolium chloride (BmimCl), 1-hexyl-3-methylimidazolium chloride (HmimCl) and 1-decyl-3-methylimidazolium chloride (DmimCl), which differ only in the length of the aliphatic carbon chain attached to the imidazolium group. In addition, the effect of the presence of sulfate in the electrolyte is also evaluated. Results confirmed that this type of ILs can be completely transformed into carbon dioxide, nitrates, ammonium (the imidazolium cation) and perchlorate and chloramines (the chloride anion) during the electrolysis of the synthetic waste containing sulfate. The electrolysis of wastes without sulfate anions leads to a much less efficient process, with the same final products in the case of the BminCl and HminCl ILs and with the formation of a polymer as the main final product in the case of the DmimCl. These

25 results are of a paramount significance from a mechanistic point of view since, because  
26 of the high conductivity of the ILs, there is not a necessity of salt addition and they inform  
27 about the pure removal of the organics by electrolysis with BDD, pointing out the  
28 important influence of peroxodisulfate on the electrolyses with diamond of organic  
29 wastes.

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32 **Keywords:** electrolysis, ionic liquid, diamond, hydroxyl radical, peroxodisulfate

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38 **Highlights**

39 - ILs based on imidazolium can be completely removed by electrolysis with BDD.

40 - Electropolymerization of Dmim<sup>+</sup> is observed during the electrolysis with BDD.

41 - Sulfate leads to a more efficient oxidation and prevents polymerization.

42 - Nitrites, nitrates and ammonium are formed from the nitrogen of the imidazolium  
43 groups.

44 - The chloride counter ion is transformed into perchlorates and chloramines.

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50 **1. Introduction.**

51 Ionic liquids (ILs) are salts that exhibit high thermal stability and low melting point [1].  
52 They may become as substitutes of conventional organic solvents [2], behaving as more  
53 environmentally-friendly species and, for this reason, they are commonly known as  
54 “green” solvents [3]. In the recent years, their use has been studied for many applications,  
55 such as the removal of carbon dioxide by absorption [4], the extraction of dyes and  
56 emerging contaminants [5, 6], the separation of hydrocarbons [7], the removal of  
57 chromium [8] or the photodegradation of organochlorine compounds [9].

58 Despite of the large number of potential applications, recently, ILs have been identified  
59 as persistent pollutants, because of their stability towards biological degradation [10]  
60 typically associated to their complex structure (cations typically consists of derivatives of  
61 imidazolium, pyridinium or phosphonium rings). Furthermore, several authors have  
62 informed about the toxicity of these compounds, as well as the environmental hazards  
63 that they may produce [11-14]. For this reason, in order to promote their applications, it  
64 is necessary to develop efficient processes that allow the removal of ILs from exhausted  
65 industrial effluents.

66 Advanced Oxidation Processes (AOPs) can be considered as suitable technologies for the  
67 treatment of wastewater polluted with ILs. AOPs are based on the production by different  
68 technologies of large amounts of hydroxyl radicals, which significantly contribute to the  
69 degradation of the pollutants present in the effluent [15, 16]. Technologies based on ozone  
70 or Fenton reagent have been the most studied AOPs for many decades [17-19]. However,  
71 from the nineties of the last century, electrolytic technologies have emerged as very  
72 promising alternatives [20-22]. These processes produce hydroxyl radicals from  
73 electrolysis of water on the anode surface (Eq. 1) [23-25], being the choice of a suitable  
74 electrode material a key to obtain a high efficiencies [26-30].



76 One of the electrodes that has awakened great interest in the recent years is boron doped  
77 diamond (BDD) [31, 32]. This material has a large electrochemical window and, hence,  
78 it allows to generate large amounts of free hydroxyl radicals [33, 34]. For this reason, it  
79 has been evaluated in the oxidation of hundreds of pollutants including ILs [22, 25, 35-  
80 39]. In this context, Fabianska et al. [40] reported the electrolysis of imidazolium-based  
81 ionic liquids with diamond electrodes, evaluating the influence of the ionic liquid anion  
82 in different media (sulfate, chloride and bromide) by cyclic voltammetries and  
83 galvanostatic electrolyses with and without membrane. They concluded that hydroxyl  
84 radical is the main oxidant for the removal of the different ionic liquids studied and, the  
85 nature of the supporting electrolyte significantly influences the IL removal. However, the  
86 electrogenerated peroxodisulfate does not play a key role on the electrolysis process in  
87 this work. Later, Pieczynska et al. [41] assessed the removal of imidazolium and  
88 pyridinium ionic liquids, studying the influence of the pH and temperature. Alkaline pHs  
89 showed a decrease in the process efficiency whereas higher temperatures slightly increase  
90 the degradation of ILs. Likewise, the removal of pyridinium salts was more efficient in  
91 comparison with the imidazolium ILs depletion. They informed that  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$  were  
92 the main oxidants responsible of the removal of ILs. Finally, more recently, García-  
93 Segura et al. [42] have described the degradation of pyridinium- and imidazolium-based  
94 ionic liquids in sulfate media by anodic oxidation, electro-Fenton and photoelectro-  
95 Fenton using BDD anodes. They concluded that photoelectro-Fenton was the most  
96 efficient technology for the removal of those ILs and proposed the potential formation of  
97 hydroxyl radicals as the main mechanism for the removal of pollutants. The production  
98 of ozone and peroxodisulfate was also described but they not seemed to be the primary  
99 responsible of the degradation.

100 Opposite to those results, other works focused on the degradation of species different of  
101 ILs indicate that peroxocompounds formed during the electrolysis with BDD may behave  
102 as the most important species to explain the mineralization processes [43-45]. Hence,  
103 there exists a real necessity to clarify the specific contribution of hydroxyl radicals and/or  
104 other electrogenerated oxidants on the removal of ILs. With this background, the main  
105 aim of this work is to shed light about the real mechanisms of electrolysis with diamond  
106 anodes for the removal of organics. To do this, three different ILs were selected: they  
107 have the same anion ( $\text{Cl}^-$ ) and different cations with an imidazolium group derivative:  
108  $\text{Bmim}^+$  (1-Butyl-3-methylimidazolium),  $\text{Hmim}^+$  (1-Hexyl-3-methylimidazolium) and  
109  $\text{Dmim}^+$  (1-Decyl-3-methylimidazolium). Solutions polluted with these compounds were  
110 electrolyzed in electrolytes with absence and presence of sulfate anions, in order to  
111 evaluate the contribution of hydroxyl radicals and electrogenerated peroxodisulfate (and  
112 related derivative species, such as radical sulfate) during the degradation of the ILs.

113

## 114 **2. Material and methods.**

### 115 **2.1. Chemicals.**

116 Analytical grade  $\text{BmimCl}$  (1-Butyl-3-methylimidazolium chloride),  $\text{HmimCl}$  (1-Hexyl-  
117 3-methylimidazolium chloride),  $\text{DmimCl}$  (1-Decyl-3-methylimidazolium chloride) and  
118 sulfuric acid were used as received. Double deionized water (Millipore Milli-Q system,  
119 resistivity:  $18.2 \text{ M}\Omega\text{cm}$  at  $25^\circ\text{C}$ ) was used to prepare all solutions.

### 120 **2.2. Analytical techniques.**

121 The concentration of ILs was measured by chromatography using an Agilent 1100 series  
122 chromatograph equipped with a UV detector and a Synergy 4 mm Polar-RP 80 A column.  
123 For the determination of  $\text{Bmim}^+$  and  $\text{Hmim}^+$ , the mobile phase consisted of 95:5 v/v

124 phosphate buffer/acetonitrile (flow rate:  $0.75 \text{ cm}^3 \text{ min}^{-1}$ ). In the case of Dmim<sup>+</sup>, the  
125 percentage of acetonitrile was increased to 40 %. The DAD detection wavelength was  
126 218 nm, the temperature was kept at 35°C and the injection volume was 20  $\mu\text{L}$ .

127 Total Organic Carbon (TOC) was monitored using a Multi N/C 3100 Analytik Jena  
128 analyzer. Inorganic ions were measured by ion chromatography using a Metrohm 930  
129 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was  
130 used to determine the anions and a Metrosep A Supp 4 column was used to analyze the  
131 cations. The mobile phase consisted of 85:15 v/v 3.6 mM Na<sub>2</sub>CO<sub>3</sub>/acetone solution for  
132 the determination of anions (flowrate:  $0.80 \text{ cm}^3 \text{ min}^{-1}$ ) and 1.7 mM HNO<sub>3</sub> and 1.7 mM  
133 2,6-pyridinedicarboxylic acid solution for the determination of cations (flowrate:  $0.90$   
134  $\text{cm}^3 \text{ min}^{-1}$ ). The temperature of the oven was 45 and 30°C for the determination of anions  
135 and cations, respectively. The volume injection was 20  $\mu\text{L}$ .

136 The molecular weight of the polymer formed was measured by Gel Permeation  
137 Chromatography (GPC) using a Viscotek chromatograph equipped with a Styragel HR2  
138 column and a Styragel HR0.5 column. The system was operated at 35°C with a flowrate  
139 of  $1 \text{ cm}^3 \text{ min}^{-1}$ . THF was used as eluent and calibration curves were obtained with  
140 polyethylene glycol standards (Waters).

### 141 **2.3. Electrochemical cell.**

142 Electrolyses were carried out in a single compartment electrochemical flow cell operating  
143 in recirculation mode ( $50 \text{ dm}^3 \text{ h}^{-1}$ ). Boron doped diamond (BDD) (WaterDiam,  
144 Switzerland) was used as anode and cathode. The electrodes were circular with a  
145 geometric area of  $78 \text{ cm}^2$ , boron concentration of  $500 \text{ mg dm}^{-3}$ , a thickness of  $2.72 \mu\text{m}$ ,  
146 sp<sup>3</sup>/sp<sup>2</sup> ratio of 220 and p-Si as support. The electrode gap between anode and cathode  
147 was 3 mm. The electric current was provided by a Delta Electronika ES030-10 power

148 supply (0-30V, 0-10A). The temperature was maintained at 25°C using a thermostated  
149 bath.

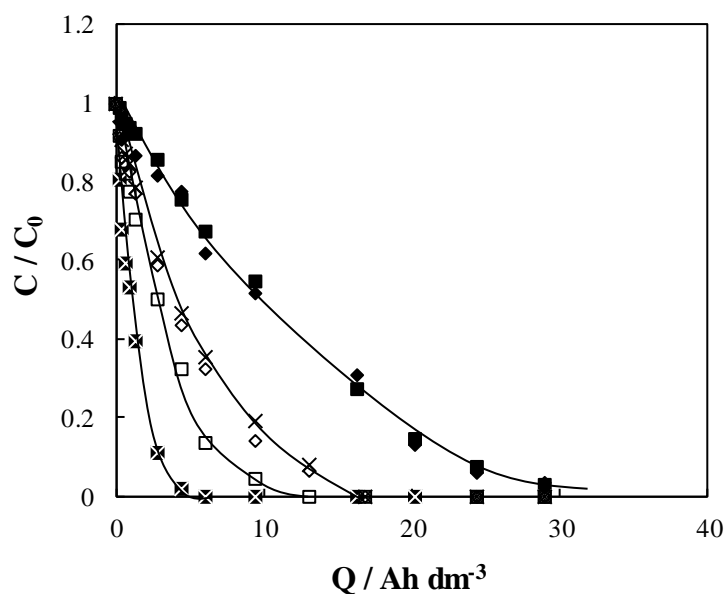
150 Synthetic wastewater consisted of a solution (1.0 dm<sup>3</sup>) containing 1 mM of ionic liquid.

151 For the study of the influence of the supporting electrolyte, 3000 mg dm<sup>-3</sup> of sulfuric acid  
152 were added to synthetic wastewater.

153

### 154 3. Results and discussion.

155 Figure 1 shows changes undergone by the concentration of the three ILs during the  
156 electrolysis at 30 mA cm<sup>-2</sup> of synthetic wastes, with presence or absence of sulfate ions  
157 in the electrolyte.



158

159 **Figure 1.** Removal of ionic liquids with the applied electric charge during the electrolysis  
160 of wastewater polluted with 1 mM of ionic liquid.  $j$ : 30 mA cm<sup>-2</sup>; (■) BmimCl; (◆)  
161 HmimCl; (x) DmimCl. Full symbols: electrolyte without SO<sub>4</sub><sup>2-</sup>; empty symbols: 3000 mg  
162 dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

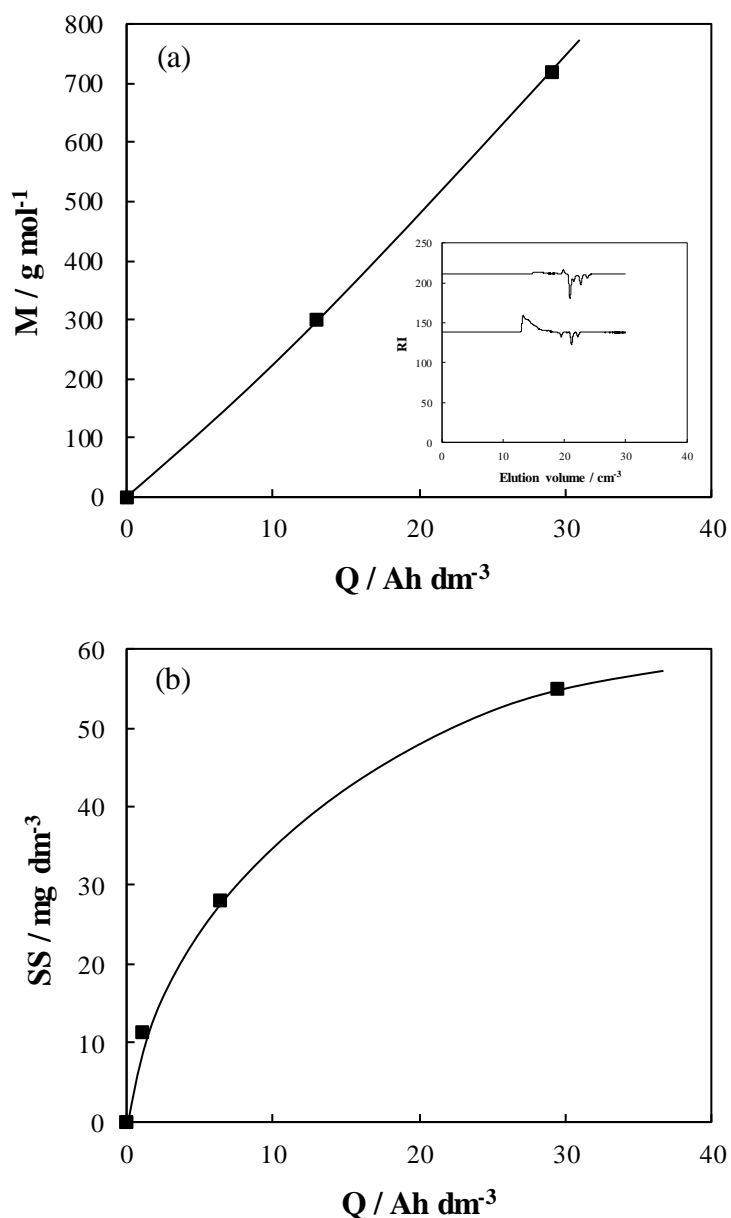
163 In every case, the concentration of ILs decreases down to almost zero, indicating that total  
164 depletion of these imidazolium ILs can be attained from the synthetic wastes using this  
165 electrochemical technology, regardless the molecular weight of the cation and the  
166 presence of sulfate anions in the electrolyte. Even so, degradation results are not  
167 overlapped but, just on the contrary, significant differences can be observed in the  
168 removal of the ILs, depending on the length of the carbon chain attached to the  
169 imidazolium ring and the electrolyte used. As indicated in the introductory section of this  
170 work, in the electrolysis of solutions without sulfate, only oxidation mediated by chlorine  
171 or by hydroxyl radicals (Eq. 1) can supplement the direct anodic oxidation, whereas in  
172 the case of the electrolysis carried out to sulfate-containing solutions, peroxosulfates and  
173 sulfates radicals are also expected to play an important role [46]. On the other hand, it is  
174 expected a slower degradation as the molecular weight of the ILs cation increases, since  
175 the degradation of linear alkane chains is known to be a low efficiency process for AOP,  
176 because of the nonexistence of functional groups to start the attack of the carbon chain.

177 A second important remark that should be pointed out is the higher efficiency observed  
178 in the degradation of the DmimCl polluted solution as compared to the results of the other  
179 two ILs. Thus, during the electrolysis tests of solutions without sulfate, the concentration  
180 of Bmim<sup>+</sup> and Hmim<sup>+</sup> cations decreases down to less than 3% of their initial value for  
181 electric current charges of 30 Ah dm<sup>-3</sup>, whereas Dmim<sup>+</sup> is completely depleted at electric  
182 current charges even lower than 10 Ah dm<sup>-3</sup>, indicating an improved efficiency in more  
183 than three times, because of the higher theoretical oxygen demand (ThOD) associated to  
184 these larger cations, in this later case. As pointed out before, this is an unexpected  
185 behavior, in particular taking into account that the molecule structure of Dmim<sup>+</sup> is much  
186 more complex than that of the other two ILs (larger carbon chain) and, hence, it was  
187 expected that its electrochemical degradation was much more difficult. However, this fact



188 can be explained in terms of the generation of a polymer during the electrolysis of Dmim  
189 with BDD anodes. In this context, the occurrence of particles and even of a thin layer of  
190 polymer was observed on the surface of the pipes and tanks of the bench-scale plant  
191 during the electrolysis, just the same behavior which was previously reported in literature  
192 for the electrolysis of nitrophenols polluted wastes with BDD anodes [47, 48], being one  
193 of the rare cases in which polymerization reactions are found during electrolysis with the  
194 powerful BDD electrodes. Therefore, the efficient removal of Dmim<sup>+</sup> in comparison with  
195 Bmim<sup>+</sup> and Hmim<sup>+</sup> during electrolysis is mainly due to the polymerization of the ionic  
196 liquid and not to its mineralization, which was the expected treatment. In order to confirm  
197 this production of polymer and to know more about its formation, the electrolysis of  
198 Dmin<sup>+</sup> was repeated three times, under exactly the same conditions, being stopped the  
199 electrolysis in each of the three tests at different electric current charge passed. Then, the  
200 solids were carefully collected and their amount (by gravimetry) and molecular weight  
201 (using GPC) were measured. Results of these experiments are shown in Figure 2 and  
202 confirms the production of a polymer whose amount and molecular weight increase  
203 during the electrolysis reaching a molecular weight of 720 mg mol<sup>-1</sup> at the end of the  
204 electrolysis.

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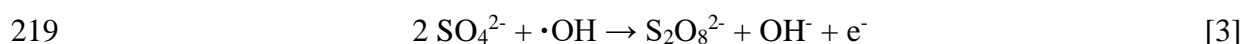
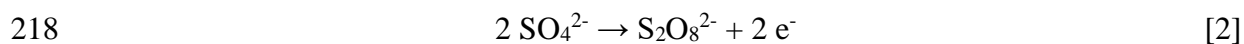
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207 **Figure 2.** Mean molecular weight (part A) and concentration (part B) of the solids  
 208 produced during the electrolysis of DminCl, obtained from three different tests operated  
 209 exactly under the same conditions.

210

211 Another important observation which can be drawn from Figure 1 is that the removal  
 212 efficiency of Bmim<sup>+</sup> and Hmim<sup>+</sup> cations is higher when sulfate ions are contained in the  
 213 electrolyte. As pointed out before, during electrolysis in sulfate media, significant

214 amounts of peroxodisulfate are produced, either by direct (Eq 2) or by hydroxyl radicals  
215 mediated (Eq. 3) mechanisms. In turn, peroxodisulfate can interact with other oxidants  
216 and produce sulfate radicals. All these species are known to be powerful oxidants that  
217 favors the removal of organic matter in wastewater [49-51].

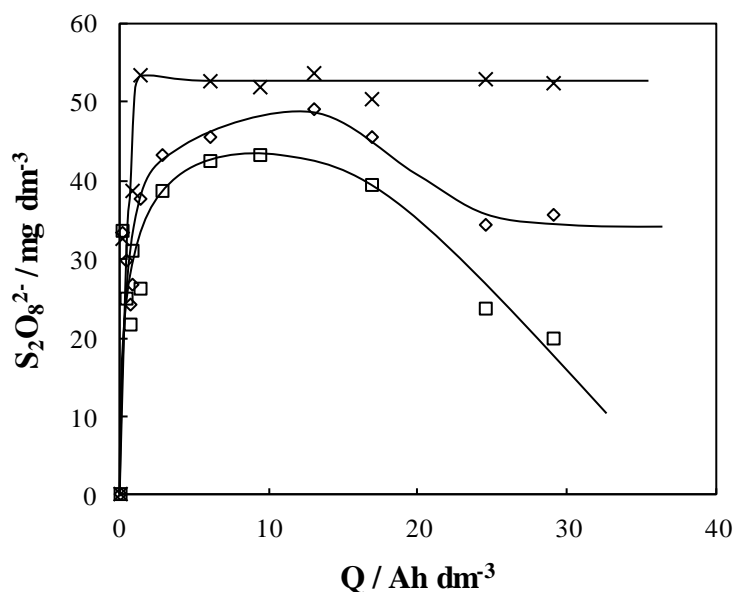


220 The trend observed in  $\text{Bmim}^+$  and  $\text{Hmim}^+$  concentration in presence of sulfate anions  
221 clearly points out the important contribution of peroxodisulfate in the electrolysis with  
222 BDD in the treatment of wastes containing sulfate, which is complementary to the  
223 contribution of the hydroxyl radicals and chlorine oxidation (if this oxidation may really  
224 occur in this system, as it will be pointed out afterwards). It is important to highlight that  
225 electrolysis of ILs is a very special case of study for the understanding of the oxidation  
226 of organics, because due to their very high ionic conductivity, it is not necessary to dope  
227 the synthetic waste with any salt in order to decrease the operation cell voltage. Hence,  
228 the oxidation of wastes in supporting electrolytes without sulfates only shows pure  
229 electrochemical mechanisms.

230 Effect observed on the degradation of  $\text{DminCl}$  is the opposite of that observed for  $\text{BminCl}$   
231 and  $\text{HminCl}$  in presence of sulfates. Thus, the concentration of  $\text{Dmin}^+$  cation decreases  
232 with the applied electric charge until reaching its total depletion at current charge values  
233 around  $17 \text{ Ah dm}^{-3}$ . This value is much higher than that obtained during the electrolysis  
234 without sulfate and, therefore, it may initially suggest a lower efficiency. However, at this  
235 point, it is important to highlight that the presence of a polymer was not detected during  
236 the electrolysis carried out when sulfate ions are contained in the electrolyte. This means  
237 that the production of peroxodisulfate does not only contributes to the more efficient

238 degradation of the ILs by electrolysis but it also prevents the formation of a polymer and,  
239 hence, the removal of Dmim<sup>+</sup> by an electropolymerization process.

240 To evaluate the significance of the formation of peroxodisulfate during the electrolysis of  
241 ILs with BDD anodes, its concentration was measured. Figure 3 shows the changes in the  
242 concentration of this oxidant with the applied electric charge in the three tests carried out  
243 to solutions containing sulfate anions.



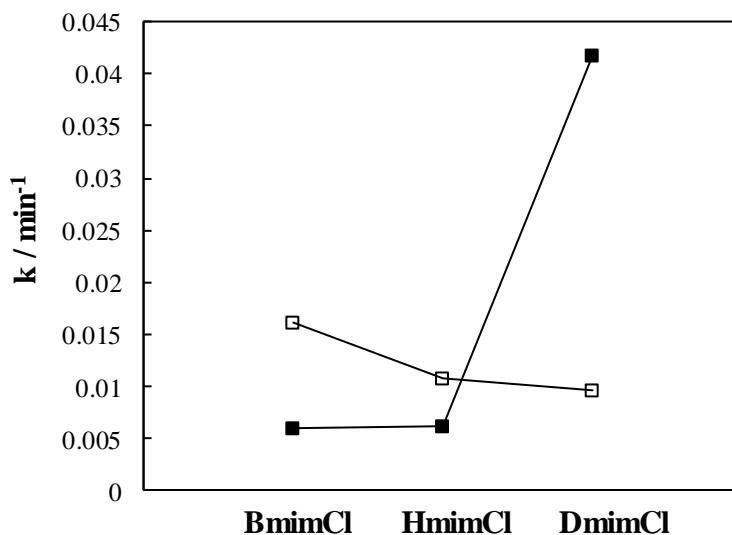
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245 **Figure 3.** Evolution of peroxodisulfate with the applied electric charge during the  
246 electrolysis of wastewater polluted with 1 mM of ILs.  $j$ : 30 mA cm<sup>-2</sup>; supporting  
247 electrolyte: 3,000 mg dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>; (□) BmimCl; (◇) HmimCl; (x) DmimCl.

248 It is important to note that, the concentration of peroxodisulfate measured corresponds to  
249 that which has not reacted with the ILs or reaction intermediates and, hence, that higher  
250 concentrations may be produced, because the observed concentration is the balance  
251 between the production and the consumption of this oxidant. As it can be observed,  
252 peroxodisulfate increases with the applied electric charge for all the tests carried out.  
253 However, different behaviors can be seen depending on the particular ionic liquid treated.  
254 In the case of Bmim<sup>+</sup> cation, the concentration of peroxodisulfate increases until reaching

255 a maximum value (for around  $10 \text{ Ah dm}^{-3}$ ) from which it starts to decrease. This means  
 256 that a higher consumption of this species takes place at intermediate stages during the  
 257 treatment process. This result agrees the removal of BmimCl previously observed (Figure  
 258 1) where this compound is completely removed at lower applied electric charges. A  
 259 similar trend can be seen during the treatment of HmimCl: an initial increase followed by  
 260 a decrease. Nonetheless, in this case, the maximum concentration measured is higher and,  
 261 the decrease observed is less marked. Finally, the peroxydisulfate concentration remains  
 262 constant (at about  $53 \text{ mg dm}^{-3}$ ) during the electrolysis of DmimCl, which suggests that  
 263 the generation and consumption rates of this species are balanced from the very early  
 264 stages of the electrolysis. The important decreases observed after the initial stages in the  
 265 case of the  $\text{Bmin}^+$  and  $\text{Hmin}^+$  cations may suggest a high affinity of the peroxydisulfate for  
 266 the intermediates formed from the oxidation of these two ILs.

267 For comparison purposes, the ILs decay was fitted to a first order kinetics and the removal  
 268 rate constants are presented in Figure 4.



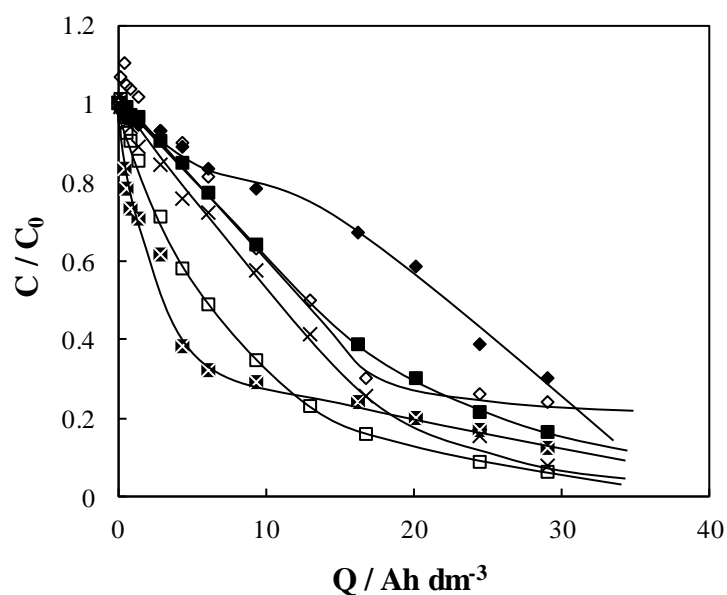
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270 **Figure 4.** Kinetic constants calculated for the removal of ionic liquids by electrolysis with  
 271 BDD anodes. Full symbols: without sulfate; empty symbols:  $3000 \text{ mg dm}^{-3} \text{ H}_2\text{SO}_4$ .

272

273 As it can be observed, the kinetic constants for Bmim<sup>+</sup> and Hmim<sup>+</sup> cations are similar  
274 during the electrolyses in absence of sulfate in the electrolyte. However, the value  
275 obtained for Dmim<sup>+</sup> is much higher, which is due to the polymerization of ionic liquid,  
276 previously described. Likewise, the use of sulfate as supporting electrolyte significantly  
277 increases the kinetic constants for BmimCl and HmimCl, being higher in the first case.  
278 In the case of DmimCl, the kinetic constant for the oxidation was expected to be higher  
279 than that obtained during the electrolysis in absence of sulfate. Unfortunately, it is not  
280 possible to compare, in terms of oxidation, both processes (with and without sulfate)  
281 because of the polymerization produced in absence of sulfate. This is not the case in the  
282 electrolysis of the ILs in solutions containing sulfates, for which the kinetic constants are  
283 observed to decrease with the molecular weight of the ionic liquid (Bmim<sup>+</sup> > Hmim<sup>+</sup> >  
284 Dmim<sup>+</sup>). This means that there is a clear influence of the molecule structure on the  
285 removal of ILs by electrolysis with BDD anodes and that it is promoted the oxidation of  
286 the ILs containing the shorter carbon chains.

287 As for many other pollutants, the electrolysis of ionic liquids may lead to the formation  
288 of other intermediate organic compounds and/or to a complete mineralization of the  
289 organic matter to carbon dioxide. Intermediates can be more harmful than the initial  
290 pollutants and, hence, they should be removed from wastewater. In this context, to  
291 provide information about the evolution of the organic matter, the concentration of TOC  
292 was monitored during the treatment. It is important to take in mind that this parameter  
293 informs only about the complete mineralization of the organic matter (conversion of  
294 organic carbon into carbon dioxide) and not about the progress of the oxidation. Results  
295 obtained are shown in Figure 5.



296

297 **Figure 5.** TOC decay as function of the applied electric charge during the electrolysis of  
 298 wastewater polluted with 1 mM of ionic liquid.  $j$ :  $30 \text{ mA cm}^{-2}$ ; (■) BmimCl; (◆) HmimCl;  
 299 (x) DmimCl. Full symbols: without sulfate; empty symbols:  $3000 \text{ mg dm}^{-3} \text{ H}_2\text{SO}_4$ .

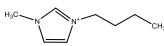
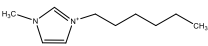
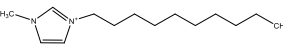
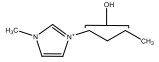
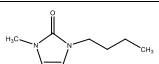



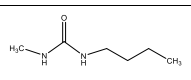


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301 As seen, TOC concentration decreases very importantly with the applied electric charge  
 302 for all the tests carried out. However, it is not possible to attain a complete mineralization  
 303 of the organic matter within the current charges applied ( $30 \text{ Ah dm}^{-3}$ ), regardless the IL  
 304 studied and the supporting electrolyte. Anyhow, trends produced clearly points out that  
 305 total depletion of the ILs can be obtained for larger applied charges.

306 The presence of sulfate leads to a more efficient TOC removal. In this context, a final  
 307 percentage removal of 93.8 and 76.2 were obtained for BmimCl and HmimCl,  
 308 respectively, whereas only 83.7 and 69.8 % were achieved for both ionic liquids in  
 309 absence of sulfate anions at the same electric current charges applied. This agrees with  
 310 the results previously obtained for the removal of the raw ILs (Figure 1), and indicates  
 311 again the positive effect of the electrogenerated peroxodisulfate, not only in the oxidation  
 312 of ILs, but also in the total removal of the intermediates formed.

313 On the other hand, the case of the DmimCl is different because of the polymerization  
 314 observed in electrolyses of electrolytes without sulfate. Thus, the formation of polymer  
 315 leads to an initial higher efficiency in the absence of sulfate, but this situation reverses at  
 316 higher charges passed and the final percentage removal of TOC was 87.6 % in wastes  
 317 without sulfate and 92.5 % when using sulfate as supporting electrolyte (polymer  
 318 formation was not observed). The intermediates detected by HPLC-MS are reported in  
 319 Table 1.

320 **Table 1.** Main intermediates found during the electrolysis of the three imidazolium ILs.

Nº	Molecular structure	Retention time (min)	m/z	Presence in Bmim <sup>+</sup>	Presence in Hmim <sup>+</sup>	Presence in Dmim <sup>+</sup>
						
1		4.5	154	Yes	Yes	No
2		4.5	154	Yes	Yes	No
3		4.5	82	Yes	Yes	Yes
4		2.5	68	Yes	Yes	Yes
5		2.5	84	Yes	Yes	Yes
6		4.8	130	Yes	No	Yes
7		2.5	102	Yes	Yes	Yes
8		4.5	73	Yes	Yes	Yes

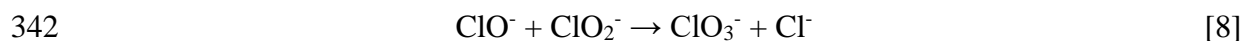
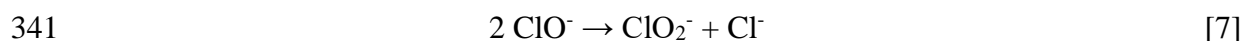
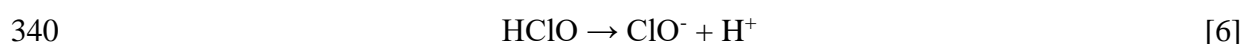
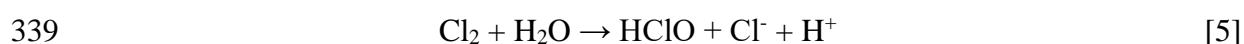
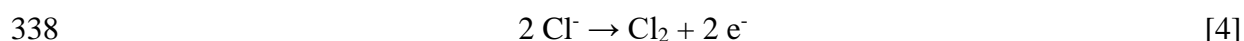
321

322 As can be observed, the electrolysis of Dmim<sup>+</sup> cation leads to the higher production of  
 323 organic intermediate compounds. Specifically, 16 compounds were detected whereas 12  
 324 and 9 were found during the electrolysis of HmimCl and BmimCl, respectively. This is  
 325 an expected behavior, taking into account that the carbon chain is the highest for Dmim<sup>+</sup>  
 326 cation. Likewise, it is important to point out that the electrolysis of the three ILs studied  
 327 with diamond electrodes favors the formation of similar intermediates compounds at the  
 328 end of the experiments. This fact suggests that the ILs are attacked on the carbon chain

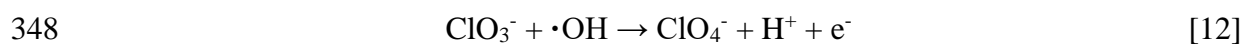
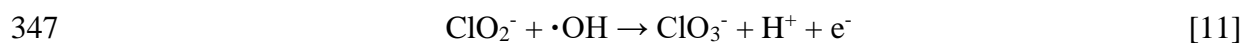
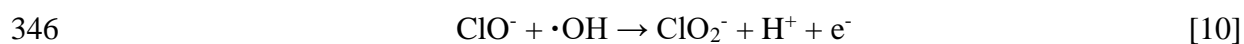
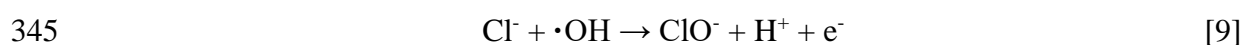


329 by electrogenerated oxidants at the beginning of the experiment followed by the ring  
330 opening.

331 The three ILs salts studied in this work contained a chloride anion. This anion is known  
332 to be oxidized during the electrolysis with BDD anodes, favoring the production of other  
333 chlorine compounds in higher oxidation state [52]. Specifically, chloride can be oxidized  
334 to chlorine gas in a first step (Eq. 4) and, depending on the pH, chlorine gas can favor the  
335 production of hypochlorous acid/hypochlorite (Eqs. 5-6). Next, these species can  
336 disproportionate to chlorate and chloride or undergo electrochemical oxidation to  
337 chlorate.

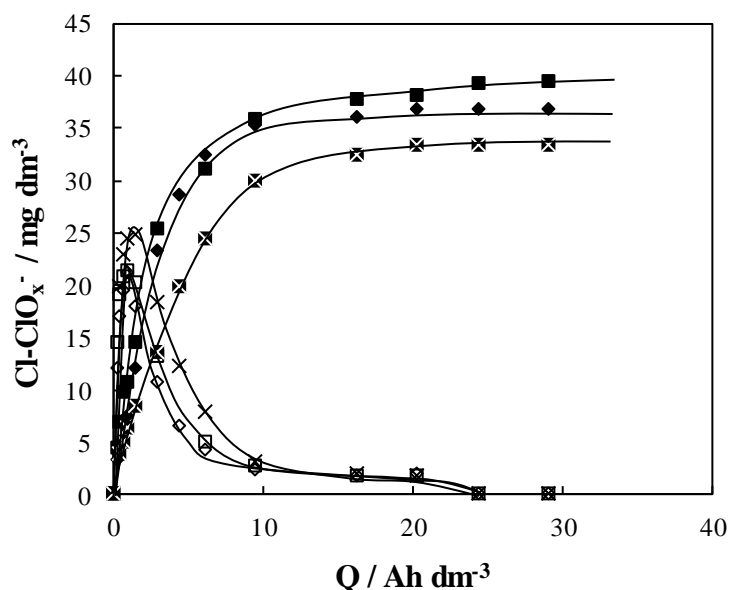


343 In addition, chloride can also react with hydroxyl radicals, favoring the production of  
344 chlorine compounds in higher oxidation state including perchlorate (Eqs. 9-12).



349 Several of these chlorinated species can contribute to the degradation of the ILs (chlorine,  
350 hypochlorite and hypochlorous acid) due to their high oxidant capacity, whereas other  
351 such as chlorate and perchlorate do not contribute, because the oxidation carried out by

352 them is not favored kinetically at room temperature. Figure 6 shows the changes in the  
 353 concentration of these two non-active ions (chlorate and perchlorate) with the applied  
 354 electric charge during the electrolysis of different ionic liquids in absence of sulfate.  
 355 Unfortunately, the presence of high concentrations of sulfate makes not possible the  
 356 analysis of different ions in the effluent and, therefore, these data cannot be shown.



357

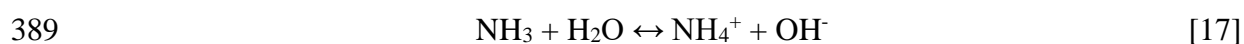
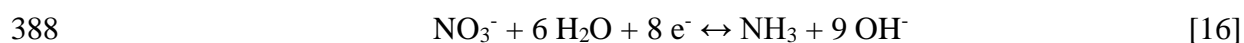
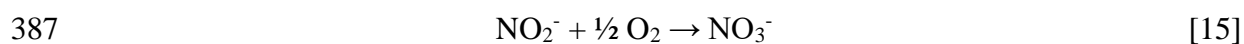
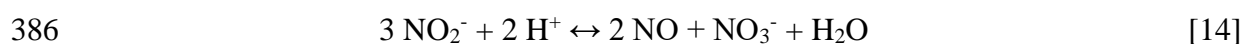
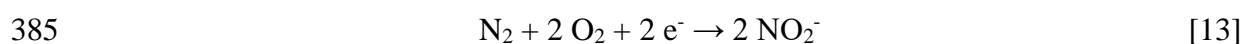
358 **Figure 6.** Chlorine speciation as function of the applied electric charge during the  
 359 electrolysis of different ionic liquids in absence of sulfuric acid.  $j$ :  $30 \text{ mA cm}^{-2}$ ; (■)  
 360 BmimCl; (◆) HmimCl; (x) DmimCl. Empty symbols: chlorate; full symbols: perchlorate.

361

362 As it can be observed, large amounts of chlorates and perchlorates are produced during  
 363 the treatment, resulting in almost total conversion of the initial chloride contained in the  
 364 solutions. Chlorate shows the typical behavior of an intermediate: there is an initial  
 365 increase associated to the disproportionation of hypochlorite (or its electro-oxidation)  
 366 followed by a later decrease until reaching zero values. The decrease observed  
 367 corresponds to the increase in the concentration of perchlorate. This species, which  
 368 behaves as final product, reaches a maximum value, from which it remains constant. The

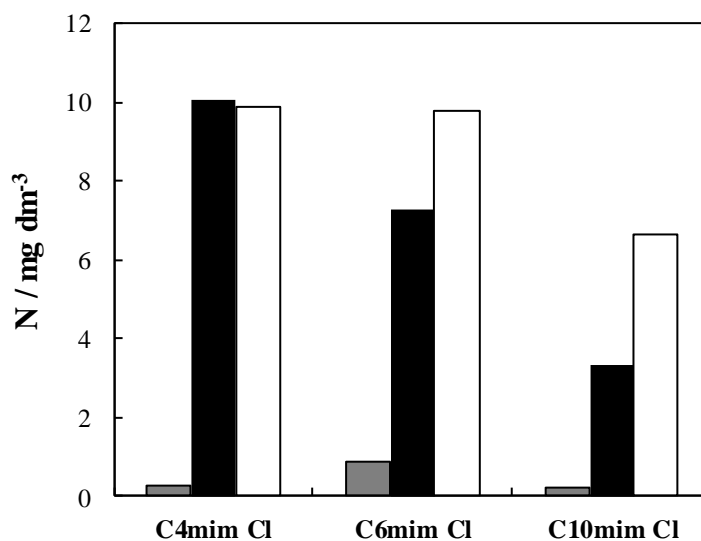
369 three ILs studied follow the same behavior during chlorine speciation. However, the total  
 370 production of perchlorate decreases in the sequence BminCl > HminCl > DmimCl,  
 371 suggesting that other final products are formed in the case of the Hmin<sup>+</sup> and the Dmin<sup>+</sup>  
 372 electrolysis [53]. From the mechanistic point of view looked for in this study, the  
 373 formation of perchlorate is very positive, because it minimizes the mediated oxidation of  
 374 the ILs by chlorinated species and, hence, results of the oxidation in the absence of sulfate  
 375 can only be caused by hydroxyl radicals mediated oxidation or, alternatively, by direct  
 376 oxidation.

377 A last important piece of information regarding the degradation of the ILs can be obtained  
 378 from the nitrogen contained in the three imidazolium cations degraded. This species can  
 379 be degraded during the electrolysis with BDD anodes, favoring the formation of inorganic  
 380 nitrogen compounds [43, 54]. In this context, organic nitrogen oxidation start with the  
 381 formation of nitrites (Eq. 13). These species are quickly oxidized into nitrates by different  
 382 mechanisms (Eqs. 14-15) and, in turn, nitrates can be cathodically reduced to ammonium  
 383 cations (Eqs. 16-17), which is the most important final product in the electrolysis of  
 384 organic nitrogen species [55].



390 Figure 7 shows the maximum nitrogen formation of each species during the electrolysis  
 391 of each ionic liquid at 30 mA cm<sup>-2</sup> in absence of sulfuric acid. Once again, inorganic

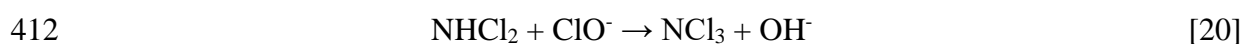
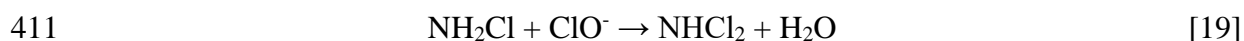
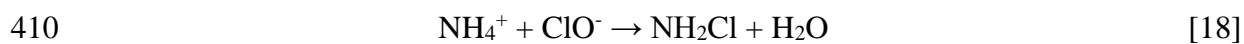
392 nitrogen measurements were not possible during the process in sulfate media and,  
393 unfortunately, data cannot be shown.



394

395 **Figure 7.** Maximum concentration of inorganic nitrogen release during the electrolysis  
396 of different ionic liquids in absence of sulfuric acid.  $j$ :  $30 \text{ mA cm}^{-2}$ ; grey bars:  $\text{NO}_2^-$ ; black  
397 bars:  $\text{NO}_3^-$ ; white bars:  $\text{NH}_4^+$ .

398 As it can be observed, nitrite presents the lower concentration in comparison with nitrate  
399 and ammonium for all the ionic liquids studied. This reveals the potential oxidation of  
400 nitrite to nitrate during the electrolysis with BDD anodes. The higher nitrite concentration  
401 was obtained for HmimCl. Regarding the evolution of nitrate, its maximum concentration  
402 is reached during the treatment of BmimCl whereas the minimum is obtained for DmimCl  
403 (in which the oxidation of the imidazolium group competes with the polymerization).  
404 Likewise, the maximum concentration of ammonium is also lower for this ionic liquid.  
405 This means that ammonium may be consumed by other way. At this point, it is important  
406 to highlight that the presence of chlorine compounds in high oxidation state can promote  
407 its reaction with ammonium. Specifically, hypochlorite can react with ammonium,  
408 favoring the production of inorganic chloramines (Eqs. 18-20) and finally nitrogen gas  
409 and chloride.



413 This is consistent with the previous chlorine speciation observed in Figure 6, where the  
414 generation rate of perchlorate (the final product of chloride oxidation) is lower during the  
415 treatment of DmimCl, followed by HmimCl and finally, BmimCl. This suggests that there  
416 were higher concentrations of hypochlorite in the solution which reacted with ammonium  
417 to form chloramines in a first stage and, eventually, gaseous nitrogen and chloride. This  
418 reactivity of the hypochlorite with the ammonium ion prevents reactivity with the organic  
419 carbon and make the electrolysis of the ILs in the absence of sulfate a very clean case of  
420 study.

421

#### 422 **4. Conclusions.**

423 From this work, the following conclusions can be drawn:

- 424 - Ionic liquids based on imidazolium group can be completely removed by  
425 electrolysis with diamond anodes.
- 426 - Despite an applied electric charge of 30 Ah dm<sup>-3</sup> is not enough to mineralize  
427 completely 1 mM of ILs, results obtained confirm that the electrolytic technology  
428 can attain the total transformation of the imidazolium ring into carbon dioxide and  
429 nitrates, being this anion later transformed into ammonium.
- 430 - Presence of sulfate in the waste electrolyzed improve the efficiency of the  
431 oxidation process, clearly pointing out that the contribution of peroxosulfate and  
432 sulfate radicals in the electrolysis with diamond anodes of organic is very  
433 important.

- 434 - The electrolysis of solutions containing 1 mM of DmimCl leads to the formation  
435 of a polymer, whose molecular weight increases during the treatment. Presence of  
436 sulfate prevents the formation of this polymer and favor the mineralization of the  
437 ILs.
- 438 - Chloride is mainly oxidized to chlorate and perchlorate during the electrolysis of  
439 the three ILs. Chloramines are also formed by the combination of the ammonium  
440 released from the imidazolium group with hypochlorite.

441

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447

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