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

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

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**Highlights**
- ILs based on imidazolium can be completely removed by electrolysis with BDD.
- Electropolymerization of Dmim⁺ is observed during the electrolysis with BDD.
- Sulfate leads to a more efficient oxidation and prevents polymerization.
- Nitrites, nitrates and ammonium are formed from the nitrogen of the imidazolium
groups.
- The chloride counter ion is transformed into perchlorates and chloramines.
1. Introduction.

Ionic liquids (ILs) are salts that exhibit high thermal stability and low melting point [1]. They may become as substitutes of conventional organic solvents [2], behaving as more environmentally-friendly species and, for this reason, they are commonly known as “green” solvents [3]. In the recent years, their use has been studied for many applications, such as the removal of carbon dioxide by absorption [4], the extraction of dyes and emerging contaminants [5, 6], the separation of hydrocarbons [7], the removal of chromium [8] or the photodegradation of organochlorine compounds [9]. Despite of the large number of potential applications, recently, ILs have been identified as persistent pollutants, because of their stability towards biological degradation [10] typically associated to their complex structure (cations typically consists of derivatives of imidazolium, pyridinium or phosphonium rings). Furthermore, several authors have informed about the toxicity of these compounds, as well as the environmental hazards that they may produce [11-14]. For this reason, in order to promote their applications, it is necessary to develop efficient processes that allow the removal of ILs from exhausted industrial effluents.

Advanced Oxidation Processes (AOPs) can be considered as suitable technologies for the treatment of wastewater polluted with ILs. AOPs are based on the production by different technologies of large amounts of hydroxyl radicals, which significantly contribute to the degradation of the pollutants present in the effluent [15, 16]. Technologies based on ozone or Fenton reagent have been the most studied AOPs for many decades [17-19]. However, from the nineties of the last century, electrolytic technologies have emerged as very promising alternatives [20-22]. These processes produce hydroxyl radicals from electrolysis of water on the anode surface (Eq. 1) [23-25], being the choice of a suitable electrode material a key to obtain a high efficiencies [26-30].
\[ \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^- \]  

[1]

One of the electrodes that has awakened great interest in the recent years is boron doped diamond (BDD) [31, 32]. This material has a large electrochemical window and, hence, it allows to generate large amounts of free hydroxyl radicals [33, 34]. For this reason, it has been evaluated in the oxidation of hundreds of pollutants including ILs [22, 25, 35-39]. In this context, Fabianska et al. [40] reported the electrolysis of imidazolium-based ionic liquids with diamond electrodes, evaluating the influence of the ionic liquid anion in different media (sulfate, chloride and bromide) by cyclic voltammetries and galvanostatic electrolyses with and without membrane. They concluded that hydroxyl radical is the main oxidant for the removal of the different ionic liquids studied and, the nature of the supporting electrolyte significantly influences the IL removal. However, the electrogenerated peroxodisulfate does not play a key role on the electrolysis process in this work. Later, Pieczynska et al. [41] assessed the removal of imidazolium and pyridinium ionic liquids, studying the influence of the pH and temperature. Alkaline pHs showed a decrease in the process efficiency whereas higher temperatures slightly increase the degradation of ILs. Likewise, the removal of pyridinium salts was more efficient in comparison with the imidazolium ILs depletion. They informed that \( \cdot\text{OH} \) and \( \text{O}_2\cdot^- \) were the main oxidants responsible of the removal of ILs. Finally, more recently, García-Segura et al. [42] have described the degradation of pyridinium- and imidazolium-based ionic liquids in sulfate media by anodic oxidation, electro-Fenton and photoelectro-Fenton using BDD anodes. They concluded that photoelectro-Fenton was the most efficient technology for the removal of those ILs and proposed the potential formation of hydroxyl radicals as the main mechanism for the removal of pollutants. The production of ozone and peroxodisulfate was also described but they not seemed to be the primary responsible of the degradation.
Opposite to those results, other works focused on the degradation of species different of ILs indicate that peroxocompounds formed during the electrolysis with BDD may behave as the most important species to explain the mineralization processes [43-45]. Hence, there exists a real necessity to clarify the specific contribution of hydroxyl radicals and/or other electrogenerated oxidants on the removal of ILs. With this background, the main aim of this work is to shed light about the real mechanisms of electrolysis with diamond anodes for the removal of organics. To do this, three different ILs were selected: they have the same anion (Cl−) and different cations with an imidazolium group derivative: Bmim+ (1-Butyl-3-methyimidazolium), Hmim+ (1-Hexyl-3-methyylimidazolium) and Dmim+ (1-Decyl-3-methyylimidazolium). Solutions polluted with these compounds were electrolyzed in electrolytes with absence and presence of sulfate anions, in order to evaluate the contribution of hydroxyl radicals and electrogenerated peroxodisulfate (and related derivative species, such as radical sulfate) during the degradation of the ILs.

2. Material and methods.

2.1. Chemicals.
Analytical grade BmimCl (1-Butyl-3-methyimidazolium chloride), HmimCl (1-Hexyl-3-methylimidazolium chloride), DmimCl (1-Decyl-3-methyimidazolium chloride) and sulfuric acid were used as received. Double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25°C) was used to prepare all solutions.

2.2. Analytical techniques.
The concentration of ILs was measured by chromatography using an Agilent 1100 series chromatograph equipped with a UV detector and a Synergy 4 mm Polar-RP 80 A column. For the determination of Bmim+ and Hmim+, the mobile phase consisted of 95:5 v/v
phosphate buffer/acetonitrile (flow rate: 0.75 cm$^3$ min$^{-1}$). In the case of Dmim$^+$, the percentage of acetonitrile was increased to 40%. The DAD detection wavelength was 218 nm, the temperature was kept at 35ºC and the injection volume was 20 µL.

Total Organic Carbon (TOC) was monitored using a Multi N/C 3100 Analytik Jena analyzer. Inorganic ions were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used to determine the anions and a Metrosep A Supp 4 column was used to analyze the cations. The mobile phase consisted of 85:15 v/v 3.6 mM Na$_2$CO$_3$/acetone solution for the determination of anions (flowrate: 0.80 cm$^3$ min$^{-1}$) and 1.7 mM HNO$_3$ and 1.7 mM 2,6-pyridinedicarboxylic acid solution for the determination of cations (flowrate: 0.90 cm$^3$ min$^{-1}$). The temperature of the oven was 45 and 30ºC for the determination of anions and cations, respectively. The volume injection was 20 µL.

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

2.3. Electrochemical cell.

Electrolyses were carried out in a single compartment electrochemical flow cell operating in recirculation mode (50 dm$^3$ h$^{-1}$). Boron doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of 78 cm$^2$, boron concentration of 500 mg dm$^{-3}$, a thickness of 2.72 µm, sp$^3$/sp$^2$ ratio of 220 and p-Si as support. The electrode gap between anode and cathode was 3 mm. The electric current was provided by a Delta Electronika ES030-10 power
supply (0-30V, 0-10A). The temperature was maintained at 25°C using a thermostatized bath.

Synthetic wastewater consisted of a solution (1.0 dm³) containing 1 mM of ionic liquid. For the study of the influence of the supporting electrolyte, 3000 mg dm⁻³ of sulfuric acid were added to synthetic wastewater.

3. Results and discussion.

Figure 1 shows changes undergone by the concentration of the three ILs during the electrolysis at 30 mA cm⁻² of synthetic wastes, with presence or absence of sulfate ions in the electrolyte.

Figure 1. Removal of ionic liquids with the applied electric charge during the electrolysis of wastewater polluted with 1 mM of ionic liquid. j: 30 mA cm⁻²; (■) BmimCl; (♦) HmimCl; (x) DmimCl. Full symbols: electrolyte without SO₄²⁻; empty symbols: 3000 mg dm⁻³ H₂SO₄
In every case, the concentration of ILs decreases down to almost zero, indicating that total depletion of these imidazolium ILs can be attained from the synthetic wastes using this electrochemical technology, regardless the molecular weight of the cation and the presence of sulfate anions in the electrolyte. Even so, degradation results are not overlapped but, just on the contrary, significant differences can be observed in the removal of the ILs, depending on the length of the carbon chain attached to the imidazolium ring and the electrolyte used. As indicated in the introductory section of this work, in the electrolysis of solutions without sulfate, only oxidation mediated by chlorine or by hydroxyl radicals (Eq. 1) can supplement the direct anodic oxidation, whereas in the case of the electrolysis carried out to sulfate-containing solutions, peroxosulfates and sulfates radicals are also expected to play an important role [46]. On the other hand, it is expected a slower degradation as the molecular weight of the ILs cation increases, since the degradation of linear alkane chains is known to be a low efficiency process for AOP, because of the nonexistence of functional groups to start the attack of the carbon chain.

A second important remark that should be pointed out is the higher efficiency observed in the degradation of the DmimCl polluted solution as compared to the results of the other two ILs. Thus, during the electrolysis tests of solutions without sulfate, the concentration of Bmim+ and Hmim+ cations decreases down to less than 3% of their initial value for electric current charges of 30 Ah dm⁻³, whereas Dmim+ is completely depleted at electric current charges even lower than 10 Ah dm⁻³, indicating an improved efficiency in more than three times, because of the higher theoretical oxygen demand (ThOD) associated to these larger cations, in this later case. As pointed out before, this is an unexpected behavior, in particular taking into account that the molecule structure of Dmim+ is much more complex than that of the other two ILs (larger carbon chain) and, hence, it was expected that its electrochemical degradation was much more difficult. However, this fact
can be explained in terms of the generation of a polymer during the electrolysis of Dmim with BDD anodes. In this context, the occurrence of particles and even of a thin layer of polymer was observed on the surface of the pipes and tanks of the bench-scale plant during the electrolysis, just the same behavior which was previously reported in literature for the electrolysis of nitrophenols polluted wastes with BDD anodes [47, 48], being one of the rare cases in which polymerization reactions are found during electrolysis with the powerful BDD electrodes. Therefore, the efficient removal of Dmim\(^+\) in comparison with Bmim\(^+\) and Hmim\(^+\) during electrolysis is mainly due to the polymerization of the ionic liquid and not to its mineralization, which was the expected treatment. In order to confirm this production of polymer and to know more about its formation, the electrolysis of Dmin\(^+\) was repeated three times, under exactly the same conditions, being stopped the electrolysis in each of the three tests at different electric current charge passed. Then, the solids were carefully collected and their amount (by gravimetry) and molecular weight (using GPC) were measured. Results of these experiments are shown in Figure 2 and confirms the production of a polymer whose amount and molecular weight increase during the electrolysis reaching a molecular weight of 720 mg mol\(^{-1}\) at the end of the electrolysis.
Figure 2. Mean molecular weight (part A) and concentration (part B) of the solids produced during the electrolysis of DminCl, obtained from three different tests operated exactly under the same conditions.

Another important observation which can be drawn from Figure 1 is that the removal efficiency of Bmim$^+$ and Hmim$^+$ cations is higher when sulfate ions are contained in the electrolyte. As pointed out before, during electrolysis in sulfate media, significant
amounts of peroxodisulfate are produced, either by direct (Eq 2) or by hydroxyl radicals mediated (Eq. 3) mechanisms. In turn, peroxodisulfate can interact with other oxidants and produce sulfate radicals. All these species are known to be powerful oxidants that favors the removal of organic matter in wastewater [49-51].

\[ 2 \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2 \text{e}^- \]  \hspace{1cm} [2]

\[ 2 \text{SO}_4^{2-} + \cdot\text{OH} \rightarrow \text{S}_2\text{O}_8^{2-} + \text{OH}^- + \text{e}^- \]  \hspace{1cm} [3]

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

Effect observed on the degradation of DminCl is the opposite of that observed for BminCl and HminCl in presence of sulfates. Thus, the concentration of Dmin\(^+\) cation decreases with the applied electric charge until reaching its total depletion at current charge values around 17 Ah dm\(^{-3}\). This value is much higher than that obtained during the electrolysis without sulfate and, therefore, it may initially suggest a lower efficiency. However, at this point, it is important to highlight that the presence of a polymer was not detected during the electrolysis carried out when sulfate ions are contained in the electrolyte. This means that the production of peroxodisulfate does not only contributes to the more efficient
degradation of the ILs by electrolysis but it also prevents the formation of a polymer and, hence, the removal of Dmim$^+$ by an electropolymerization process.

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

**Figure 3.** Evolution of peroxodisulfate with the applied electric charge during the electrolysis of wastewater polluted with 1 mM of ILs. j: 30 mA cm$^{-2}$; supporting electrolyte: 3,000 mg dm$^{-3}$ H$_2$SO$_4$; (□) BmimCl; (◊) HmimCl; (x) DmimCl.

It is important to note that, the concentration of peroxodisulfate measured corresponds to that which has not reacted with the ILs or reaction intermediates and, hence, that higher concentrations may be produced, because the observed concentration is the balance between the production and the consumption of this oxidant. As it can be observed, peroxodisulfate increases with the applied electric charge for all the tests carried out. However, different behaviors can be seen depending on the particular ionic liquid treated.

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

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

**Figure 4.** Kinetic constants calculated for the removal of ionic liquids by electrolysis with BDD anodes. Full symbols: without sulfate; empty symbols: 3000 mg dm$^{-3}$ H$_2$SO$_4$. 
As it can be observed, the kinetic constants for Bmim$^+$ and Hmim$^+$ cations are similar during the electrolyses in absence of sulfate in the electrolyte. However, the value obtained for Dmim$^+$ is much higher, which is due to the polymerization of ionic liquid, previously described. Likewise, the use of sulfate as supporting electrolyte significantly increases the kinetic constants for BmimCl and HmimCl, being higher in the first case. In the case of DmimCl, the kinetic constant for the oxidation was expected to be higher than that obtained during the electrolysis in absence of sulfate. Unfortunately, it is not possible to compare, in terms of oxidation, both processes (with and without sulfate) because of the polymerization produced in absence of sulfate. This is not the case in the electrolysis of the ILs in solutions containing sulfates, for which the kinetic constants are observed to decrease with the molecular weight of the ionic liquid (Bmim$^+$ > Hmim$^+$ > Dmim$^+$). This means that there is a clear influence of the molecule structure on the removal of ILs by electrolysis with BDD anodes and that it is promoted the oxidation of the ILs containing the shorter carbon chains.

As for many other pollutants, the electrolysis of ionic liquids may lead to the formation of other intermediate organic compounds and/or to a complete mineralization of the organic matter to carbon dioxide. Intermediates can be more harmful than the initial pollutants and, hence, they should be removed from wastewater. In this context, to provide information about the evolution of the organic matter, the concentration of TOC was monitored during the treatment. It is important to take in mind that this parameter informs only about the complete mineralization of the organic matter (conversion of organic carbon into carbon dioxide) and not about the progress of the oxidation. Results obtained are shown in Figure 5.
Figure 5. TOC decay as function of the applied electric charge during the electrolysis of wastewater polluted with 1 mM of ionic liquid. j: 30 mA cm$^{-2}$; (■) BmimCl; (♦) HmimCl; (x) DmimCl. Full symbols: without sulfate; empty symbols: 3000 mg dm$^{-3}$ H$_2$SO$_4$.

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

The presence of sulfate leads to a more efficient TOC removal. In this context, a final percentage removal of 93.8 and 76.2 were obtained for BmimCl and HmimCl, respectively, whereas only 83.7 and 69.8 % were achieved for both ionic liquids in absence of sulfate anions at the same electric current charges applied. This agrees with the results previously obtained for the removal of the raw ILs (Figure 1), and indicates again the positive effect of the electrogenerated peroxodisulfate, not only in the oxidation of ILs, but also in the total removal of the intermediates formed.
On the other hand, the case of the DmimCl is different because of the polymerization observed in electrolyses of electrolytes without sulfate. Thus, the formation of polymer leads to an initial higher efficiency in the absence of sulfate, but this situation reverses at higher charges passed and the final percentage removal of TOC was 87.6 % in wastes without sulfate and 92.5 % when using sulfate as supporting electrolyte (polymer formation was not observed). The intermediates detected by HPLC-MS are reported in Table 1.

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

<table>
<thead>
<tr>
<th>Nº</th>
<th>Molecular structure</th>
<th>Retention time (min)</th>
<th>m/z</th>
<th>Presence in Bmim⁺</th>
<th>Presence in Hmim⁺</th>
<th>Presence in Dmim⁺</th>
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<tr>
<td>1</td>
<td><img src="image1" alt="Molecular structure" /></td>
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<td>154</td>
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<td>Yes</td>
<td>No</td>
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<tr>
<td>2</td>
<td><img src="image2" alt="Molecular structure" /></td>
<td>4.5</td>
<td>154</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Molecular structure" /></td>
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<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
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<td>Yes</td>
</tr>
<tr>
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<td>Yes</td>
</tr>
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<td>Yes</td>
</tr>
<tr>
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<td>4.5</td>
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</tr>
</tbody>
</table>

As can be observed, the electrolysis of Dmim⁺ cation leads to the higher production of organic intermediate compounds. Specifically, 16 compounds were detected whereas 12 and 9 were found during the electrolysis of HmimCl and BmimCl, respectively. This is an expected behavior, taking into account that the carbon chain is the highest for Dmim⁺ cation. Likewise, it is important to point out that the electrolysis of the three ILs studied with diamond electrodes favors the formation of similar intermediates compounds at the end of the experiments. This fact suggests that the ILs are attacked on the carbon chain
by electrogenerated oxidants at the beginning of the experiment followed by the ring opening.

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

\[
2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^- \quad [4]
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad [5]
\]

\[
\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+ \quad [6]
\]

\[
2 \text{ClO}^- \rightarrow \text{ClO}_2^- + \text{Cl}^- \quad [7]
\]

\[
\text{ClO}^- + \text{ClO}_2^- \rightarrow \text{ClO}_3^- + \text{Cl}^- \quad [8]
\]

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

\[
\text{Cl}^- + \cdot \text{OH} \rightarrow \text{ClO}^- + \text{H}^+ + \text{e}^- \quad [9]
\]

\[
\text{ClO}^- + \cdot \text{OH} \rightarrow \text{ClO}_2^- + \text{H}^+ + \text{e}^- \quad [10]
\]

\[
\text{ClO}_2^- + \cdot \text{OH} \rightarrow \text{ClO}_3^- + \text{H}^+ + \text{e}^- \quad [11]
\]

\[
\text{ClO}_3^- + \cdot \text{OH} \rightarrow \text{ClO}_4^- + \text{H}^+ + \text{e}^- \quad [12]
\]

Several of these chlorinated species can contribute to the degradation of the ILs (chlorine, hypochlorite and hypochlorous acid) due to their high oxidant capacity, whereas other such as chlorate and perchlorate do not contribute, because the oxidation carried out by
them is not favored kinetically at room temperature. Figure 6 shows the changes in the
concentration of these two non-active ions (chlorate and perchlorate) with the applied
electric charge during the electrolysis of different ionic liquids in absence of sulfate.
Unfortunately, the presence of high concentrations of sulfate makes not possible the
analysis of different ions in the effluent and, therefore, these data cannot be shown.

![Graph showing chlorine speciation as function of the applied electric charge during the
electrolysis of different ionic liquids in absence of sulfuric acid.](image)

**Figure 6.** Chlorine speciation as function of the applied electric charge during the
electrolysis of different ionic liquids in absence of sulfuric acid. j: 30 mA cm\(^{-2}\); (■) B mimCl; (●) H mimCl; (x) D mimCl. Empty symbols: chlorate; full symbols: perchlorate.

As it can be observed, large amounts of chlorates and perchlorates are produced during
the treatment, resulting in almost total conversion of the initial chloride contained in the
solutions. Chlorate shows the typical behavior of an intermediate: there is an initial
increase associated to the disproportionation of hypochlorite (or its electro-oxidation)
followed by a later decrease until reaching zero values. The decrease observed
corresponds to the increase in the concentration of perchlorate. This species, which
behaves as final product, reaches a maximum value, from which it remains constant. The
three ILs studied follow the same behavior during chlorine speciation. However, the total production of perchlorate decreases in the sequence BminCl > HminCl > DmimCl, suggesting that other final products are formed in the case of the Hmin\(^+\) and the Dmin\(^+\) electrolysis [53]. From the mechanistic point of view looked for in this study, the formation of perchlorate is very positive, because it minimizes the mediated oxidation of the ILs by chlorinated species and, hence, results of the oxidation in the absence of sulfate can only be caused by hydroxyl radicals mediated oxidation or, alternatively, by direct oxidation.

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

\[
\begin{align*}
N_2 + 2 O_2 + 2 e^- & \rightarrow 2 NO_2^- \quad [13] \\
3 NO_2^- + 2 H^+ & \leftrightarrow 2 NO + NO_3^- + H_2O \quad [14] \\
NO_2^- + \frac{1}{2} O_2 & \rightarrow NO_3^- \quad [15] \\
NO_3^- + 6 H_2O + 8 e^- & \leftrightarrow NH_3 + 9 OH^- \quad [16] \\
NH_3 + H_2O & \leftrightarrow NH_4^+ + OH^- \quad [17]
\end{align*}
\]

Figure 7 shows the maximum nitrogen formation of each species during the electrolysis of each ionic liquid at 30 mA cm\(^{-2}\) in absence of sulfuric acid. Once again, inorganic
nitrogen measurements were not possible during the process in sulfate media and, unfortunately, data cannot be shown.

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

As it can be observed, nitrite presents the lower concentration in comparison with nitrate and ammonium for all the ionic liquids studied. This reveals the potential oxidation of nitrite to nitrate during the electrolysis with BDD anodes. The higher nitrite concentration was obtained for HmimCl. Regarding the evolution of nitrate, its maximum concentration is reached during the treatment of BmimCl whereas the minimum is obtained for DmimCl (in which the oxidation of the imidazolium group competes with the polymerization).

Likewise, the maximum concentration of ammonium is also lower for this ionic liquid. This means that ammonium may be consumed by other way. At this point, it is important to highlight that the presence of chlorine compounds in high oxidation state can promote its reaction with ammonium. Specifically, hypochlorite can react with ammonium, favoring the production of inorganic chloramines (Eqs. 18-20) and finally nitrogen gas and chloride.
NH\(_4^+\) + ClO\(^{-}\) → NH\(_2\)Cl + H\(_2\)O  \[18\]

NH\(_2\)Cl + ClO\(^{-}\) → NHCl\(_2\) + H\(_2\)O  \[19\]

NHCl\(_2\) + ClO\(^{-}\) → NCl\(_3\) + OH\(^-\)  \[20\]

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


From this work, the following conclusions can be drawn:

- Ionic liquids based on imidazolium group can be completely removed by electrolysis with diamond anodes.

- Despite an applied electric charge of 30 Ah dm\(^{-3}\) is not enough to mineralize completely 1 mM of ILs, results obtained confirm that the electrolytic technology can attain the total transformation of the imidazolium ring into carbon dioxide and nitrates, being this anion later transformed into ammonium.

- Presence of sulfate in the waste electrolyzed improve the efficiency of the oxidation process, clearly pointing out that the contribution of peroxosulfate and sulfate radicals in the electrolysis with diamond anodes of organic is very important.
- The electrolysis of solutions containing 1 mM of DmimCl leads to the formation of a polymer, whose molecular weight increases during the treatment. Presence of sulfate prevents the formation of this polymer and favors the mineralization of the ILs.

- Chloride is mainly oxidized to chlorate and perchlorate during the electrolysis of the three ILs. Chloramines are also formed by the combination of the ammonium released from the imidazolium group with hypochlorite.

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