Sono and photo-electrocatalytic processes for the removal of ionic liquids based on 1-butyl-3-methylimidazolium cation

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Abstract

In this work, synthetic wastewaters polluted with ionic liquids 1-Butyl-3-methylimidazolium acetate (BmimAc) and chloride (BmimCl) undergo electrolysis with diamond anodes. Results obtained were compared to those attained by enhancing bare electrolysis with the irradiation of UV light or with the application of high-frequency ultrasound (US). Despite its complex heterocyclic structure, $Bmim^+$ cation is successfully depleted with the three technologies tested, being mainly transformed into four different organic intermediates, inorganic nitrogen species and carbon dioxide. Regardless of the technology evaluated, removal of the heterocyclic ring is much less efficient (and so, much slower) than the oxidation of the counter ion. In turn, the counter ion influences on the rate of the removal of the ionic liquid cation. Thus, the electrolysis and photoelectrolysis of the BmimAc is much less efficient than its sonoelectrolysis, while these differences becomes much less important in the case of the BmimCl. In this later

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case, the most efficient technology is photoelectrolysis. This fact is directly related to the generation of free radicals in the solution by the irradiation of UV light to the electrochemical system which significantly contribute to the removal of $Bmim^+$. As the results obtained in those tests do not depend on the action of external oxidants (typically produced from the additional supporting electrolyte typically added to decrease cell voltage to suitable values), this mechanistic information is very interesting to understand the complex processes undergone in electrolysis with diamond.

Keywords

Electrolysis; photoelectrolysis; sonoelectrolysis; ionic liquid; 1-Butyl-3-methylimidazolium

Highlights

- 1-Butyl-3-methylimidazolium can be easily transformed into intermediates and mineralized

- Chloride and acetate anions are removed more efficiently than $Bmim^+$ cation

- During oxidation of $Bmim^+$, nitrites, nitrates and ammonium are formed in the bulk

- Sonoelectrolysis is the most efficient technology for the mineralization of BmimAc

- Photoelectrolysis attains the faster mineralization of the BmimCl.

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1. Introduction

Electrolysis is known to be an effective wastewater treatment, highly recommended for the depletion of pollutants that become refractory to other treatment technologies [1-3]. In the last two decades, the development of conductive-diamond coatings and their application as electrodes has contributed definitively to this success and, nowadays, there are hundreds of papers that have reported the outstanding efficiencies and mineralization got in the treatment of a great variety of species, ranging from very simple carboxylic acids to the very complex organic dyes [2, 4]. For this reason, it is important for this technology to be confronted to new challenges, in order to better understand the mechanisms involved in the removal of organics.

In the recent years, the high-performance of the electrolysis with diamond has been improved by its combination with the irradiation of UV light and ultrasounds [5]. In the first case, the main mechanisms promoted is the activation of oxidants formed on the anode (peroxosulfates, peroxophosphates, peroxocarbonates, chlorine, etc.) and cathode (hydrogen peroxide) surfaces by the formation of the corresponding radicals [5-7]. In the second case, improvement in the mass transport (for low frequency US) or promotion in the formation of radicals (not only by activation of electrogenerated oxidant but also by the sonochemical oxidation of water) are the expected mechanisms to explain the changes caused by the irradiation [8].

The treatment of ionic liquids (ILs) can be one of the most important challenges still needed to be studied, not only because of the very complex structure of these molecules, often containing heterocycles, but also because of their conductivity, high enough to allow the electrolysis of wastes polluted with them at suitable cell voltages, without the addition of further supporting electrolyte salts. This is a very important point, because of the well-known formation of oxidants from the anions contained in the supporting

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electrolyte salts (chloride, sulfates, phosphates, etc.) added in high concentration during the electrochemical treatment, which definitively affects to the process performance and efficiency [9, 10].
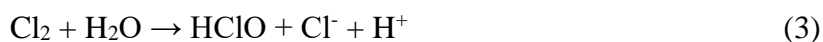
These compounds (ILs) are commonly formed by a cation such as pyridinium, imidazolium, sulfonium, phosphonium, among others, and acetate, halides, NTf_2 (bis(trifluoromethanesulfonimide)) or PF_6 (hexafluorophosphate) as the anions most used [11-13]. One of the most representative ionic liquids is 1-Butyl-3-methylimidazolium ($Bmim^+$), which can be purchased as different salts. Two of them are the chloride (BmimCl) and the acetate (BmimAc) salts, which only differs in the counter ion. The common heterocyclic imidazolium ring, usually classified as diazole, presents non-adjacent nitrogen atoms in its structure where carbon chains are joined to form $Bmim^+$ cation [14, 15]. On the other hand, it is important to highlight that these ILs based on $Bmim^+$ are used for different industrial applications [16]: enzymatic reactions [17], solvents [18, 19], catalysis [20, 21], extraction and purification [22], Li-ion batteries [23], capacitors [24] or fuel cells [25] among others. Likewise, these industries produce large volumes of wastewater containing these compounds in low concentration, which are not biologically degraded [26, 27]. Likewise, these compounds present high toxicity and they can produce environmental hazards [26-29]. For this reason, it is necessary to develop clean and efficient technologies that allow the removal of these compounds in wastewater, such as electrochemical techniques [30, 31].

Taking into account these points, this work reports the results obtained during the electrolysis of synthetic wastewater polluted with two different ionic liquids with the same cation ($Bmim^+$) and two different anions: acetate and chloride. This study was initially planned for understanding better the mechanisms of the electrochemical oxidation with diamond anodes. In the particular case of the ionic liquids used, as because

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of their high conductivity (BmimAc and BmimCl), it is not necessary the addition of different salts to perform electrolysis at a reasonable cell voltage. This means that only peroxoacetate could be expected to be formed, in addition to hydroxyl radicals and to oxidants formed from them (hydrogen peroxide and ozone) by the oxidation of acetate anion contained in the IL molecule during the electrolysis of BmimAc (Eq. (1)) [32].

$$CH_3COO^- + 2 \cdot OH \rightarrow CH_3COOO^- + H_2O \qquad (1)$$

As peroxoacetate is not efficient in the oxidation of organics, electrolysis of BmimAc will inform about the most pure mechanisms for the oxidation of organics by electrolysis with diamond. Opposite, in the case of the chloride salt, other active chlorine species could be present in addition to hydroxyl radicals, ozone and hydrogen peroxide by the electrochemical oxidation of chloride anion (Eqs. (2)-(4)) [33].

$$2 \, Cl^- \rightarrow Cl_2 + 2 \, e^- \qquad (2)$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (3)$$

$$HClO \leftrightarrows H^+ + ClO^- \qquad (4)$$

2. Materials and Methods

2.1. Chemicals.

Bmim (1-butyl-3-methylimidazolium) acetate and chloride were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Sodium carbonate and acetone (Sigma-Aldrich, Spain) were used as mobile phase for the determination of ions. Double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at $25°C$) was used to prepare all solutions.

2.2. Analytical methods.

Samples were filtered with 0.22 μm nylon filters Scharlau provided by Scharlab. The concentration of $Bmim^+$ cation was followed by reversed-phase chromatography. The chromatography system was an Agilent 1100 series coupled a UV detector. A Synergy 4 mm Polar-RP 80 A analytical column was used. The mobile phase consisted of 95:5 phosphate buffer/acetonitrile (flow rate: 0.75 cm^3 min^{-1}). The UV detection wavelength was 218 nm, the temperature was maintained at 35ºC and the injection volume was 20 μL. TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. In this case, samples were directly measured without filtration in order to quantify all the organic carbon present in the system. Ions concentration was measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used for the determination. The mobile phase consisted of 85:15 v/v 3.6 mM Na_2CO_3/acetone with a flow rate of 0.8 mL min^{-1}. The temperature of the oven was 45 ºC and the volume injection was 20 μL. Likewise, a Metrosep A Supp 4 column was used to analyze the cations, mainly ammonium (NH_4^+). The mobile phase consisted of 1.7 mM HNO_3 and 1.7 mM 2,6-pyridinedicarboxylic acid with a flow rate of 0.9 ml min^{-1}. The temperature of the oven was 30ºC. Intermediates found during the degradation of the ionic liquids were followed by HPLC-MS (LC/MS SQ Agilent). The system employed an ACE Excel 3 C18-Amide, 150x4.6 mm column at 40 ºC as stationary phase and a mixture of water and formic acid (99.9:0.1 v/v) as mobile phase (flow rate: 5 cm^3 min^{-1}). Mass spectra were collected in the m/z range of 40-400.

2.3. Electrochemical cell.

Electrolyses were carried out in a single compartment electrochemical flow cell. Boron doped diamond (BDD) with a geometric area of 78 cm^2 (WaterDiam, Switzerland) was used as anode and cathode. However, to allow the irradiation of UV light inside the

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electrochemical cell, the cathode material consisted of a stainless steel grid and one of the cell covers was made of quartz. The inter-electrode gap between both electrodes was 9 mm. A low pressure Hg vapor UV lamp VL-215MC (Vilber Lourmat), $\lambda = 254$ nm, intensity of 930 μW/cm^2 and energy 4.89 eV irradiated 4 W directly to the quartz cover. A high-frequency ultrasound (Epoch 650 ultrasound horn, Olympus) was used to provide waves into the system at 10 MHz. The power of ultrasound was 200 W. A Delta Electronika ES030-10 power supply (0-30 V, 0-10 A) provided the electric current. Wastewater was stored in a glass tank (0.6 dm^3). BDD anode presents a 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. Experiments were carried out under galvanostatic conditions (30 mA cm^{-2}) and discontinuous mode.

3. Results and Discussion

Figure 1 shows the decay observed in the concentration of Bmim$^+$ cation along the electrolysis of BmimCl and BmimAc aqueous solutions (1 mM). No other chemicals were added to the synthetic wastewater. Hence, and opposite to what happened in other electrolysis works, in which it is found a key role of electro-generated oxidants produced from the oxidation of the supporting electrolyte salts [34], here the decay can only be associated to three mechanisms, directly related to the degradation of the pollutant: direct electrolysis, hydroxyl radicals mediated oxidation (including ozone and hydrogen peroxide) or to chemical oxidation promoted by oxidants electro-generated from the anions of the ionic liquid salt, i.e. chlorine/hypochlorite and peroxoacetic acid.
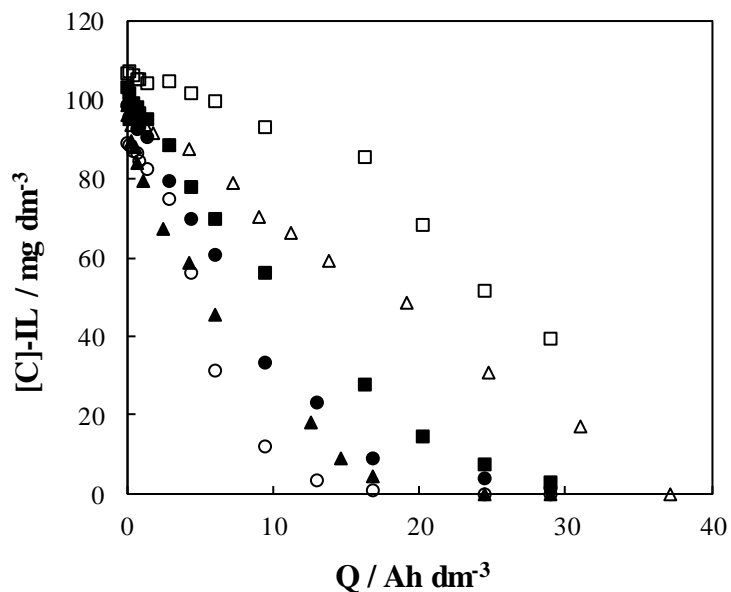
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Figure 1. Changes observed in the concentration of Bmim$^+$ cation during the electrolysis of BmimCl (black symbols) and BmimAc (white symbols). (■) electrolysis; (●) sonoelectrolysis; (▲) photoelectrolysis. [IL]$_0$: 1 mM; pH$_0$: 6.18; j: 30 mA cm^{-2}.

As it can be seen in Figure 1, in every case, the concentration of Bmim$^+$ cation decreases down to complete depletion, although differences in the efficiency associated to the technology applied and to the counter ion are very remarkable. Thus, except for the sonoelectrolysis, the removal of Bmim$^+$ cation is much more efficient in the presence of the chloride ion as compared to the electrolysis with acetate. This fact can be related to a competitive oxidation during the treatment of BmimCl between Bmim$^+$ and Cl$^-$ while the oxidation of the cation seems to be the main process during the removal of BmimAc. The irradiation of UV light or high-frequency US shows always positive effect on the removal efficiency, which is very interesting because this is not always the expected situation as it was pointed out before elsewhere [9, 35]. In the electrolysis of BmimCl, differences among the three technologies are lower than in the case of BmimAc, where the results of the sonoelectrolysis becomes estrange and can only be explained by taking into account

that high-frequency sonolysis is energetic-enough to produce very high concentrations of hydroxyl radicals from water in the bulk [8, 36], while the photolysis is much less efficient in this process. The enhanced supply of hydroxyl radicals (electrolysis and sonolysis) can help to explain the very remarkable increase in the oxidation rate of $Bmim^+$.

An additional observation that can be made is related to the shape of the concentration vs Q plots. While in the case of the electrolysis of BmimCl, it follows a typical exponential decay, in the case of the BmimAc the decay is linear and from a given moment the rate increases importantly, which is a totally unexpected result. The exponential decay is typically associated to the electrolytic treatment of wastewater and it is typically understood by first order kinetic model, associated either to mass transport limitations in direct electrolysis or to the proportionality of the rate with concentration in the case of the kinetic control by mediated oxidation processes [37].

Once discussed the oxidation of $Bmim^+$, it is important to take into account that not only the cation is oxidized by the electrolytic technologies, but also the counter ions. Figure 2 shows the oxidation of chloride and acetate, two well-known anions in terms of electrochemical reactivity.
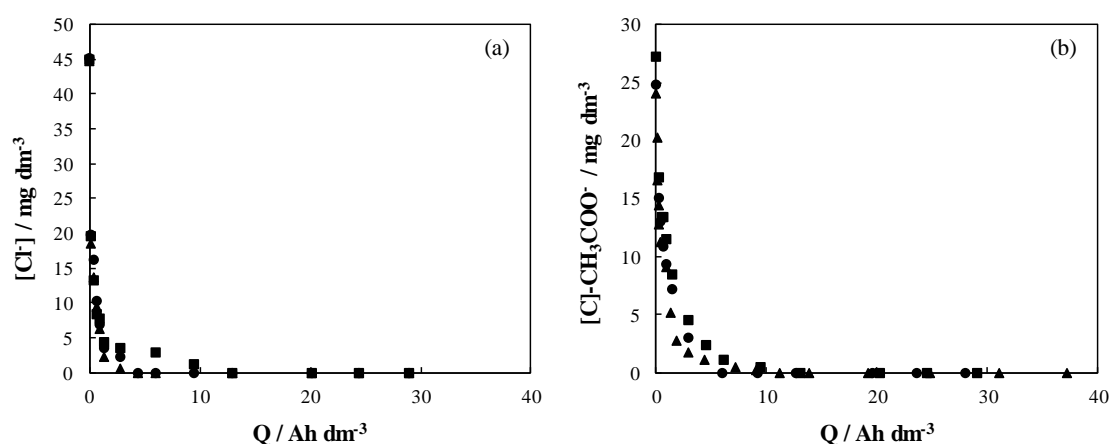

Figure 2. Changes in the concentration of chloride (a) and acetate (b) found during the electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl and BmimAc, respectively. $[IL]_0$: 1 mM; pH_0: 6.18; j: 30 mA cm^{-2}.

The first important observation that should be made from the plot is that oxidation of the counter ions is much faster than oxidation of $Bmim^+$. Here, the electrostatic effects on the pollutants (pointed out before) should be clearly claimed. The negative charge of the anions allows a better interaction with the positively charge surface of the anode and this fact, together with the much lower number of electrons required to be exchanged, explains the faster removal. In comparing the technologies, it may be stated that both US and UV irradiation have a very positive effect on the removal rate, being photoelectrolysis slightly more efficient than sonoelectrolysis. Oxidation of the anion leads to the formation of reaction intermediates and final products (Figure 3).
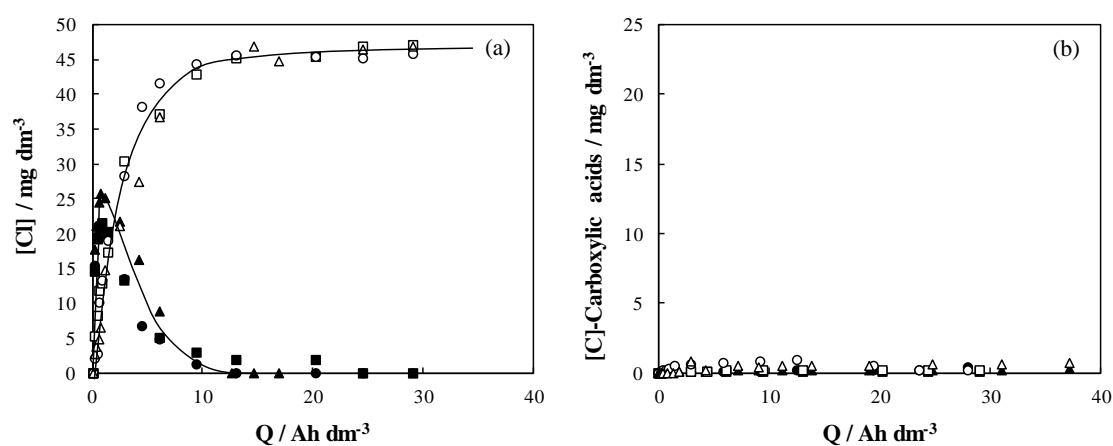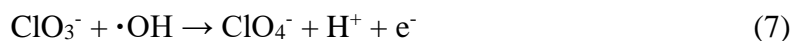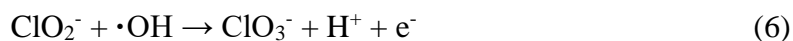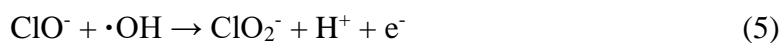

Figure 3. Concentrations of a) chlorate (black symbols) and perchlorate (white symbols) and b) oxalic acid (black symbols) and formic acid (white symbols) found during the electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl and BmimAc, respectively. $[IL]_0$: 1 mM; pH_0: 6.18; j: 30 mA cm^{-2}.

In the case of chloride, hypochlorite is the first species formed during the electrolysis with BDD anodes (Eqs. (2)-(4)). This compound can react with the organic matter present in wastewater favoring its degradation. On the other hand, hypochlorite can be rapidly

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oxidized by hydroxyl radicals to other chlorine compounds in high oxidation state such as chlorate and perchlorate (Eqs. (5)-(7)).

$$ClO^- + \cdot OH \rightarrow ClO_2^- + H^+ + e^- \tag{5}$$

$$ClO_2^- + \cdot OH \rightarrow ClO_3^- + H^+ + e^- \tag{6}$$

$$ClO_3^- + \cdot OH \rightarrow ClO_4^- + H^+ + e^- \tag{7}$$

Perchlorate is the final oxidation product and there is quantitative conversion of the chloride contained initially in the solution. This is a toxic and harmful compound for humans and the environment. For this reason, its production should be avoided and future researches should be focused on not only the removal of organics but also the minimization of this type of inorganic pollutants. Chlorate is the main intermediate and the only important difference found when comparing the technologies is a slightly faster oxidation in the case of the sonoelectrolysis, which can be explained in terms of the higher $\cdot OH$ production rate in the sonoelectrochemical process. Opposite to what it is observed in the case of chloride, role of intermediates in the case of the oxidation of acetate is almost negligible, as expected according to previous works [38], in which it is suggested an almost direct cold combustion for these species and concentrations of oxalic and formic acid formed are always below 1 ppm. Despite carboxylic acids are typically difficult to be oxidized by AOPS, mineralization of carboxylic acids by electrolysis with diamond is not a difficult process although it is usually much slower, and hence less efficient, than oxidation of aromatic species. The effective mineralization observed in this work is a very valuable information, because of the absence of other oxidants typically found in the electrolysis of organics such as peroxosulfates or chlorine/hypochlorite. Thus, as carboxylic acids are refractory to hydroxyl radicals and direct electrolysis is the only different mechanisms that can develop in the system (in comparison with another

raw AOP), this observation points out that direct electrolysis has a key role in the depletion of the carboxylic acids as it was proposed by Savall and coworkers and Brillas´ group in previous studies [39, 40].

Regarding the oxidation of $Bmim^+$ cation, this species consists of a heterocyclic ring that contains nitrogen. Figure 4 shows the concentration of nitrites, nitrates and ammonium released to the solution during the treatment. It is important to take in mind that electrochemistry of inorganic nitrogen species in solution is not easy from a mechanistic point of view. According to previous works, main product in the oxidation of C-N bond is not ammonium but oxidized nitrogen [41]. This explains the concentration of nitrites and nitrates observed. Both species behaves as intermediates because nitrites are oxidized either electrochemically or chemically by dissolved oxygen into nitrates which, in turn, are reduced cathodically to ammonium ions over BDD and stainless steel electrodes, explaining the large concentrations of this cations found [42, 43]. Oxidation of ammonium to nitrates is not favored because of the important electrostatic repulsion forces that prevents a good interaction of this cation with the anodic surface. On the other hand, the oxidation of C-N bond can also lead to the formation of other volatile NO_x species during the electrochemical treatment with BDD anodes [44]. Nonetheless, its concentration is much lower than nitrite, nitrate and ammonium.
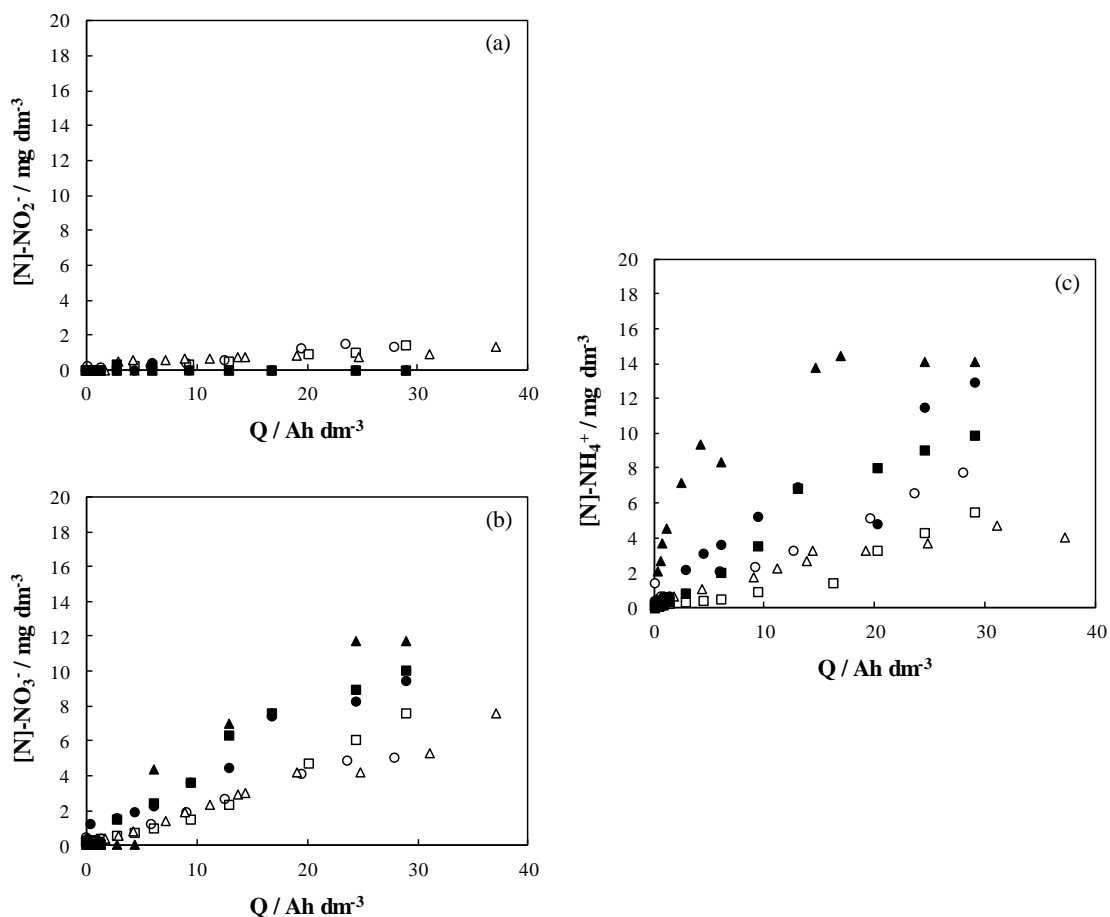
Figure 4. Inorganic nitrogen species found during the electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl (black symbols) and BmimAc (white symbols). (a) NO_2^-; (b) NO_3^-; (c) NH_4^+. $[IL]_0$: 1 mM; pH_0: 6.18; j: 30 mA cm^{-2}.

Total concentration of ammonium is much lower in the case of the electrolysis of the chloride salt. This observation may be explained in terms of the interaction of hypochlorite with ammonium to form sequentially mono, dichloramine, nitrogen trichloride and to regenerate chloride and produce nitrogen gas [45].

By HPLC, four organic intermediates were found. They were identified by mass spectrometry as: i1 (which was not clearly identified but it may correspond to an intermediate with MW 102 g mol^{-1}), isopropanol (i2), n,n-dimetylformamide (i3) and chlorosulfonic acid (i4). Figure 5 shows the chromatographic area of different

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intermediates as function of the applied electric charge during the electrolytic and electro-irradiated treatment of the ionic liquids.
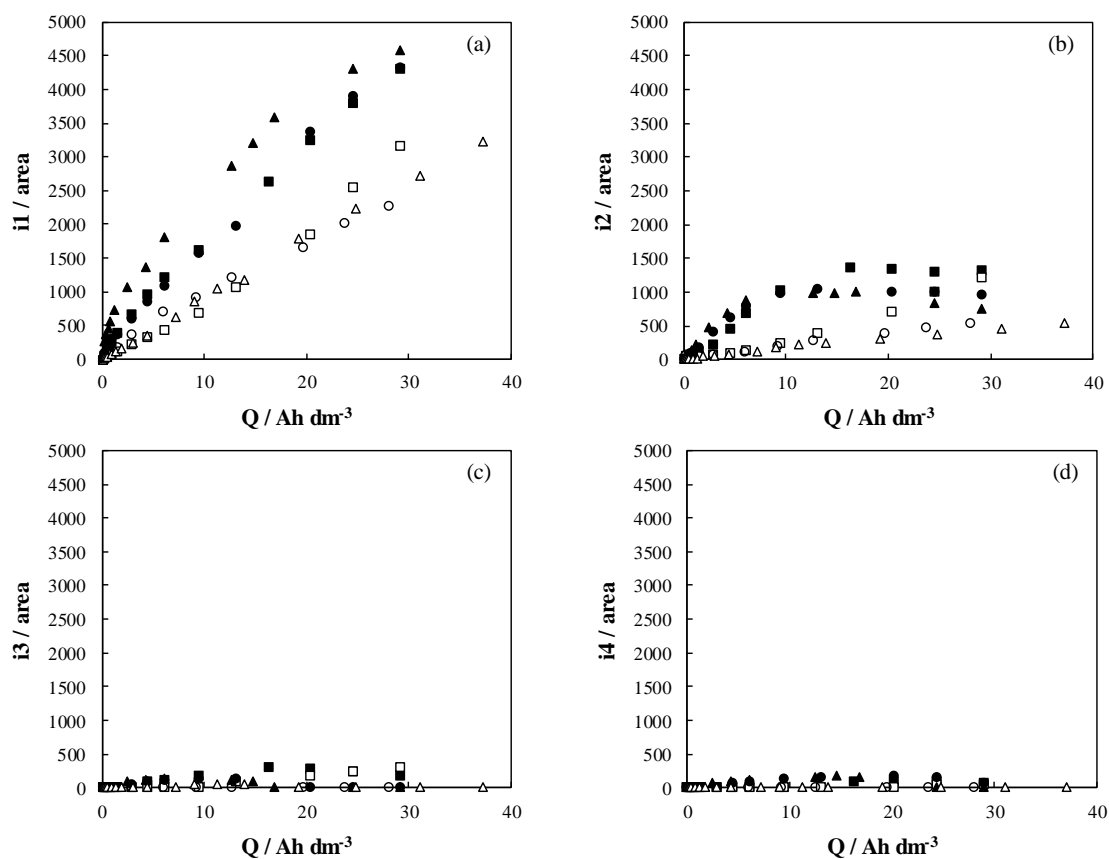

Figure 5. Intermediates found during the electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl (black symbols) and BmimAc (white symbols). $[IL]_0$: 1 mM; pH_0: 6.18; j: 30 mA cm^{-2}.

As it can be observed, there is only one intermediate (i1) which shows a significant area during the process, following an increase trend for all the tests carried out. Likewise, i2 profile, identified as isopropanol, initially increases followed by a decrease. Finally, i3 and i4 (n,n-dimetylformamide and chlorosulfonic acid, respectively) shows the lowest signal during the process. At this point, it is important to highlight that all concentrations are very low according to the TOC mass balance, regardless the area registered by HPLC analysis.

Taking into account these results, the mechanism described in Figure 6 can be proposed for the degradation of $Bmim^+$ cation by electrolysis with diamond electrodes.
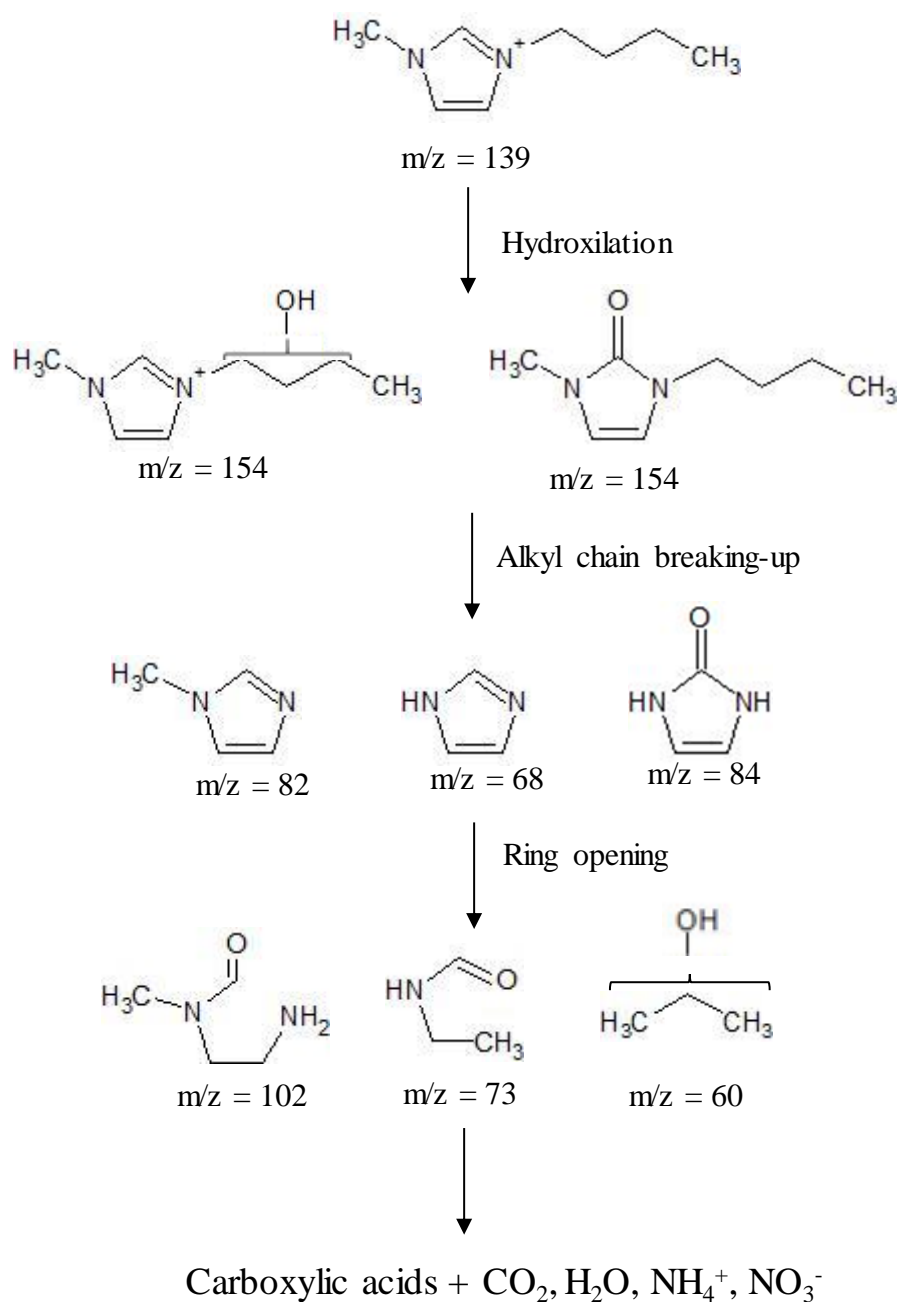

Figure 6. Pathway proposed for the degradation of $Bmim^+$ cation by electrolysis.

Figure 7 shows the changes in the mineralization and it also summarizes the oxidation rates discussed. As it can be seen, $Bmim^+$ cation is fully depleted but the waste is not fully mineralized for the 40 Ah dm^{-3} of charge applied. Oxidation of the acetate salt is less

efficient except for the case of the sonoelectrolysis, and differences found with the oxidation of chloride salts have to be explained by the chlorine mediated oxidation. In the case of the electrolysis of the chloride salt, irradiation of light has a clear positive effect which can be explained by the formation of Cl· radicals, which in addition to delay the formation of chlorate, contribute to a faster oxidation of the $Bmim^+$ cation. This is not the case in the electrolysis of acetate salts, in which the irradiation of light does not show this clear improvement.
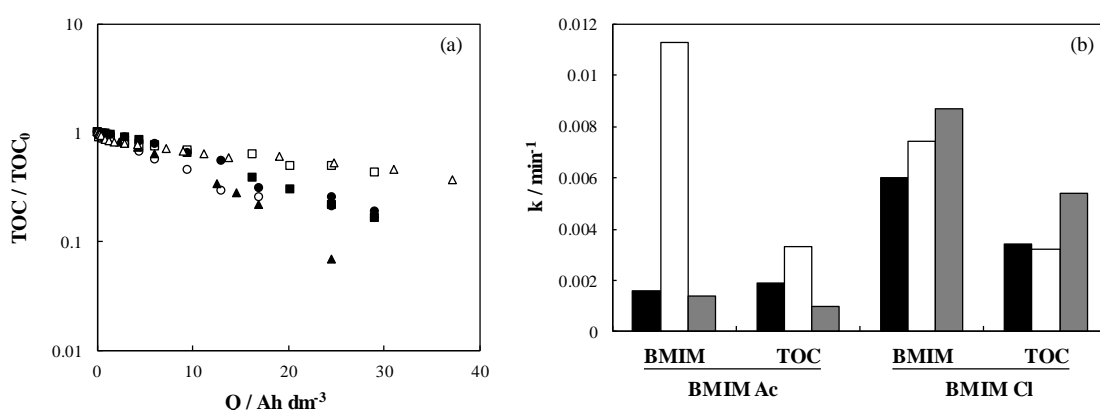

Figure 7. (a) Mineralization of the ILs evaluated in this work: (black symbols) BmimCl; (white symbols) BmimAc. (■) electrolysis; (●) sonoelectrolysis; (▲) photoelectrolysis. (b) First-order kinetic constants for the $Bmim^+$ cation depletion and for the mineralization of the ILs. Black: electrolysis; white: photoelectrolysis; grey: sonoelectrolysis. $[IL]_0$: 1 mM; pH_0: 6.18; j: 30 mA cm^{-2}.

Opposite, the effect of high-frequency US clearly improves the oxidation of the TOC and $Bmim^+$ cation in the electrolysis of the acetate salt and becomes the more efficient process. Massive formation of hydroxyl radicals not only in the anode surface but also in the bulk and an increase in the mass transport can help to explain this observation.

Conclusions

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From this work, the following conclusions can be drawn:

- 1-Butyl-3-methylimidazolium cation can be fully oxidized by electrolysis with diamond electrodes, leading to the formation of carbon dioxide, ammonium, nitrite and nitrate ions. Efficiency of the depletion depends on the counter ion and on the irradiation of high-frequency US and UV light.

- The depletion of the counter ion is much more efficient than the oxidation of the $Bmim^+$ cation. In the case of the BmimCl, the final product in the oxidation of the anion is perchlorate and the main intermediate chlorate. There are no differences among the technologies except for a faster reaction in the case of the sonoelectrolysis. In the case of the BmimAc, oxalic and formic acids are the key intermediates and carbon dioxide the final product. The reluctance of hydroxyl radicals to the oxidation of carboxylic acids and the impossibility of other alternative oxidation mechanisms, point out the importance of the direct electrolysis in the oxidation of carboxylic acids.

- Oxidation of $Bmim^+$ leads to the formation of hydroxylated-Bmim molecules as the main organic intermediate species and to nitrates and ammonium as the final nitrogen products. Because of the non-favored electrochemical oxidation of ammonium cation to nitrate anion, this speciation confirms that nitrate is the product obtained in the oxidation of the C-N bonds.

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