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

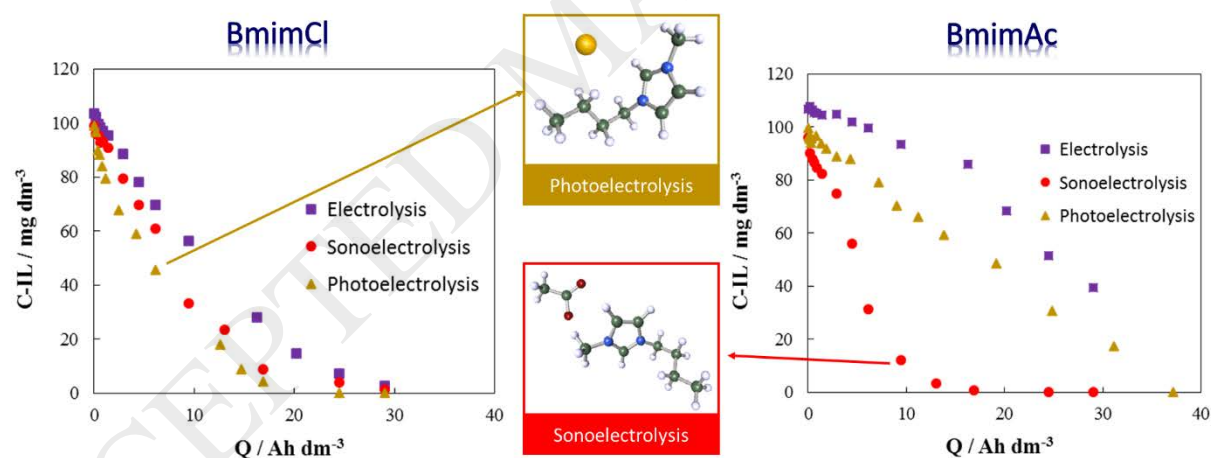
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Graphical Abstract



HighlightsAbstract

In this work, sono- and photoelectrolysis of synthetic wastewaters polluted with the ionic liquids 1-Butyl-3-methylimidazolium acetate (BmimAc) and chloride (BmimCl) were investigated with diamond anodes. The results were compared to those attained by enhancing bare electrolysis with irradiation by UV light or with the application of high-frequency ultrasound (US). Despite its complex heterocyclic structure, the Bmim⁺ cation

was successfully depleted with the three technologies that were tested and was mainly transformed into four different organic intermediates, an inorganic nitrogen species and carbon dioxide. Regardless of the technology that was evaluated, removal of the heterocyclic ring is much less efficient (and much slower) than oxidation of the counter ion. In turn, the counter ion influences the rate of removal of the ionic liquid cation. Thus, the electrolysis and photoelectrolysis of BmimAc are much less efficient than sonoelectrolysis, but their differences become much less important in the case of BmimCl. In this later case, the most efficient technology is photoelectrolysis. This result is directly related to the generation of free radicals in the solution by irradiation of the electrochemical system with UV light, which contributes significantly to the removal of Bmim⁺.

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

- 1-Butyl-3-methylimidazolium can be easily transformed into intermediates and can be mineralized
- Chloride and acetate anions are removed more efficiently than the Bmim⁺ cation
- During the oxidation of Bmim⁺, nitrites, nitrates and ammonium are formed in bulk
- Sonoelectrolysis is the most efficient technology for mineralizing BmimAc
- Photoelectrolysis results in faster mineralization of BmimCl

1. Introduction

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

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

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

in supporting electrolyte salts (chloride, sulfates, phosphates, etc.) that are added in high concentrations during the electrochemical treatment, which definitively affects the process performance and efficiency [9, 10].

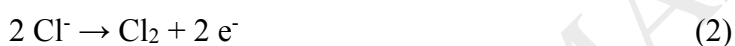
Ionic liquids (ILs) commonly consist of a cation such as pyridinium, imidazolium, sulfonium, or phosphonium (among others) and an anion such as acetate, a halide, NTf₂ (bis(trifluoromethanesulfonimide)) or PF₆ (hexafluorophosphate) [11-13]. One of the most representative ionic liquids is 1-Butyl-3-methylimidazolium (Bmim⁺), which can be purchased as different salts, e.g., the chloride (BmimCl) and acetate (BmimAc) salts, which only differ in their counter ions. The common heterocyclic imidazolium ring, usually classified as diazole, presents non-adjacent nitrogen atoms in its structure where carbon chains join to form the Bmim⁺ cation [14, 15]. However, it is important to highlight that these ILs that are based on Bmim⁺ are used for different industrial applications [16] including enzymatic reactions [17], solvents [18, 19], catalysis [20, 21], extraction and purification [22], Li-ion batteries [23], capacitors [24], fuel cells [25] and others. Likewise, these industries produce large volumes of wastewater that contain these compounds in low concentrations, which are not biologically degraded [26, 27]. Likewise, these compounds have high toxicity and can produce environmental hazards [26-29]. For this reason, it is necessary to develop clean and efficient technologies that allow for the removal of these compounds from wastewater, such as electrochemical techniques [30, 31].

Considering these points, this work reports results that were obtained during electrolysis of synthetic wastewater that was polluted with two different ionic liquids with the same cation (Bmim⁺) and two different anions (acetate and chloride). This study was initially planned to elucidate the mechanisms of electrochemical oxidation with diamond anodes. In the specific case of the ionic liquids that were used, because of their high conductivity

(BmimAc and BmimCl), the addition of different salts is not necessary to perform electrolysis at a reasonable cell voltage. Thus, only peroxyacetate was expected to form in addition to hydroxyl radicals and oxidants that formed from them (hydrogen peroxide and ozone) through the oxidation of the acetate anion within the IL molecule during the electrolysis of BmimAc (Eq. (1)) [32].



Because peroxyacetate is not efficient in the oxidation of organics, the electrolysis of BmimAc will provide information about the most fundamental mechanisms for the oxidation of organics by electrolysis with diamonds. In contrast, in the case of the chloride salt, other active chlorine species ~~chlorinated oxidants~~ could be present in addition to hydroxyl radicals, ozone and hydrogen peroxide through the electrochemical oxidation of chloride anion (Eqs. (2)-(4)) [33].



2. Materials and Methods

2.1. Chemicals.

Bmim (1-butyl-3-methylimidazolium) acetate and chloride were of analytical grade and were used as received. HPLC-grade acetonitrile (Sigma-Aldrich, Spain) was used for the mobile phase. Sodium carbonate and acetone (Sigma-Aldrich, Spain) were used as mobile phases 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 Scharlau filters provided by Scharlab. Determining the concentration of the Bmim⁺ cation was followed by reversed-phase chromatography. The chromatography system was an Agilent 1100 series coupled with 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 $\text{cm}^3 \text{min}^{-1}$). The UV detection wavelength was 218 nm, the temperature was maintained at 35°C, and the injection volume was 20 μL . The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. In this case, samples were directly measured without filtration to quantify all of the organic carbon that was present in the system. Ion concentrations 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 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 °C, 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 30°C. Intermediates found during the degradation of the ionic liquids were followed by HPLC-MS.

2.3. Electrochemical cell

Electrolysis experiments were performed in a single-compartment electrochemical flow cell. Boron-doped diamond (BDD) with a geometric area of 78 cm^2 (WaterDiam, Switzerland) was used as the anode and cathode. However, to allow for irradiation with UV light inside the 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 $930 \mu\text{W}/\text{cm}^2$ and energy 4.89 eV irradiated the quartz cover directly at 4 W. High-frequency ultrasound (Epoch 650 ultrasound horn, Olympus) was used to introduce waves into the system at 10 MHz. The power of the 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). The BDD anode presents a boron concentration of 500 mg dm^{-3} , a thickness of $2.72 \mu\text{m}$ and an sp^3/sp^2 ratio of 220 , and it is supported on p-Si. Experiments were performed under galvanostatic conditions (30 mA cm^{-2}) and a discontinuous mode.

3. Results and Discussion

Figure 1 shows the decay observed in the concentration of the Bmim^+ cation during the electrolysis of the BmimCl and BmimAc aqueous solutions (1 mM). No other chemicals were added to the synthetic wastewater. Hence, opposite to what has occurred in other electrolysis experiments in which it was found that electro-generated oxidants that are produced from the oxidation of the supporting electrolyte salts have a key role [34]. Here, the decay can only be associated with three mechanisms that are directly related to the degradation of the pollutant: direct electrolysis, hydroxyl-radical-mediated oxidation (including ozone and hydrogen peroxide), or chemical oxidation promoted by oxidants electro-generated from the anions of the ionic liquid salt (i.e., chlorine/hypochlorite and peroxyacetic acid).

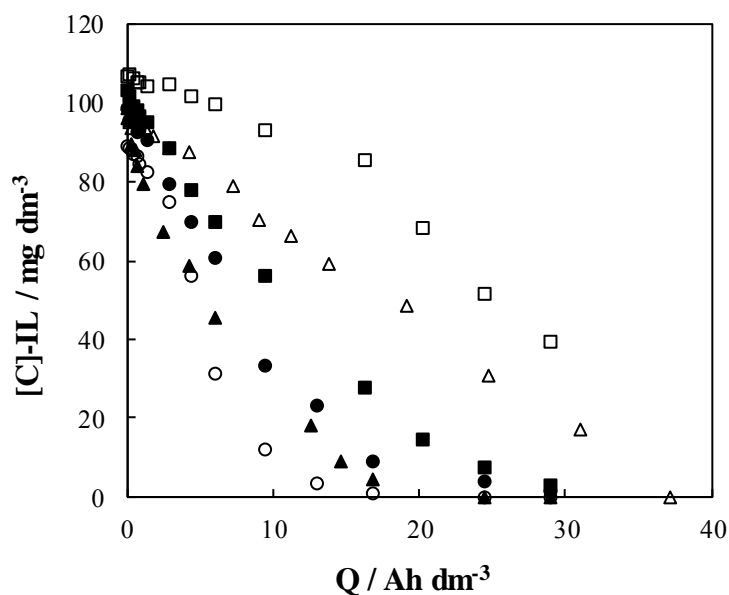


Figure 1. Changes observed in the concentration of the Bmim^+ cation during the electrolysis of BmimCl (black symbols) and BmimAc (white symbols). (■) electrolysis; (●) sonoelectrolysis; (▲) photoelectrolysis. $[\text{IL}]_0$: 1 mM; pH_0 : 6.18; j : 30 mA cm^{-2} .

As shown in Figure 1, the concentration of Bmim^+ cation decreases to complete depletion in every case, but the differences in the efficiency associated with the applied technology and the counter ion are very remarkable. Thus, except for sonoelectrolysis, the removal of the Bmim^+ cation is much more efficient in the presence of the chloride ion compared to electrolysis with acetate. This result can be attributed to competitive oxidation between Bmim^+ and Cl^- during the treatment of BmimCl , whereas the oxidation of the cation seems to be the main process that occurs during the removal of BmimAc . Irradiation by UV light or high-frequency US always shows a positive effect on the removal efficiency, which is interesting because this is not always the expected outcome, as was reported in previous studies [9, 35]. In the electrolysis of BmimCl , differences among the three technologies are smaller than in the case of BmimAc , where the results of the sonoelectrolysis differ significantly. This can only be explained by taking into account that high-frequency sonolysis is sufficiently energetic to produce very high

concentrations of hydroxyl radicals from bulk water [8, 36], whereas photolysis is much less efficient in this process. The enhanced supply of hydroxyl radicals (electrolysis and sonolysis) may help to explain the remarkable increase in the oxidation rate of Bmim^+ .

An additional observation that can be made regards the shape of the concentration *versus* Q plots. During the electrolysis of BmimCl , it follows a typical exponential decay, whereas during the electrolysis of BmimAc , the decay is linear, and the rate increases significantly from any given moment, which is a totally unexpected result. Exponential decay is typically associated with the electrolytic treatment of wastewater, and it is typically understood using a first-order kinetic model. This behavior is associated with either mass transport limitations in direct electrolysis or the proportionality of the rate to concentration in the case of kinetic control by mediated oxidation processes [37].

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

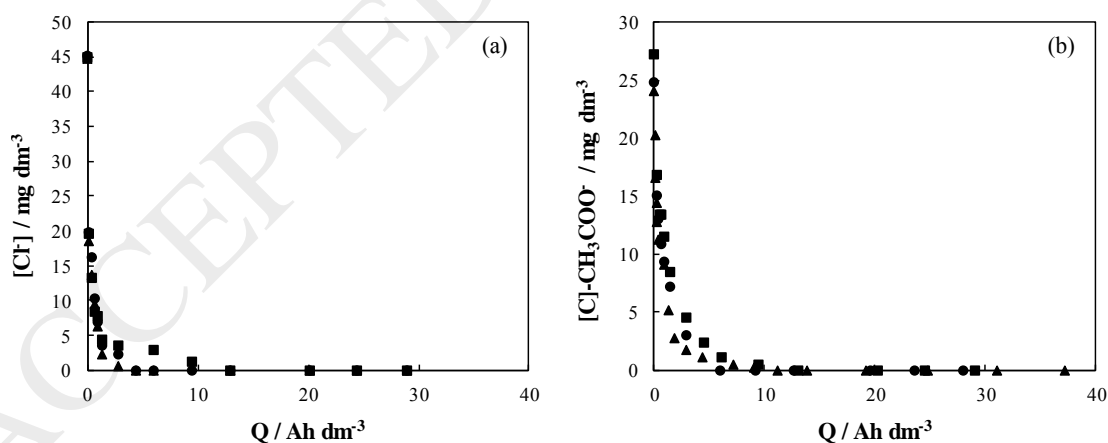


Figure 2. Changes in the concentration of chloride (a) and acetate (b) observed during electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl and BmimAc , respectively. $[\text{IL}]_0$: 1 mM; pH_0 : 6.18; j : 30 mA cm^{-2} .

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

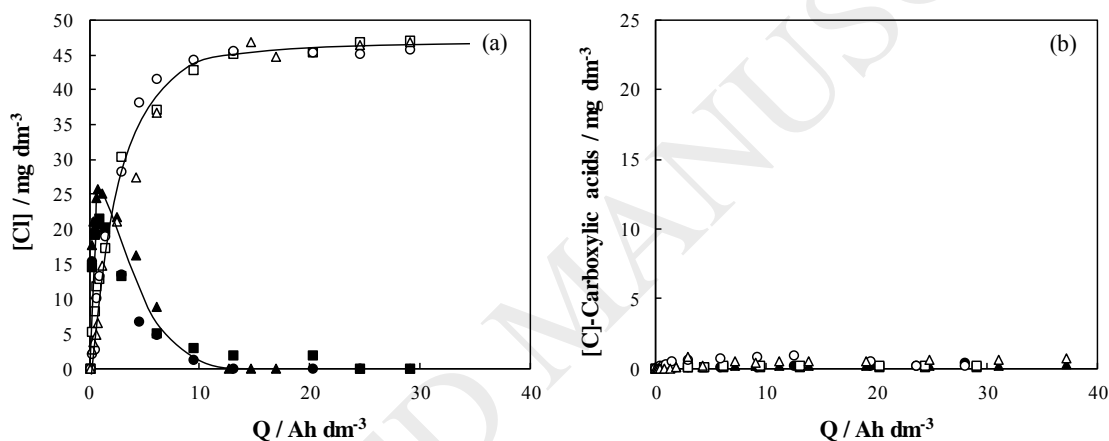
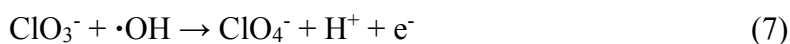
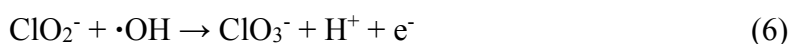
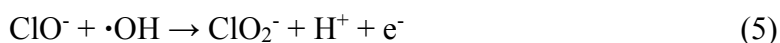


Figure 3. Concentrations of a) chlorate (black symbols) and perchlorate (white symbols) and b) oxalic acid (black symbols) and formic acid (white symbols) that were observed during electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl and BmimAc , respectively. $[\text{IL}]_0$: 1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

In the case of chloride, hypochlorite is the first species that formed during electrolysis with BDD anodes (Eqs. (2)-(4)). This compound can react with organic matter that is present in wastewater, favoring its degradation. However, hypochlorite can be rapidly oxidized by hydroxyl radicals to other chlorine compounds in a high oxidation state, such as chlorate and perchlorate (Eqs. (5)-(7)).



Perchlorate is the final oxidation product, and there is quantitative conversion of the chloride that was initially contained in the solution. Perchlorate is a toxic and harmful compound for humans and the environment. For this reason, perchlorate production should be avoided, and future investigations should focus not only on the removal of organics but also the minimization of this type of inorganic pollutant. Chlorate is the main intermediate, and the only important difference that was observed when comparing the technologies was slightly faster oxidation with sonoelectrolysis, which can be explained by the higher $\cdot\text{OH}$ production rate in the sonoelectrochemical process. In contrast to what it was observed for chloride, the role of intermediates during the oxidation of acetate is almost negligible, as is expected according to previous works [39], which suggest that there is nearly direct cold combustion for these species, and the concentrations of oxalic and formic acid that form are always below 1 ppm. Although carboxylic acids are typically difficult to oxidize by AOPS, the mineralization of carboxylic acids through electrolysis with diamond is not a difficult process. However, it is usually much slower, and thus less efficient, than oxidation of the aromatic species. The effective mineralization that is observed in this work is very valuable information because of the absence of other oxidants that are typically found in the electrolysis of organics, such as peroxosulfates or chlorine/hypochlorite. Thus, because carboxylic acids are refractory to hydroxyl radicals, and direct electrolysis is the only different mechanism that can develop in the system (in comparison to another raw AOP), this observation indicates that direct electrolysis plays a key role in the depletion of carboxylic acids, as was proposed by Savall and coworkers and Brillas' group in previous studies [40, 41].

Regarding the oxidation of the Bmim⁺ cation, this species consists of a heterocyclic ring that contains nitrogen. Figure 4 shows the concentrations of nitrites, nitrates and ammonium that were released to the solution during the treatment. It is important to consider that the electrochemistry of inorganic nitrogen species in solution is not simple from a mechanistic point of view. According to previous work, the main product in the oxidation of C-N bond is not ammonium but oxidized nitrogen [42]. This result explains the concentrations of nitrites and nitrates that were observed. Both species behave as intermediates because nitrites are oxidized, either electrochemically or chemically by dissolved oxygen, into nitrates that are, in turn, reduced cathodically to ammonium ions over BDD and stainless steel electrodes, explaining their large observed concentrations [38, 43]. The oxidation of ammonium to nitrates is not favored because of significant electrostatic repulsion forces that prevent the good interaction of this cation with the anodic surface. However, the oxidation of the C-N bond can also lead to the formation of other volatile NO_x species during electrochemical treatment with BDD anodes [44]. Nonetheless, its concentration is much lower than those of nitrite, nitrate and ammonium.

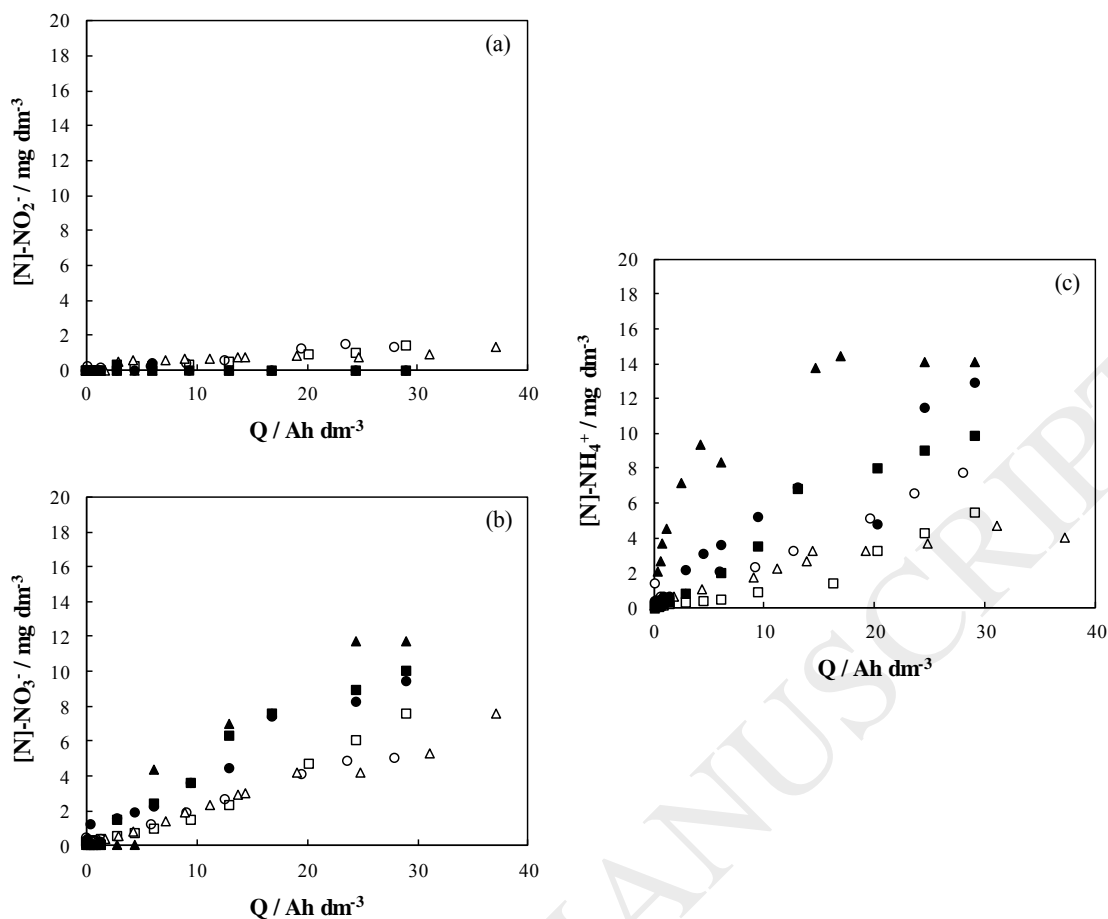


Figure 4. Inorganic nitrogen species observed during electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl (black symbols) and BmimAc (white symbols). (a) NO_2^- ; (b) NO_3^- ; (c) NH_4^+ . $[\text{IL}]_0$: 1 mM; pH_0 : 6.18; j : 30 mA cm^{-2} .

The total concentration of ammonium is much lower during electrolysis of the chloride salt. This observation can be explained by the interaction of hypochlorite with ammonium to sequentially form mono-, dichloramine, and nitrogen trichloride, as well as to regenerate chloride and produce nitrogen gas [45].

Using 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 $\text{MW } 102 \text{ g mol}^{-1}$), isopropanol (i2), *n,n*-dimethylformamide (i3) and chlorosulfonic acid (i4). Figure 5 shows the chromatographic areas of the different

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

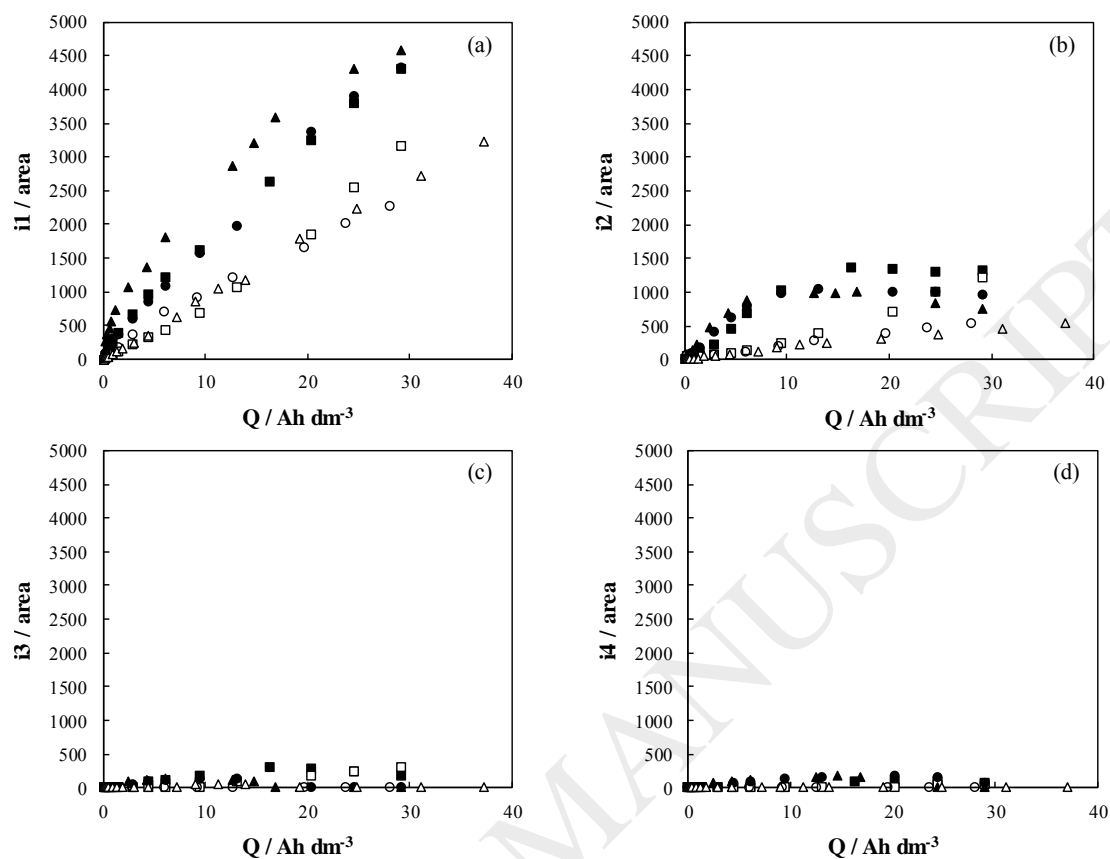


Figure 5. Intermediates observed during electrolysis (■), sonoelectrolysis (●) and photoelectrolysis (▲) of BmimCl (black symbols) and BmimAc (white symbols). [IL]₀: 1 mM; pH₀: 6.18; j: 30 mA cm⁻².

It is apparent that there is only one intermediate (i1) that has a significant area during the process, following an increasing trend for all tests that were performed. Likewise, the i2 profile, identified as isopropanol, initially increases and is followed by a decrease. Finally, i3 and i4 (n,n-dimethylformamide and chlorosulfonic acid, respectively) show the lowest signals during the process. At this point, it is important to note that all concentrations are very low according to the TOC mass balance, regardless of the area that was registered in the HPLC analysis.

Considering these results, the mechanism that is described in Figure 6 is proposed for the degradation of the Bmim⁺ cation by electrolysis with diamond electrodes.

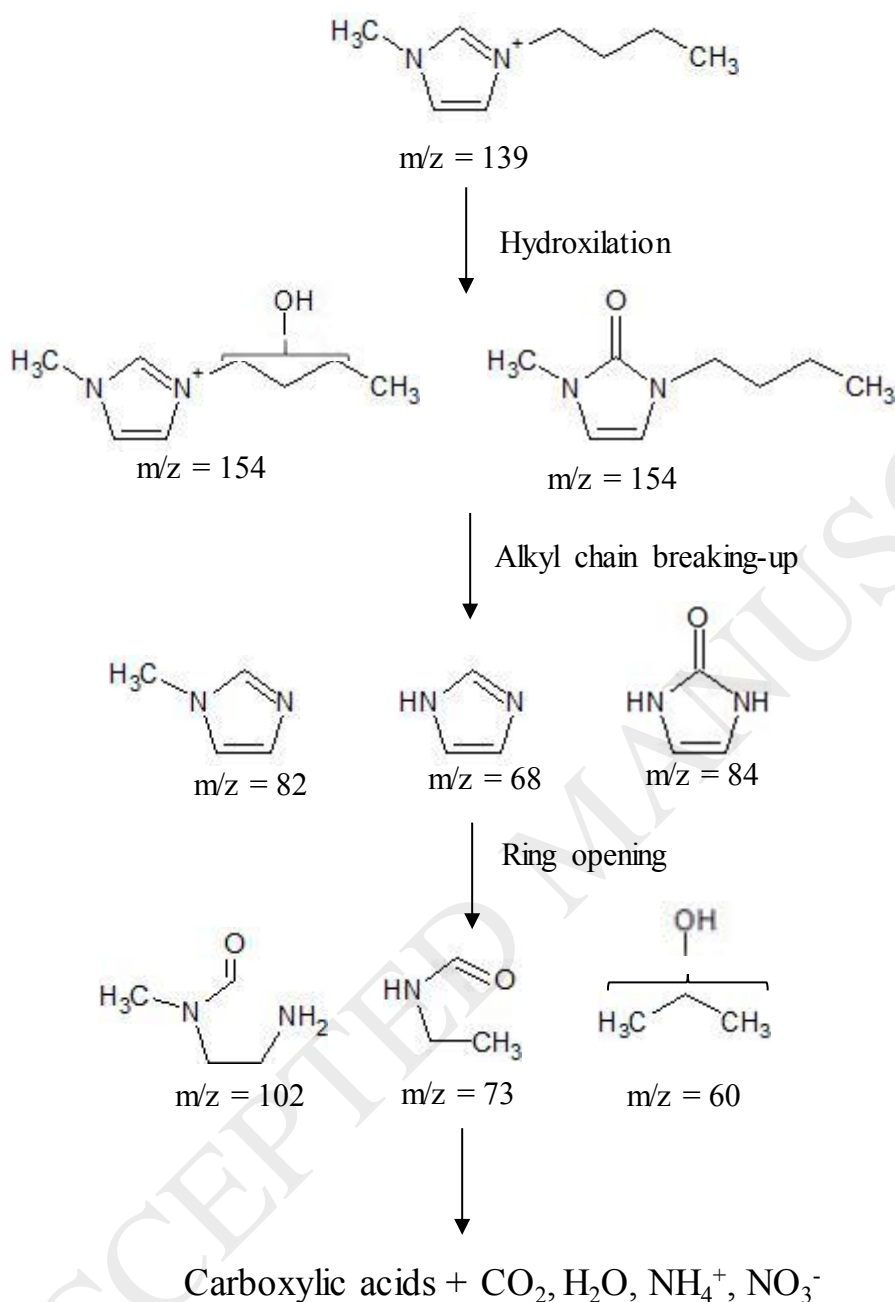


Figure 6. Pathway proposed for the degradation of the Bmim⁺ cation by electrolysis.

Figure 7 shows the changes in mineralization and summarizes the oxidation rates that were discussed above. The Bmim⁺ cation is fully depleted, but the waste is not fully mineralized at the 40 Ah dm⁻³ of charge applied. The oxidation of the acetate salt is less efficient, except for sonoelectrolysis, and the differences that were observed during the

oxidation of chloride salts must be explained by chlorine mediated oxidation. During electrolysis of the chloride salt, irradiation with light has a clear positive effect. This result can be explained by the formation of $\text{Cl}\cdot$ radicals, which contribute to faster oxidation of the Bmim^+ cation, in addition to delaying the formation of chlorate. This is not the case in the electrolysis of acetate salts, in which the irradiation by light does not show a similar clear improvement.

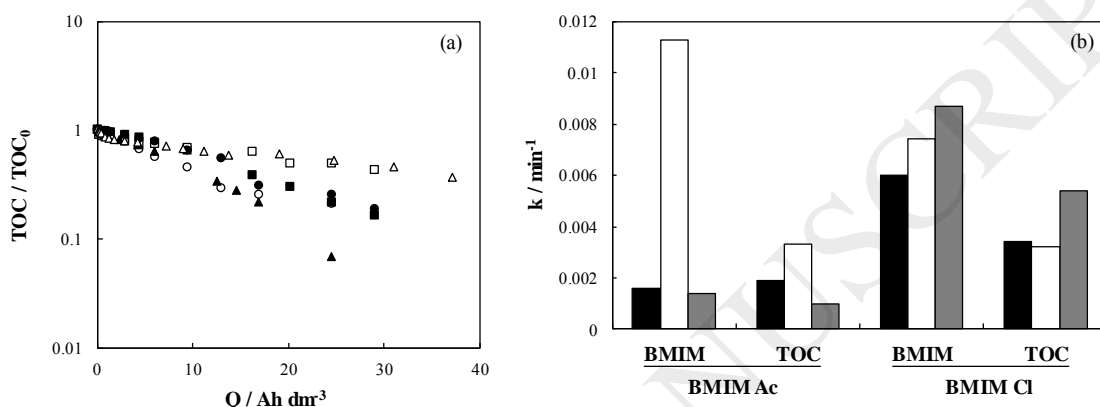


Figure 7. (a) Mineralization of the ILs evaluated in this work: (black symbols) BmimCl; (white symbols) BmimAc. (b) First-order kinetic constants for the depletion of the Bmim^+ cation and for the mineralization of the ILs. (■) electrolysis; (●) sonoelectrolysis; (▲) photoelectrolysis. $[\text{IL}]_0$: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

In contrast, the effect of high-frequency US clearly improves the oxidation of the TOC and the Bmim^+ cation during the electrolysis of acetate salts, becoming the more efficient process. The massive formation of hydroxyl radicals, not only at the anode surface but also in the bulk, and the increase in mass transport can help to explain this observation.

Conclusions

From this work, the following conclusions can be drawn:

- The 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. The efficiency of the depletion depends on the counter ion and on irradiation by 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 BmimCl, the final product in the oxidation of the anion is perchlorate, and the main intermediate is chlorate. There are no differences among the technologies except for a faster reaction time in the case of sonoelectrolysis. In the case of BmimAc, oxalic acid and formic acid are the key intermediates, and carbon dioxide is the final product. The reluctance of hydroxyl radicals in the oxidation of carboxylic acids and the impossibility of other alternative oxidation mechanisms illustrate the importance of direct electrolysis in the oxidation of carboxylic acids.
- The 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 the ammonium cation to a nitrate anion, this speciation confirms that nitrate is the product obtained in the oxidation of C-N bonds.

Acknowledgements

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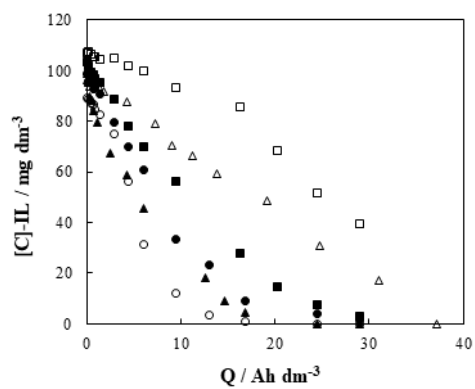
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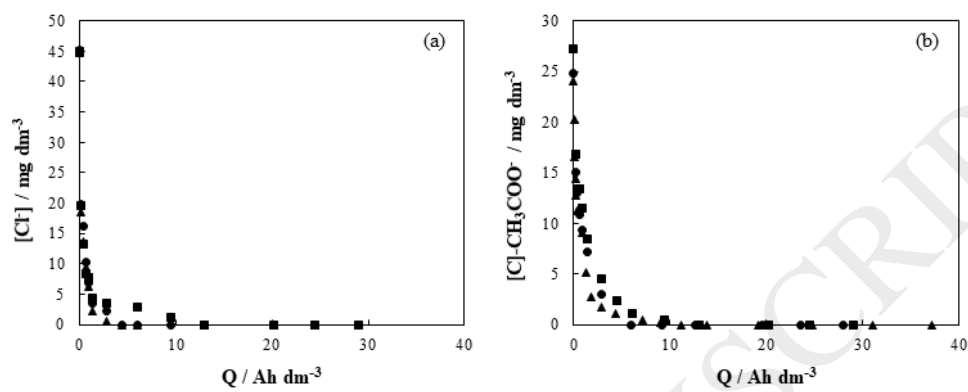
Figure Caption

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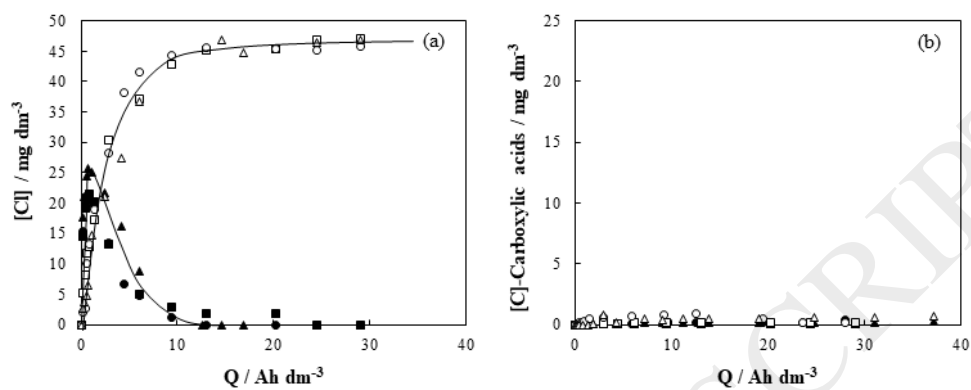
Figr-1



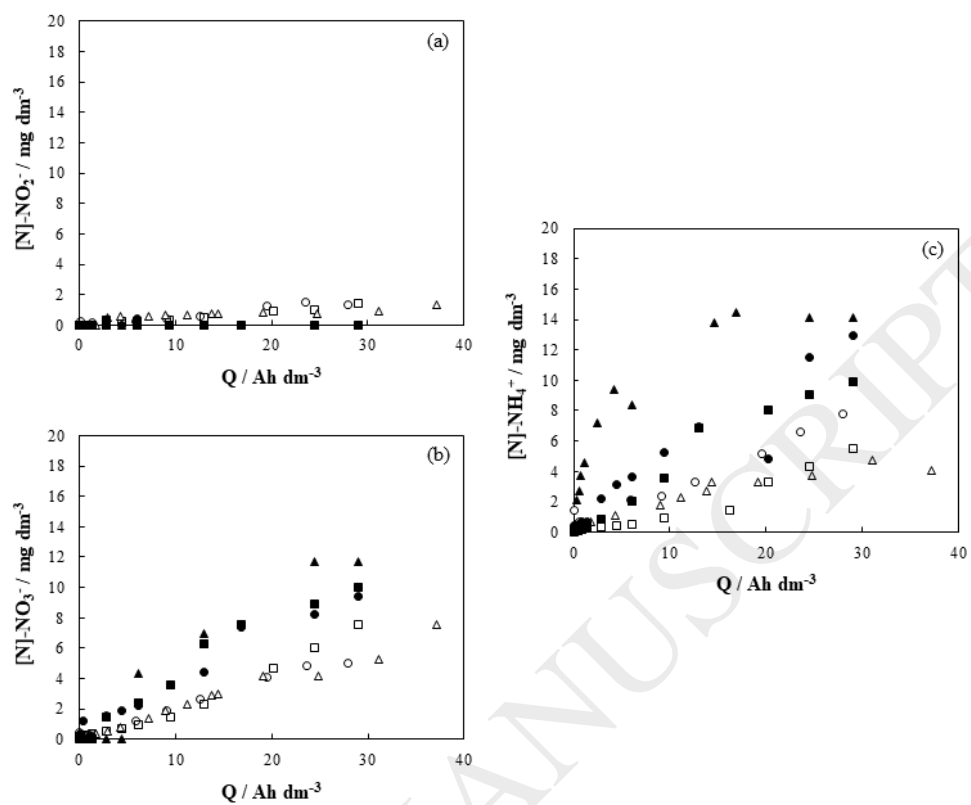
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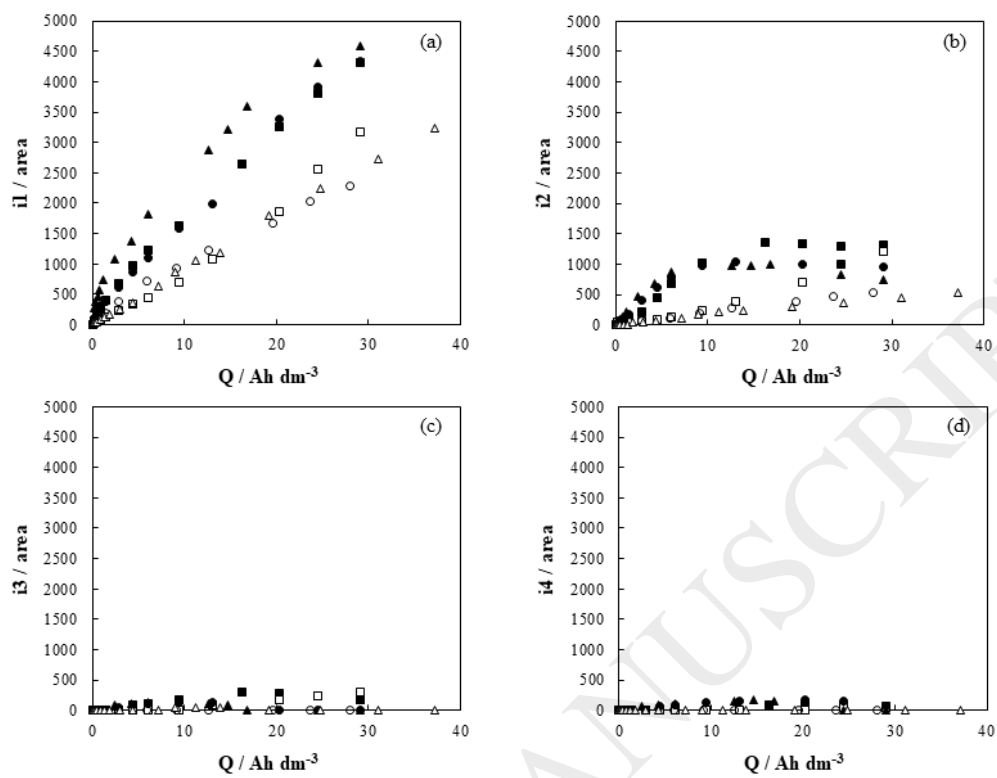
Figr-3



Figr-4



Figr-5



Figr-6

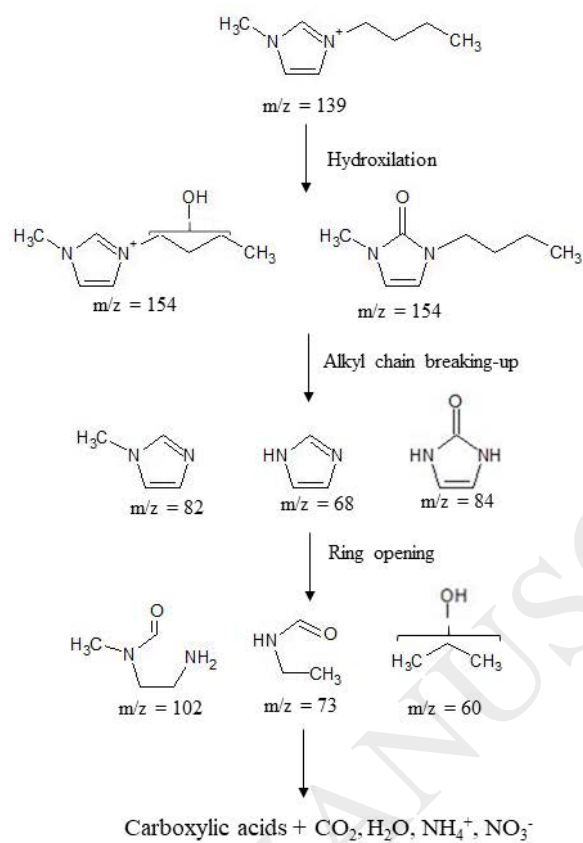


Fig-7

