Electrolysis with diamond anodes: Eventually, there are refractory species!

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Abstract

In this work, synthetic wastewater polluted with ionic liquid 1-butyl-3-methylimidazolium (Bmim) bis(trifluoromethanesulfonyl)imide (NTf₂) undergoes four electrolytic treatments with diamond anodes (bare electrolysis, electrolysis enhanced with peroxosulfate promoters, irradiated with UV light and with US) and results obtained were compared with those obtained with the application of Catalytic Wet Peroxide Oxidation (CWPO). Despite its complex heterocyclic structure, Bmim⁺ cation is successfully depleted with the five technologies tested, being transformed into intermediates that eventually can be mineralized. Photoelectrolysis attained the lowest concentration of intermediates, while CWPO is the technology less efficient in their degradation. However, the most surprising result is that concentration of NTf₂⁻ anion does not change during the five advanced oxidation processes tested, pointing out its strong refractory character, being the first species that exhibits this character in wastewater undergoing

electrolysis with diamond. This means that the hydroxyl and sulfate radicals mediated oxidation and the direct electrolysis are inefficient for breaking the C-S, C-F and S-N bounds of the NTf₂⁻ anion, which is a very interesting mechanistic information to understand the complex processes undergone in electrolysis with diamond.

Keywords

Refractory; ionic liquid; bis(trifluoromethanesulfonyl)imide; 1-butyl-3-methylimidazolium; electrolysis

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Highlights

- 1-Butyl-3-methylimidazolium can be easily transformed into intermediates and mineralized
- Bis(trifluoromethanesulfonyl)imide anion is refractory to electrolysis with diamond
- CWPO leads to the formation of more intermediates than electrolysis with diamond
- Sonoelectrolysis is the most efficient technology for the mineralization of wastes polluted with Bmim
- Photoelectrolysis attains an almost direct mineralization of the Bmim⁺ cation

Introduction

Over the last two decades, hundreds of papers have demonstrated the outstanding performance of the electrolysis of different types of wastewater with diamond anodes. Very high current efficiencies, exceptional robustness and lack of refractory species can be considered as the three most important labels for this technology (Rodrigo et al., 2010) and, all together, they explain why, even after having passed by more than 20 years from the beginning of the massive study of applications, currently electrolysis with diamond is still a hot scientific topic (Sires et al., 2014; Martinez-Huitle et al., 2015).

To attain these conclusions, thousands of products have been tested, ranging from very high-molecular weight dyes (Martinez-Huitle and Brillas, 2009; Brillas and Martinez-Huitle, 2015) to small carboxylic acid molecules (Gandini et al., 2000), from linear aliphatic (Cañizares et al., 2003; Cañizares et al., 2008) to highly heterocyclic molecular structures (Cañizares et al., 2007) and from natural (Raut et al., 2013) to anthropogenic molecules (Oturán et al., 2012). Likewise, different matrixes have been studied, ranging from real wastewater (Cabeza et al., 2007) to synthetic solutions enriched in salts (Cañizares et al., 2009a), passing through other different types of matrixes such as soil washing & soil flushing wastes (dos Santos et al., 2015) or pollutant-intensified matrixes. Results have been always the same: rate could be higher or lower but eventually, all organic molecules are fully degraded and, for non-heterocyclic compounds (or in the absence of chloride), mineralization, that is, conversion of organic carbon into carbon dioxide, is complete. To explain the impressive performance of this process, the combined action of many different oxidations mechanisms is proposed (Sires et al., 2014; Martinez-Huitle et al., 2015). Thus, in addition to the formation of hydroxyl radical, first demonstrated at the turn of the century (Marselli et al., 2003), formation of many other oxidants is known to occur via direct and hydroxyl mediated processes, giving chance to

the formation of a very important oxidants' cocktail (Cañizares et al., 2009b). Thus, presence of sulfates, carbonates and/or phosphates in the wastewater leads to the production of peroxosulfates, peroxocarbonates and/or peroxophosphates, respectively. Occurrence of chloride leads to the formation of hypochlorite/chlorine for low electric charge passed and, unfortunately, to chlorates and perchlorates for higher charges. Ozone and hydrogen peroxide are also known to be formed by interaction of hydroxyl radicals with water or oxygen. In addition, all these compounds can be transformed into more powerful oxidants by activation with UV light, high frequency US and even, with the simple interactions among them.

Taking into account these points, this work reports the results obtained during the electrolysis of an ionic liquid, the salt 1-butyl-3-methylimidazolium (Bmim) bis(trifluoromethanesulfonyl)imide (NTf₂). This compound presents a melting point about 2°C and a density of 1.44 g mL⁻¹. As most of the ionic liquids, it exhibits high thermal stability and it is very difficult to remove by biological degradation (Liwarska-Bizukojc and Gendaszewska, 2013). For this reason, this compound is considered as persistent pollutant and, hence, its presence in water should be avoided. The study was initially planned for understanding better the mechanisms of the electrochemical oxidation with diamond anodes, as because of the high conductivity of the pollutant used (BmimNTf₂), it is not necessary to add different salts in order to perform electrolysis at a reasonable cell voltage. However, in the results obtained, we found that bis(trifluoromethanesulfonyl)imide anion is refractory to the electrolysis with diamond, which is a very interesting result which, in turn, gives very valuable mechanistic information about this very important environmental electrochemical technology.

Materials and Methods

2.1. Chemicals

Analytical grade BminNTf₂ (C₁₀H₁₅F₆N₃O₄S₂) 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.

Bmin⁺ cation was quantified by reverse-phase chromatography using an Agilent 1100 system coupled a UV detector. A Synergy 4 mm Polar-RP 80 A column was used and the mobile phase consisted of 95:5 phosphate buffer/acetonitrile (flow rate: 0.75 mL min⁻¹; λ: 218 nm; T: 35 °C; V_{injection}: 20 μL, retention time: 9 min). NTf₂⁻ anion was identified by liquid chromatography coupled with mass spectrometry (Agilent Technologies 6120 Quadrupole LC/MS). An ACE Excel 3 C18-Amide column at 40 °C as stationary phase. The mobile phase consisted of 10:90 formic acid (0.1 % v)/acetonitrile (flow rate: 0.2 mL min⁻¹; V_{injection}: 1 μL, retention time: 4.7 min). Inorganic nitrogen species were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector (Rubí-Juárez et al., 2016a). The mobile phase consisted of 85:15 v/v 3.6 mM Na₂CO₃/acetone solution for the determination of anions (flowrate: 0.80 mL min⁻¹) and 1.7 mM HNO₃ and 1.7 mM 2,6-pyridinedicarboxylic acid solution for the determination of cations (flowrate: 0.90 mL min⁻¹). The temperature of the oven was 45 and 30 °C for the determination of anions and cations, respectively. The volume injection was 20 μL. TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.

2.3. Electrochemical cell.

Electrolyses were carried out using the experimental setup and methodology described elsewhere (Cotillas et al., 2016). Boron doped diamond (BDD) with a geometric area of 78 cm² (WaterDiam, Switzerland) was used as anode and cathode. However, to allow the

irradiation of 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 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 (0-30V, 0-10A) provided the electric current. Wastewater was stored in a glass tank (0.6 L). BDD anode presents a boron concentration of 500 mg L^{-1} , a thickness of $2.72 \mu\text{m}$, sp^3/sp^2 ratio of 220 and p-Si as support. Experiments were carried out under galvanostatic conditions and discontinuous mode. The current density employed was 30 mA cm^{-2} . This value was selected to guarantee the potential production of hydroxyl radicals during the process (Marselli et al., 2003).

Synthetic wastewater was prepared by dissolving 419 mg L^{-1} (1 mM) of BmimNTf₂ in double deionized water. For the study of the influence of the supporting electrolyte, 3000 mg L^{-1} of sulfuric acid were added to synthetic wastewater.

2.4. Catalytic Wet Peroxide Oxidation experiments

Catalytic Wet Peroxide Oxidation (CWPO) experiments were performed with a Fe/ γ -Al₂O₃ catalyst prepared by incipient wetness impregnation of γ -Al₂O₃ (supplied by Merck) with an aqueous solution of Fe(NO₃)₃·9H₂O (Bautista et al., 2010a; Bautista et al., 2010b). The Fe load was adjusted to a nominal 4% (w/w). After impregnation, the catalyst was left at room temperature for 2 h, dried at 60 °C for 18 h and calcined at 300 °C for 4 h.

Oxidation experiments were carried out in batch in 400 mL glass batch reactor with temperature control and a magnetic stirring velocity of 500 rpm. The catalysts were used in powdered form ($d_p < 100 \text{ nm}$) and at 1 g L^{-1} . The operating conditions were: $[\text{IL}]_0 = 419 \text{ mg L}^{-1}$ (correspond to a concentration of 1 mM), $\text{pH} = 3$, $T = 80^\circ\text{C}$ and H_2O_2 starting concentration corresponding to the theoretical stoichiometric dose to achieve the complete mineralization (1377 mg L^{-1}).

Results and Discussion

Figure 1 compares the time-course of normalized TOC after the application of electrolysis with diamond anodes for 8 h to 1.0 L of a solution containing 419 mg L^{-1} of the ionic liquid BmimNTf₂. Data of the raw electrolysis are marked with a continuous line. The other series show results of improved electrolysis technologies attained by the combination of this technique with UV light or US irradiation or by adding H_2SO_4 to the solution, a precursor for the formation of peroxosulfate. The trends of these results are not marked with lines in order to avoid a messy plot. These three technologies are known to yield synergistic effects according to the literature (Martinez-Huitle et al., 2015), and hence to improve the performance of the process as compared to the raw electrolytic process. In addition, for comparison purposes, despite the very different type of technology, results obtained during the CWPO of the same synthetic wastewater are also plotted and marked with a discontinuous line (mass ratio oxidant / pollutant 3.3:1; 80°C , 8 h). This technology allows removing organic pollutants by hydroxyl radical-mediated oxidation (Mena et al., 2017) while electrolysis with diamond anodes not only favors the production of these species ($\cdot\text{OH}$), but also other oxidants such as ozone or hydrogen peroxide. Therefore, a comparison of both technologies can serve to learn on the real contribution of hydroxyl radicals in the removal of BmimNTf₂.

Figure 1. Mineralization of BmimNTf₂ with (■) Electrolysis; (+) CWPO; (▲) Sonoelectrolysis; (◆) Photoelectrolysis; (●) Electrolysis with addition of H₂SO₄.

As it can be observed, the complete mineralization of the synthetic wastes is not attained by any of the technologies tested. Nonetheless, the trends observed suggest that it would be possible to achieve a complete TOC removal by increasing the operation time during the electrochemical treatments. In addition, great differences can be found among the different electrolytic treatments, indicating the great significance of mediated oxidation processes promoted in each of them. At this point, the most efficient result is obtained with the addition of sulfates to the synthetic waste and this clearly points out the significant role of persulfate and sulfate radicals formed by its activation in the electrolysis with diamond anodes (Eqs. (1)-(6)) (Almazán-Sánchez et al., 2017; Cotillas et al., 2018).

This better performance is especially relevant at very low TOC concentrations, where it clearly overcomes the results obtained by sonoelectrolysis, which behaves as the most efficient technology for higher TOC concentrations. This behavior is directly related to the nature of the organics present in wastewater (Cañizares et al., 2007). In this context, heterocyclic compounds are the predominant species at the beginning of the experiment which are easily attacked by electrogenerated hydroxyl radicals, promoting the formation of aliphatics. However, those compounds are known not to be largely affected by these radicals and, hence, sonoelectrolysis is more efficient at higher TOC concentrations (high concentration of heterocyclic compounds) because of the generation of large amounts of hydroxyl radicals during this process. On the other hand, the presence of persulfate in wastewater (from the oxidation of sulfate) contributes to the potential degradation of aliphatic compounds which are formed at higher operation times (low TOC concentration). Therefore, electrolysis in sulfate-containing medium shows the highest efficiency at the end of the experiment. Performance of photoelectrolysis is worse than those exhibited by these other two combined technologies, although the mineralization attained is faster and more important than the observed with the raw electrolysis. Finally, in comparing electrolysis and CWPO, it can be clearly seen that the electrolytic technology lead to higher mineralization within the same experimental period, although this comparison is not relevant because of great difference between the technologies and the operation conditions.

Hence, BmimNTf₂ is a complex pollutant and the application of the different technologies reached very different mineralization and efficiencies, clearly indicating that the oxidants produced in each of them affects the organic in different ways. For this reason, it is important to compare the evolution of the different species involved. Figure 2a shows the TOC time-course associated to Bmim⁺ and NTf₂⁻ concentration. As it can be seen, Bmim⁺ concentration decreases for all the technologies tested and there are great differences in the rates of the processes, which, as pointed out before, indicates the occurrence of different oxidation mechanisms.

Figure 2. Time-course of Bmim⁺ (symbols) and NTf₂⁻ (discontinuous line) (a) and intermediates (oxalic and formic acids) (b) according to C mass balance measured during the (■) Electrolysis; (+) CWPO; (▲) Sonoelectrolysis; (◆) Photoelectrolysis; (●) Electrolysis with addition of H₂SO₄ of synthetic wastewater polluted with 120 mg L⁻¹ of BmimNTf₂.

In comparing the removal of Bmim, results are not surprising. As expected, the CWPO is the fastest process for the removal of the raw ionic liquid. In this case, only the oxidation by hydroxyl radicals is expected, which is known to be very efficient for molecular structures like the heterocycle Bmim⁺ (Cañizares et al., 2007). As the CWPO was run in discontinuous mode, by mixing the total concentration of hydrogen peroxide and

wastewater at the beginning, the rate is expected to be higher than in the electrolytic processes, where current is progressively applied during the 8-hour tests. This means that the production of large amounts of hydroxyl radicals takes place at the beginning of the experiment during CWPO whereas electrolysis favors the generation of these radicals along the treatment. Hence, CWPO leads to higher efficiencies on Bmim⁺ removal. Anyhow, there are outstanding differences among the four electrolytic technologies tested, which are particularly relevant in the case of the chemically-enhanced electrolysis and in the sonoelectrolysis. In the first case, the role of the peroxosulfate and radicals sulfate can help to explain the better performance. On the other hand, high-frequency sonoelectrolysis promotes the formation of hydroxyl radicals from the oxidation of water (Thompson and Doraiswamy, 1999) and the higher supply rate of these radicals (the addition of the electrochemically and sonochemically produced) can help to explain the much better performance. In addition, direct electrolysis in sonoelectrochemical processes is also expected to be enhanced because of the increase in the turbulence produced by ultrasounds, which significantly affects to the mass transport of pollutant towards the anode surface (Souza et al., 2013; de Vidales et al., 2015). This is not the case for the photoelectrolysis, for which almost no differences are found in the destruction of the ionic liquid as compared with the bare electrolysis, although UV-light irradiation is also known to promote the formation of hydroxyl radicals.

However, the most interesting result is the refractory behavior of the NTf₂⁻ anion for all the technologies tested, including CWPO. The concentration of this anion is kept constant during the five oxidation tests carried out. Despite the occurrence of refractory species is not excluded in most of the advanced oxidation technologies, it is the first time that it is reported such refractory behavior with diamond anodes and previous research demonstrated that very different types of molecules ranging from heterocyclic or dyes to

carboxylic acids or alcohols are satisfactorily degraded with this technology (Panizza and Cerisola, 2009). At this point, it is worth to take into account that NTf₂⁻ anion cannot be considered a real organic compound, despite having two carbon atoms per molecule, because of the rather inorganic structure of the molecule. It also points out that hydroxyl radicals, direct electrolysis and radical sulfate/persulfate oxidation are not able to break the C-F ($\Delta H = 513.8 \text{ kJ mol}^{-1}$), C-S ($\Delta H = 713.3 \text{ kJ mol}^{-1}$) or S-N ($\Delta H = 467 \text{ kJ mol}^{-1}$) bonds of the NTf₂⁻ molecule. This is a very relevant mechanistic information because to the authors' knowledge it has not been reported before and it is clearly observed in this work (Cañizares et al., 2007; Martinez-Huitle and Andrade, 2011).

Figure 2b shows the concentration of total intermediates according to the TOC mass balance calculated taking into account the theoretical TOC values from Bmim⁺ and NTf₂⁻ and the measured TOC ($\text{TOC}_{\text{intermediates}} = \text{TOC}_{\text{measured}} - \text{TOC}_{\text{Bmim}^+} - \text{TOC}_{\text{NTf}_2^-}$). From the HPLC analysis, two peaks were observed corresponding to oxalic and formic acids. However, it was considered to be most suitable for this work the quantification of intermediate by TOC mass balance. As expected, CWPO is less efficient than the electrolytic technologies in the oxidation of already oxidized intermediate molecules. Thus, it has been reported (Cañizares et al., 2008) that carboxylic acids are oxidized much faster by electrolysis with diamond than by Fenton oxidation or ozonation. This was explained in terms of the contribution of oxidation mechanisms different of those directly associated to the hydroxyl radical, such as the direct electrolysis. In comparing the electrolytic technologies, it has to be pointed out that no great differences in terms of concentration of intermediates are found by comparing bare electrolysis with the sulfate-enhanced electrolysis and the sonoelectrolysis. Just the maximum is obtained at lower times and it can be explained in terms of the more efficient oxidation in these two technologies, which showed higher rate of removal of the Bmim⁺. Opposite, the behavior

of photoelectrolysis becomes a real surprise in terms of efficiency as the concentrations detected is much lower and in fact negligible during most of the oxidation tests. This informs about an almost direct mineralization of the Bmim⁺ cation under those conditions where the production of large amounts of free radicals can take place by the photo-activation of the electrogenerated oxidants. Hence, direct mineralization process is favored versus the formation of intermediates.

A last important observation is related to the nitrogen speciation, which is illustrated in Figure 3.

Figure 3. Time-course of Bmim⁺ (symbols), NTf₂ (discontinuous line) (a) and intermediates (nitrate and ammonium) (b) according to N mass balance measured during the electrolysis (black symbols); sonoelectrolysis (white symbols) and photoelectrolysis (grey symbols). (■) Bmim; (▲) Nitrate; (●) Ammonium.

Bmim⁺ concentration decreases, as can be previously observed for electrolytic technologies tested (Figure 3a). Nitrates and ammonium ions (nitrogen intermediate species) were the final degradation products in the electrolysis of Bmim⁺. The time-course of these nitrogen species is shown in Figure 3b. According to literature, the degradation of the C-N bond lead to the formation of nitrates (Rubí-Juárez et al., 2016a, b), which can be cathodically reduced to ammonium ions, being the direct anodic oxidation of these

latter species not promoted because of the electrostatic repulsion between the anode surface and the cation charge. This repulsion is also expected in the case of the Bmim⁺ cation, although the larger size of this species can help to explain the lower impact detected in the performance of the process. Anyhow, it also helps to explain the lowest efficiency of the raw electrolysis, as compared to the other three electrochemically assisted processes. Finally, it is important to highlight that the oxidation of organics containing nitrogen atoms can lead to the release of oxidized nitrogen species such as NO and NO₂ (Garcia-Segura et al., 2017). In this context, the results obtained in Figure 3 suggest that these species are formed during the process since the mass balance of nitrogen is not closed only with the organic and inorganic compounds analyzed.

Conclusions

From this work, the following conclusions can be drawn:

- The concentration of the anion bis(trifluoromethanesulfonyl)imide is kept constant during the five oxidation tests carried out, being the first time that it is reported a refractory behavior in electrolysis with diamond anodes. Hydroxyl radicals, direct electrolysis and radical sulfate /persulfate oxidation are not able to break the C-F, C-S or S-N bounds of the NTf₂ molecule.
- Cation 1-butyl-3-methylimidazolium can be fully oxidized by electrolysis with diamond electrodes, leading to the complete mineralization and to the formation of ammonium and nitrates ions. Concentrations of intermediates formed depends on the particular technology used being photoelectrolysis the technology which shows the lowest concentration, that is, the almost direct transformation of the Bmim⁺ into the final products

- The efficiency in the treatment of ionic liquid BmimNTf₂ decreases in the sequence sonoelectrolysis, electrolysis enhanced with peroxosulfate promoters, photoelectrolysis and bare electrolysis.

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