



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



Ismael F. Mena^a, Salvador Cotillas^b, Elena Díaz^a, Cristina Sáez^c, Juan J. Rodríguez^a, P. Cañizares^c, Ángel F. Mohedano^a, Manuel A. Rodrigo^{c,*}

^a Sección de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049, Madrid, Spain

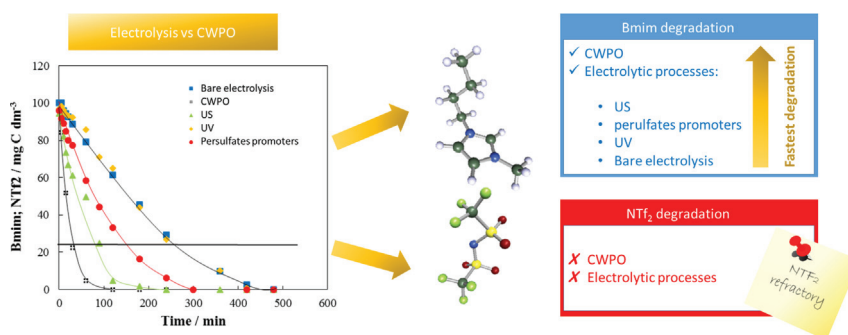
^b Department of Chemical Engineering, School of Industrial Engineering, University of Castilla-La Mancha, Avenida de España S/N, 02071, Albacete, Spain

^c Department of Chemical Engineering, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, Avenida Camilo José Cela 12, 13005, Ciudad Real, Spain

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.

GRAPHICAL ABSTRACT



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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.

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* Corresponding author.

E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

1. 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; Martínez-Huitle et al., 2015).

To attain these conclusions, thousands of products have been tested, ranging from very high-molecular weight dyes (Martínez-Huitle and Brillas, 2009; Brillas and Martínez-Huitle, 2015) to small carboxylic acid molecules (Gandini et al., 2000), from linear aliphatic (Cañizares et al., 2003, 2008) to highly heterocyclic molecular structures (Cañizares et al., 2007a) 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; Martínez-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-Bizuko 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.

2. 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 3C18-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 (Water-Diam, 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), λ = 254 nm, intensity of 930 μW/cm² 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 Elektronika ES030-10 power supply (0–30 V, 0–10 A) 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 μm, sp³/sp² 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

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