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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 BmimCl and HmimCl 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 these compounds by electrolysis with BDD, pointing out the important influence of peroxodisulfate on the electrolyses with diamond of organic wastes.

1. Introduction

Ionic liquids (ILs) are salts that exhibit high thermal stability and low melting point [1]. They can be used as substitutes of conventional organic solvents [2] and they are more environmentally-friendly species. 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 proved 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 wasted 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 of large amounts of hydroxyl radicals by different technologies, which significantly contribute to the degradation of the pollutants present in the effluents [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 high efficiencies [26–30].



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

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[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 for 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 ILs. To do this, three different ILs were selected: they have the same anion (Cl^-) and different cations with an imidazolium group derivative: Bmim⁺ (1-Buthyl-3-methylimidazolium), Hmim⁺ (1-Hexyl-3-methylimidazolium) and Dmim⁺ (1-Decyl-3-methylimidazolium). 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-Buthyl-3-methylimidazolium chloride), HmimCl (1-Hexyl-3-methylimidazolium chloride), DmimCl (1-Decyl-3-methylimidazolium chloride) and sulfuric acid were used as received. Double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩcm 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 cm³ 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 35 °C 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 Na₂CO₃/acetone solution for the determination of anions (flowrate: 0.80 cm³ min⁻¹) and 1.7 mM HNO₃ and 1.7 mM 2,6-pyridinedicarboxylic acid solution for the determination of cations (flowrate: 0.90 cm³ 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.

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 35 °C with a flowrate of 1 cm³ 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 dm³ h⁻¹). Boron doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of 78 cm², boron concentration of 500 mg dm⁻³, a thickness of 2.72 μm, sp³/sp² 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 (0–30 V, 0–10 A). The temperature was maintained at 25 °C using a thermostated 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. The initial conductivity of wastewater without sulfuric acid was within the range 103–137 μS cm⁻¹ whereas values around 8 mS cm⁻¹ were obtained when sulfate ions were added to the solution.

3. Results and discussion

Fig. 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.

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

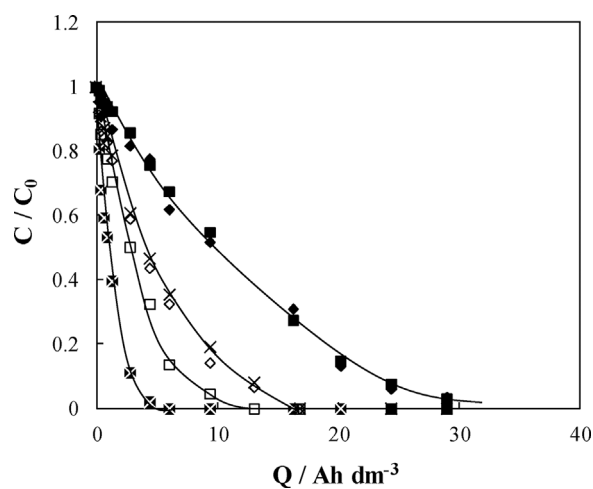


Fig. 1. Removal of ionic liquids with the applied electric charge during the electrolysis of wastewater polluted with 1 mM of ionic liquid. j: 30 mA cm⁻²; (■) BmimCl; (◆) HmimCl; (x) DmimCl. Full symbols: electrolyte without SO₄²⁻; empty symbols: 3000 mg dm⁻³ H₂SO₄.

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