



Ionic liquids breakdown by Fenton oxidation



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ABSTRACT

Fenton oxidation has proved to be an efficient treatment for the degradation of ionic liquids (ILs) of different families *viz.* imidazolium, pyridinium, ammonium and phosphonium, in water. The intensification of the process, defined as the improvement on the efficiency of H₂O₂ consumption, by increasing the temperature is necessary to avoid high reaction times and the need of large excess of H₂O₂. In this work, temperatures within the range of 70–90 °C have been used, which allowed an effective breakdown of the ILs tested (1 g L⁻¹ initial concentration) with the stoichiometric amount of H₂O₂ and a relatively low Fe³⁺ dose (50 mg L⁻¹). Under these conditions conversion of the ILs was achieved in less than 10 min, with TOC reductions higher than 60% upon 4 h reaction time, except for the phosphonium IL. The remaining TOC corresponded mainly to short-chain organic acids. The treatment reduced substantially the ecotoxicity up to final values below 0.01 TU in most cases and a significant improvement of the biodegradability was achieved. Upon Fenton oxidation of the four ILs tested hydroxylated compounds of higher molecular weight than the starting ILs, fragments of ILs partially oxidized and short-chain organic acids were identified as reaction by-products. Reaction pathways are proposed.

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1. Introduction

Room temperature ionic liquids (ILs) are a novel, broad class of semi-organic salts or salt mixtures that are liquid below 100 °C. They are gaining increasing attention due to their unique properties, such as extremely low vapor pressure, high thermal and chemical stabilities, non-flammability and high solvent capacity [1,2]. Thus, these materials are often branded as “environmentally friendly” or “green solvents”, and have been suggested as ideal replacements for volatile organic solvents [3–5].

A huge number of different ILs can be synthesized by the combination of different anion and cation cores, or by modifying their alkyl chain length or introducing oxygenated groups. Thus, ILs have been termed “designer solvents” since polarity, solvent miscibility and hydrophobicity can be tuned by a suitable combination of anion and cation [6]. In this sense, they have been found suitable for catalysis, biocatalytic processing, extraction, electrochemistry or separation [1,7], and the number of their commercial applications as well as patents on IL technology has been rising exponentially for the last years [8]. Questions regarding the potential impact of ILs on the environment have been raised recently.

Although the low vapor pressure of ILs may reduce the costs and environmental risks of air pollution, release of these compounds into aquatic environment may lead to water pollution because of their high solubility in aqueous phase. In fact, industrial application of ILs usually involves water streams in the process and the synthesis routes of ILs frequently include aqueous media. Thus it can be expected the presence of varying amounts of ionic liquids in effluents related with their manufacture and use. This represents an important concern due to their high stability and toxicity [3–5,9,10]. Romero et al. [11] pointed out that the low vapor pressure of ILs is not by itself sufficient to consider them “green solvents” since ILs are poorly biodegradable and can be more toxic than conventional solvents.

The relatively high solubility of ILs in water has important environmental consequences and should be taken into account for the design of processes involving ILs. In this sense, it is essential to improve those processes, minimizing the discharge of ILs to the aquatic media. On the other hand, downstream separation or treatment steps must be required to remove the ILs from the wastewater streams at the end of these processes. Although adsorption on activated carbon has proved to be an effective method for the uptake of ILs [12], current studies have also evidenced that steric effects restrict the adsorption of those with large molecular volumes [13]. Moreover, the recovery of ILs from the exhausted adsorbent is essential and implies the use of conventional volatile

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solvents [13]. On the other hand, destructive methods allow the degradation of ILs to less harmful intermediates and partial mineralization. The application of biological treatments is seriously limited due to the high toxicity and low biodegradability of ILs [11,14–17]. Wells and Coombe [16] studied the ecotoxicity and the microbial degradation of a wide number of IL families (ammonium, imidazolium, phosphonium and pyridinium), concluding that ILs display high ecotoxicity and are strongly resistant to biodegradation. These authors claimed that those ILs are far from displaying the green image that is often accepted in the literature. Due to the high stability and resistance to biodegradation, chemical treatments would represent the best alternative for the removal of ILs. In this context, Advanced Oxidation Processes (AOPs), based on the action of hydroxyl radicals at near ambient temperature and pressure, can be regarded as a potential solution. Among them, Fenton oxidation using H_2O_2 and iron salts ($\text{Fe}^{2+}/\text{Fe}^{3+}$) is recognized as one of the most cost-effective treatments [18]. It has been successfully applied in the treatment of a wide range of organic pollutants (phenols, chlorophenols, nitrophenols, formaldehydes, toluenes, chlorobenzenes, amines or halomethanes [19]) as well as real industrial wastewaters [19,20]. However, so far only few works have been reported dealing with the degradation of ILs by Fenton oxidation [21–23]. Those studies have been focused only on the destruction of imidazolium ILs at ambient conditions. Complete conversion of the IL ([emim][Cl]) was achieved within 90 min reaction time using large excess of H_2O_2 ($[\text{IL}]_0 = 1 \text{ mM}$; $[\text{Fe}^{3+}]_0 = 1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 400 \text{ mM}$, which represents 24 times the theoretical stoichiometric amount for the complete oxidation of IL) [21]. Those authors did not provide information about the evolution of total organic carbon (TOC) or ecotoxicity of the effluents, which is crucial in order to evaluate the potential application of Fenton oxidation.

The aim of this work is to analyze the capability of the Fenton process for the degradation of different IL families *viz.* imidazolium, pyridinium, ammonium and phosphonium. Following this objective, the effect of temperature and catalyst load has been investigated. The identification of the reaction by-products has been accomplished for the sake of elucidating the oxidation pathways. Besides, the biodegradability and ecotoxicity of the ILs and the resulting Fenton effluents have been evaluated.

2. Materials and methods

2.1. Chemicals

All the chemicals were analytical grade reagents and were used without further purification. The four ILs tested, 1-ethyl-3-methylimidazolium chloride ([emim][Cl]), 1-butyl-4-methylpyridinium chloride ([bmpyr][Cl]), tetrabutylammonium chloride ([tbN][Cl]) and tetrabutylphosphonium chloride ([tbP][Cl]), were purchased from Iolitec, Fluka and Sigma-Aldrich. Hydrogen peroxide solution (30% w/w) in stable form, nitric acid (65%) and formic acid (95%) were purchased from Sigma-Aldrich. Iron (III) nitrate nonahydrate (98%), sodium chloride (99.5%) and sodium hydroxide (>98%) were purchased from Panreac. Titanium oxysulfate (>99%) was purchased from Fluka. Acetonitrile (99.8%) was purchased from Scharlau.

2.2. Fenton experiments

The oxidation runs were carried out at atmospheric pressure in a 500 mL glass batch reactor equipped with a magnetic stirrer (700 rpm) and temperature control. The initial pH value was adjusted to 3 with nitric acid. The starting concentration of IL was always 1 g L^{-1} and the theoretical stoichiometric amount of H_2O_2 for complete mineralization was used in all the experiments

(3.9, 5.0, 5.5 and 6.0 g L^{-1} for [emim][Cl], [bmpyr][Cl], [tbN][Cl] and [tbP][Cl], respectively). The Fe^{3+} dose was varied within the range of 10 to 125 mg L^{-1} and temperatures between 50 and 90°C were tested. Temperature above the ambient is used in order to increase the efficiency of hydrogen peroxide consumption and reduce the reaction time [20]. As recently demonstrated, increasing the temperature does not imply an extra cost since heat can be recovered from the exit stream and it has also to be considered the exothermic character of the oxidation process [24].

Blank experiments in the absence of catalyst were carried out at all the temperatures tested and negligible conversions of all ILs (<5%) were always observed. All the experiments were performed by duplicate being the standard deviation lower than 5% in all cases.

2.3. Analytical methods

The progress of the reactions was followed by periodically withdrawing, cooling and immediately analyzing liquid samples from the reactor. Ionic liquids were quantified by liquid chromatography–mass spectrometry (LC/MS SQ Agilent 6120) equipped with a quadrupole detector using a Synergy 4 mm Polar-RP 80 Å column (15 cm length, 4.6 mm diameter) (Phenomenex) as the stationary phase. The analyses were carried out at ambient temperature and a flow rate of 0.5 mL min^{-1} . The elution profiles were monitored at 230 nm. The mobile phase was a mixture of water (0.1% formic acid) and acetonitrile in gradient elution. The MS analysis was performed with electrospray ionization (ESI) interface in the positive mode with a capillary voltage of 2000 V. The nebulizer gas (N_2) pressure was set to 60 psi and the drying gas flow was 5 L min^{-1} . The drying gas temperature was set at 250°C . All MS data acquisition and processing were carried out using the software package LC/MSD ChemStation. External mass calibration for the positive ESI mode was conducted prior to analysis in the mass range of m/z 100–900. The quantification of the four ionic liquids studied in this work was carried out using external standard calibration. Five levels of calibration were used: 1, 2.5, 5, 10 and 20 mg L^{-1} (r^2 ([emim][Cl]) = 0.987; r^2 ([bmpyr][Cl]) = 0.994; r^2 ([tbN][Cl]) = 0.991; r^2 ([tbP][Cl]) = 0.989, being r^2 linear correlation coefficient). Three replicates of each calibration point were carried out being the standard deviation less than 5% in all cases. This method achieves detection limits at or below 0.5 mg L^{-1} , whereas the quantification ones were 1.0 mg L^{-1} . Those analyses were also used for the tentative identification of the reaction by-products. Total organic carbon (TOC) was measured with a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H_2O_2 concentration was determined by the titanium sulfate method [25] using an UV 1603 Shimadzu UV/vis spectrophotometer. Chemical oxygen demand (COD) measurements were performed by the Moore method [26]. Short-chain organic acids were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a $3.2 \text{ mM Na}_2\text{CO}_3$ aqueous solution as the mobile phase.

2.4. Ecotoxicity tests

The ecotoxicity of the IL solutions and the samples from reaction was determined by the Microtox toxicity test (ISO 11348-3, 1998). The bioluminescence was measured in a M500 Microtox Analyzer (Azur Environmental). The toxicity tests were performed using a range of concentrations (from 0 to 100%) of each IL solution or Fenton sample. The light output of the luminescent bacteria was measured and compared with that of a blank negative control sample. We used as positive control a solution of phenol (100 mg L^{-1} , whose EC_{50} value is 16 mg L^{-1}). The test was conducted at 15°C ,

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