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ADVANCED OXIDATION PROCESSES FOR WATER/WASTEWATER TREATMENT

Removal of imidazolium- and pyridinium-based ionic liquids by Fenton oxidation

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Abstract

The oxidation of imidazolium (1-hexyl-3-methylimidazolium chloride, HmimCl) and pyridinium (1-butyl-4-methylpyridinium chloride, BmpyrCl) ionic liquids (ILs) by Fenton's reagent has been studied. Complete conversion was achieved for both ILs using the stoichiometric H_2O_2 dose at 70 °C, reaching final TOC conversion values around 45 and 55% for HmimCl and BmpyrCl, respectively. The decrease in hydrogen peroxide dose to substoichiometric concentrations (20–80% stoichiometric dose) caused a decrease in TOC conversion and COD removal and the appearance of hydroxylated oxidation by-products. Working at these substoichiometric H_2O_2 doses allowed the depiction of a possible degradation pathway for the oxidation of both imidazolium and pyridinium ILs. The first step of the oxidation process consisted in the hydroxylation of the ionic liquid by the attack of the ·OH radicals, followed by the ring-opening and the formation of short-chain organic acids, which could be partially oxidized up to CO_2 and H_2O. At H_2O_2 doses near stoichiometric values (80%), the resulting effluents showed non-ecotoxic behaviour and more biodegradable character (BOD_5/COD ratio around 0.38 and 0.58 for HmimCl and BmpyrCl, respectively) due to the formation of short-chain organic acids.

Keywords Ionic liquids · Imidazolium · Pyridinium · Fenton oxidation · Degradation pathway · Ecotoxicity

Introduction

Ionic liquids (ILs) are a novel class of room temperature salts, formed by an organic cation and an organic or inorganic anion, being able to combine both components giving rise to "designer solvents" (Plechkova and Seddon 2007). In the last decades, ionic liquids (ILs) have acquired special interest due to their low vapor pressure, non-flammability, thermal stability, and high solubility in water (Yue et al. 2011). The increase of the number of publications and patents related with ILs and changes in their solubility, polarity, and hydrophobicity is in agreement with the importance of these compounds in industrial treatments and applications: catalysis, separation processes, electrochemistry, or chemical synthesis (Kubisa 2004; Vekariya 2017).

ILs are considered as "environmental friendly" compounds which have been proposed as optimal alternative for volatile organic solvents (Ventura et al. 2013). However, their release into aquatic environment could lead to water pollution due to the high solubility of these compounds. The moderate toxicity and poor biodegradability (Wells and Coombe 2006; Docherty et al. 2007) leaves the environmental image of ILs away from "green solvents". In this sense, it is necessary to develop powerful oxidation processes for the removal of these compounds and to avoid their possible discharge into the aquatic media.

Advanced oxidation processes (AOPs), based on the hydroxyl radicals action over the target compound, are considered a promising alternative for the degradation of a large number of pollutants. However, less is known about the application of AOPs for the oxidation of ionic liquids in liquid phase. Fenton oxidation is considered one of the most appropriate treatments in terms of cost-effectiveness, based on the catalytic decomposition of H_2O_2 by means of iron salts to produce hydroxyl radicals. It has been applied for the oxidation of a wide range of pollutants and real wastewaters

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(Bautista et al. 2008; Pliego et al. 2012). However, only few works dealt with the removal of ILs by Fenton oxidation (Siedlecka et al. 2008; Czerwicka et al. 2009; Siedlecka et al. 2012; Munoz et al. 2015a, b). Siedlecka et al. (2008) studied the effect of pH and catalyst concentration, mainly focused in the removal of imidazolium ILs at ambient conditions, while Munoz et al. (2015a, b) established the optimal conditions to achieve high mineralization degrees of imidazolium and pyridinium ILs. Photocatalytic and electrochemical processes have been also studied for the degradation of ILs (Stepnowski and Zaleska 2005). Siedlecka et al. (2013) evaluated the mechanism of imidazolium degradation with different types of electrodes. Several works revealed that anodic oxidation (AO) was an efficient process for the degradation of ILs, concluding that the mineralization rate decreased as the number of carbons in the side chain increased (Siedlecka et al. 2012). AO, electro-Fenton, and photoelectro-Fenton processes were compared by Garcia-Segura et al. (2016) for the removal of pyridinium and imidazolium ILs. Among the AOP's studies, UVA irradiation in photoelectro-Fenton was the most powerful treatment with total mineralization around 95% for both ILs.

The aim of this work is to study the feasibility of Fenton process for the removal in aqueous phase of two ionic liquids commonly used: 1-hexyl-3-methylimidazolium chloride (HmimCl) and 1-butyl-4-methylpyridinium chloride (BmpyrCl). The oxidation kinetic will be analyzed and the possible pathways will be established. Finally, the ecotoxicity and biodegradability of the effluents obtained upon Fenton oxidation will be evaluated for both target compounds.

Materials and methods

Chemicals

1-hexyl-3-methylimidazolium chloride, HmimCl (98% of purity) and 1-butyl-4-methylpyridinium chloride, BmpyrCl (98% of purity) were purchased from Sigma-Aldrich®. Hydrogen peroxide (33 wt.%), hydrochloric acid (37 wt.%), iron (III) nitrate nonahydrate (98 wt.%), and sodium hydroxide (98 wt.%) were provided by Panreac.

Fenton oxidation

Fenton oxidation experiments were carried out in a 1-L glass reactor with controlled temperature (70 °C) at 200 rpm and pH 3. Each IL, with a starting concentration of 1 g L^{-1}, was placed in the reactor with different doses of H_2O_2, ranged from the stoichiometric concentration (calculated as the theoretical concentration necessary for the complete mineralization of ILs, 4.9 g L^{-1} for HmimCl and 5.1 g L^{-1} for BmpyrCl) to a 20% of that value, maintaining a Fe^{3+}/H_2O_2 ratio of 1/10 (M/M). Samples were collected during the reaction course until the complete depletion of H_2O_2, neutralized with NaOH (6 N) and filtered (Albert FV-C) for their subsequent analysis.

Total organic carbon (TOC) and total nitrogen (TN) were measured using a TOC-Vcsh apparatus from Shimadzu. COD was analyzed following the APHA procedure 5220A (APHA, 1992). BOD_5 was determined in a Velps Scientifica equipment, following the standard procedure 5210 (APHA, 1992), using 500 mL of sample volume. Hydrogen peroxide concentration was determined by colorimetric titration through the method of sulfate titanium (Eisenberg 1943), using a Shimazdu UV-1603 spectophotometer.

The ecotoxicity of the imidazolium- and pyridinium-based IL solutions and effluents upon Fenton oxidation was determined by Microtox® toxicity test (ISO 11348-3 1998). The results were expressed as toxicity units (TU).

HmimCl and BmpyrCl were quantified by HPLC (Varian Prostar 325) with a UV-vis detector at 218 nm. A Synergy 4 mm Polar-RP 80 A column (15 cm length, 4.6 mm diameter, Phenomenex) was used as the stationary phase and phosphate buffer and acetonitrile at different ratios (5 and 40% for $Hmim^+$ and $Bmpyr^+$, respectively) were used as mobile phase with a constant flow of 0.75 mL min^{-1}. Ion chromatography with chemical suppression (Metromh 790 IC) and a conductivity detector was employed to quantify short-chain organic acids, nitrate and nitrite. Metrosep A suppp 2-250 column (25 cm length, 4 m i.d.) was used as the stationary phase and an aqueous solution of 1 mM $NaHCO_3$ and 3.2 mM Na_2CO_3 as mobile phase, with a constant flow of 0.7 mL min^{-1}. Other reaction by-products were detected by HPLC/MS (Agilent, Quadrupole LC/MS). An ACE Excel 3 C-18-amide column (15 cm length, 4.6 mm diameter) was used as the stationary phase and an aqueous solution of formic acid (0.1%) and ACN gradient with a constant flow of 0.5 mL min^{-1} as a mobile phase. Mass spectrometry was performed by electrospray ionization with a drying gas flow of 9 L min^{-1}.

Results and discussion

Figure 1 shows the time-course of normalized concentration of $Hmim^+$ and $Bmpyr^+$ cations, TOC/TOC_0 and conversion of H_2O_2 upon Fenton oxidation. Both cations were completely removed in very short reaction times, being the removal rate higher in case of $Hmim^+$. The elimination of the target compounds was higher at early stages of Fenton oxidation, showing a less pronounced variation after the first hour reaching final TOC conversions of 54 and 44% for HmimCl and BmpyrCl, respectively. Siedlecka et al. (2008) reported complete degradation of imidazolium ILs at 25 °C, although the

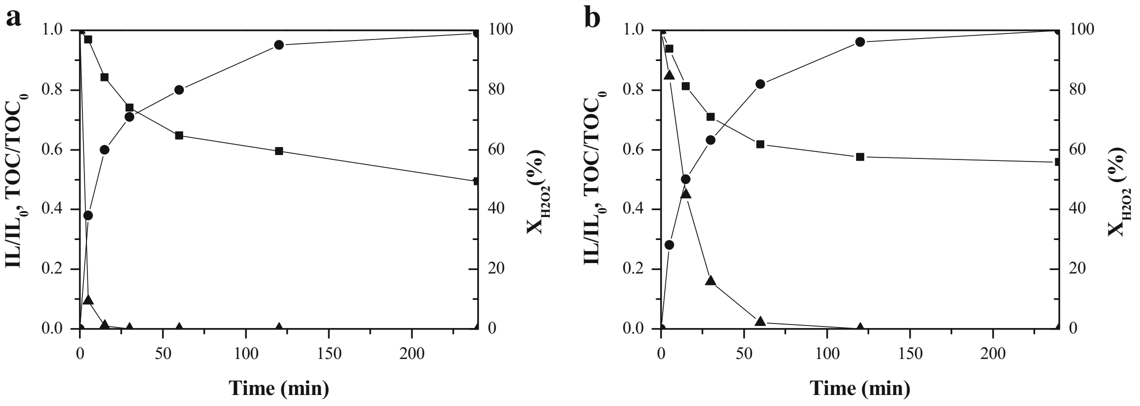

Fig. 1 Time-course of IL/IL_0 (filled triangle), TOC/TOC_0 (filled square), and H_2O_2 conversion (filled square) upon Fenton oxidation (70 °C) at stoichiometric dose of H_2O_2 for HmimCl (**a**) and BmpyrCl (**b**)

time required to reach total conversion of the pollutant was increased to 90 min due to the lower temperature used.

The apparent kinetic order and rate constants of IL and TOC removal and H_2O_2 consumption for both ILs are shown in Table 1. IL removal and H_2O_2 consumption could be described by a first order while TOC reduction was fit as a second-order kinetics. As can be seen, the kinetic constant values for Fenton oxidation of HmimCl were higher than for BmpyrCl, with a more pronounced increase in the case of IL depletion, corroborating the results showed in Fig. 1. The H_2O_2 consumption rate is quite similar for both ILs. Siedlecka et al. (2008) also described as a pseudo-first-order kinetics the removal of 1-butyl-3-methylimidazolium chloride (BmimCl).

Figure 2 shows $Hmim^+$ and $Bmpyr^+$, COD and TOC conversion after 4h reaction time at substoichiometric H_2O_2 doses. Only a complete conversion of both ILs was achieved in reactions with H_2O_2 doses higher than 60% of stoichiometric value. $Hmim^+$ showed greater resistance to be removed at low H_2O_2 doses, reaching values of 50% removal for 20% H_2O_2 dose. The relationship between the decrease of COD and TOC conversion with H_2O_2 dose is nearly lineal. In case of pyridinium IL, TOC conversion and COD degradation obtained at 20% of H_2O_2 dose were negligible, indicating that the by-products generated during the oxidation showed a strong refractory character to mineralization. Final COD and TOC values, far from the total conversion, implied a refractory character of the cation ring to the complete mineralization (Matzke et al. 2010). Although several authors dealt with Fenton oxidation for the removal of ILs, only Munoz et al. (2015a) provided information about the evolution of TOC at stoichiometric dose, reaching final conversion values next to those obtained in Fig. 1.

The identification of the oxidation by-products upon Fenton oxidation were carried out by HPLC/MS, based on the m/z ratio. Among the large number of compounds detected, the results showed hydroxylated compounds with molecular weight higher than the starting compounds at low H_2O_2 doses for both ILs. Figure 3 depicts a possible reaction pathway for HmimCl and BmpyrCl Fenton oxidation. Intermediates with m/z of 182 for imidazolium IL and m/z of 166 and 242 for pyridinium IL were identified. As the H_2O_2 dose increased, compounds with different breaks in the alkyl-chain were also observed. In the last oxidation stages, the breakdown of the imidazolium and pyridinium ring took place, given rise to the formation of short-chain organic acids, which could be oxidized to CO_2 and H_2O, final oxidation products along with oxidized nitrogen species (Garcia-Segura et al. 2016) such as NO and NO_2. Those short-chain organic acids, final oxidation products, were only detected at high H_2O_2 doses. An additional assay using a 10% of the stoichiometric H_2O_2 dose, performed with the aim to detect the oxidation by-products formed at early oxidation stages, allowed the identification of further compounds ($m/z = 197$ and 154 for HmimCl and $m/z = 165$ for BmpyrCl). Munoz et al. (2015a) only detected the $m/z = 166$ and $m/z = 100$ compounds for BmpyrCl oxidation. Siedlecka et al. (2013) observed the intermediates with $m/z = 82$, $m/z = 185$, and $m/z = 154$ for HmimCl oxidation by an electrocatalytic process, while Pieczyska et al. (2015) detected further compounds with $m/z = 155$ and $m/z = 182$ for HmimCl and $m/z = 166$ and $m/z = 165$ for BmpyrCl, using the same oxidation process. Garcia-Segura et al. (2016) found the m/z = 97 compound using photoelectro-Fenton and anoxic oxidation processes.

Table 1 Kinetic constants for IL removal, H_2O_2 consumption, and TOC reduction rates upon Fenton oxidation at stoichiometric dose of H_2O_2

	HmimCl			BmpyrCl		
	Order	k (min^{-1})	R^2	Order	k (min^{-1})	R^2
IL	1	0.2933	0.963	1	0.0651	0.998
H_2O_2	1	0.0271	0.984	1	0.0256	0.992
	Order	k (M^{-1} min^{-1})	R^2	Order	k (M^{-1} min^{-1})	R^2
TOC	2	$8.4{\cdot}10^{-5}$	0.969	2	$6.0{\cdot}10^{-5}$	0.966

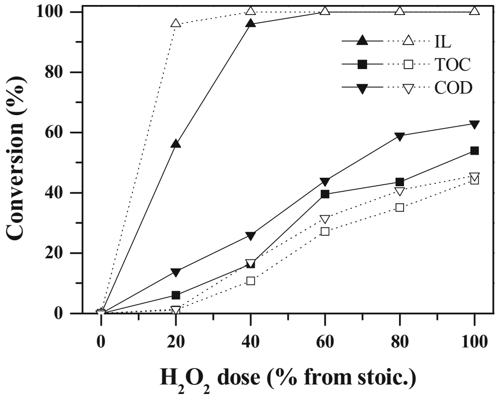

Fig. 2 Conversion of IL, COD, and TOC (%) upon Fenton oxidation (70 °C) at different substoichiometric H_2O_2 doses for HmimCl (filled symbols) and BmpyrCl (empty symbols)

Figure 4 depicts the short-chain organic acids (acetic, formic, oxalic, malonic, and fumaric acids) found in the effluents upon Fenton oxidation of both ILs using H_2O_2 from 20% to stoichiometric doses. For HmimCl oxidation, formic acid concentration showed a maximum at 20% of reactant dose decreasing at increasing H_2O_2 dose, while acetic, oxalic, malonic and fumaric acids exhibited constant concentration values for doses higher than 40% of the stoichiometric, which is in agreement with the refractory character of those acids (Barrault et al. 2005). On the other hand, for BmpyrCl, the concentration of acetic acid increased at increasing H_2O_2 percentage, reaching the highest value (230 mg L^{-1}) at stoichiometric H_2O_2 dose. Oxalic and malonic acids also increased at H_2O_2 doses higher than 60% of the stoichiometric. In this case, formic acid described a plateau instead of the decreasing trend found for HmimCl oxidation.

The carbon and nitrogen balance closure for HmimCl and BmpyrCl was shown in Fig. 5. Identified TOC and TN corresponded to short-chain organic acids and inorganic nitrogen species, respectively. Comparing these results with measured TOC and TN for both ILs, it could be shown a decrease in the measured TOC up to 50% for the stoichiometric dose in HmimCl effluents, while a less value was achieved for pyridinium effluents (40%). Measured TN has been reduced over 5–10% at stoichiometric H_2O_2 dose, compared with TN of both starting compounds. The balance closure for carbon and nitrogen increased with the H_2O_2 dose, with the exception of the effluent from HmimCl oxidation using 20% of H_2O_2 dose. In this assay, the low removal of $Hmim^+$ cation caused an increase in the identified TOC fraction even though the TOC corresponding to short-chain organic acids is minimal compared to effluents with higher doses of reactant. The TOC identified as short-chain organic acids mostly corresponds to acetic acid for both ILs, as can be seen in Fig. 4.

The TN quantified as nitrate and nitrite corresponded with the 20–30% of the measured TN, being the nitrate concentration of 20 mg L^{-1} at stoichiometric H_2O_2 dose, while the nitrite concentration was 8 mg L^{-1} for that effluent. On the other hand, for effluents of Fenton oxidation with lower H_2O_2 doses, the concentration of nitrite and nitrate became more similar (4 mg L^{-1} for NO_2^- and 4.5 mg L^{-1} for NO_3^-), indicating an increase in the oxidation rate was related with the high conversion of nitrite in nitrate. For all the H_2O_2 doses, the nitrogen mass balance was incomplete, due to the possible formation of nitrogen-containing by-products as chloramines (De Vidales et al. 2016) and NO_x species in gas phase (Garcia-Segura et al. 2017).

Knowing the structure of the compounds present in the effluents, the ratio C:N could be established, comparing between the starting compound and the effluents obtained after oxidation process. Likewise, the C:N ratios for the starting ILs were higher than for the effluents at stoichiometric H_2O_2 dose, which indicated the greater degradation of alkyl-chains (more accused in $Hmim^+$ oxidation due to the length of the side chain) while the imidazolium and pyridinium rings was more persistent to degradation (Deng et al. 2015).

Ecotoxicity values of the different effluents from Fenton oxidation using Microtox® assay are shown in Table 2. As the reactant dose increased, the TU (toxicity units) decreased, reaching non-ecotoxic values at effluents of stoichiometric H_2O_2 dose for both ILs. However, the effluents treated with lower reactant doses presented higher ecotoxicity than the starting IL, indicating that the hydroxylated compounds were more harmful to aquatic environments than the target compounds. This effect was more pronounced in the case of pyridinium ionic liquid, where effluents of Fenton oxidation with H_2O_2 doses higher than 80% were the only ones that could be considered less toxic than BmpyrCl. The ecotoxicity values obtained for the starting ILs, 1.5 and 0.9 mM for HmimCl and BmpyrCl, respectively, were in a good agreement with those found in the literature (Docherty and Kulpa 2005; Munoz et al. 2015b). Table 2 also shows the biodegradability index (BOD_5/COD ratio) and TOC/COD ratio for the effluents from Fenton oxidation of ILs. The increase of the concentration of H_2O_2 gave rise to more biodegradable effluents than the starting compound for both ILs. Those results were related with an increase in BOD_5 values and the scarce decay in COD values, increasing the biodegradability index due to the formation of organic by-products at low H_2O_2 doses. However, from H_2O_2 doses of 60% for $Hmim^+$ and 80% for $Bmpyr^+$ cations, BOD_5/COD reached a constant value which implied a reduction of BOD_5 proportional to COD one, because of the elimination of by-products aforementioned and the subsequent formation of short-chain organic acids with lower biological and chemical oxygen demand. TOC/COD ratio for effluents from HmimCl oxidation increased with the H_2O_2 dose, whereas the ratio was maintained constant for all the H_2O_2 concentrations tested for BmpyrCl effluents. The decay in COD values was more pronounced than TOC for imidazolium IL.

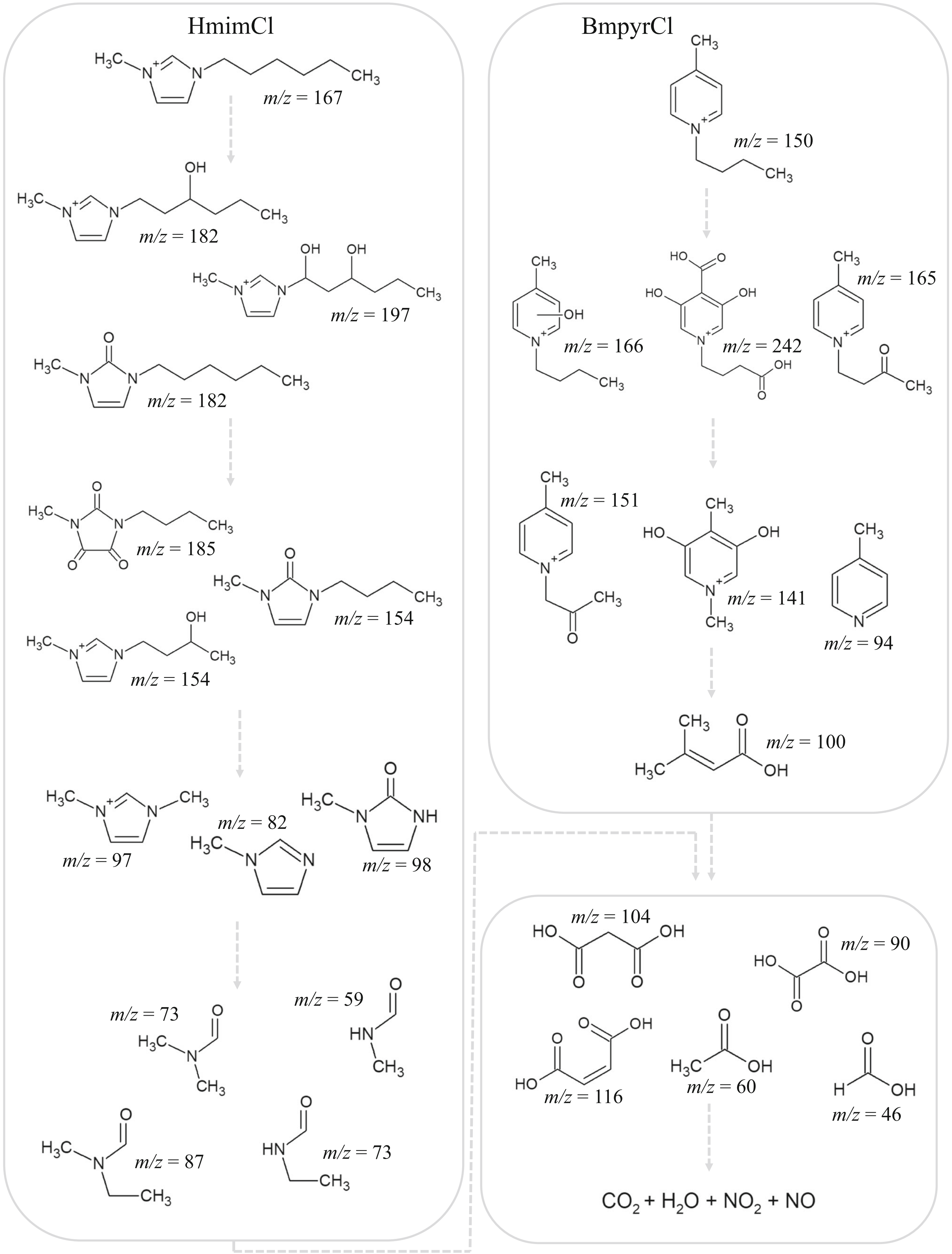

Fig. 3 Proposed pathways for HmimCl and BmpyrCl oxidation by Fenton s reagent

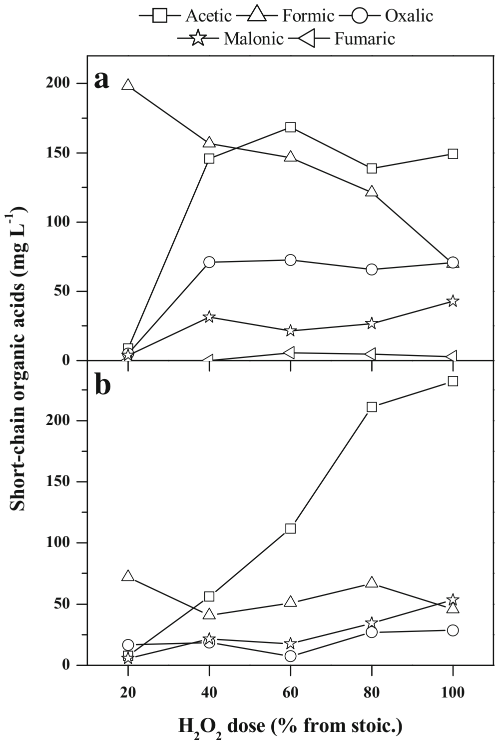

Fig. 4 Short-chain organic acids in effluents from Fenton oxidation at different substoichiometric doses of H_2O_2 of HmimCl (a) and BmpyrCl (b)

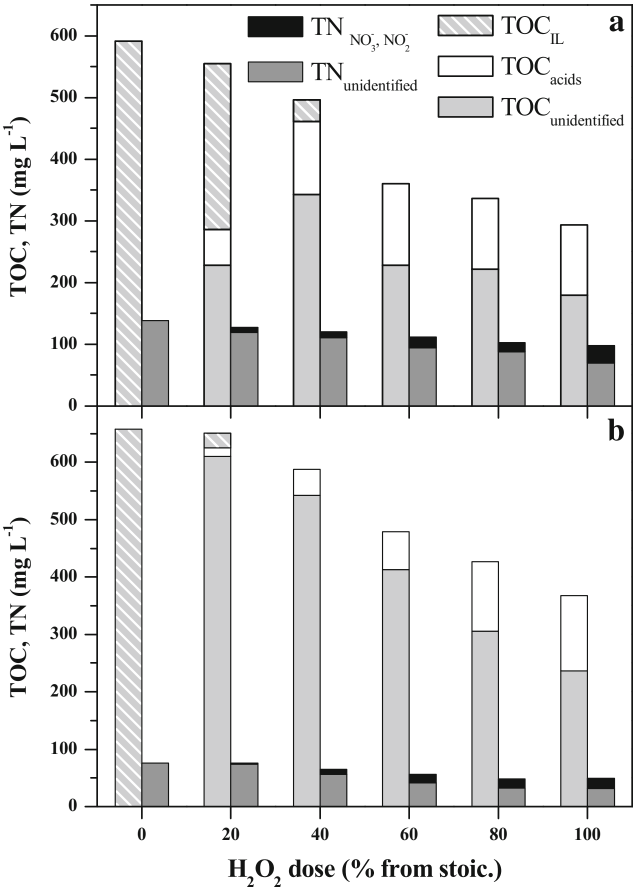

Fig. 5 Measured and unidentified TN and TOC balance closure from Fenton oxidation at different substoichiometric H_2O_2 doses for HmimCl (a) and BmpyrCl (b)

An additional Fenton oxidation experiment with both ionic liquids (HmimCl and BmpyrCl) has been carried out, in order to study the behavior of the mixture in a synthetic matrix maintaining the operating conditions aforementioned. The ionic liquid concentration was fixed to 1 g L^{-1} for each compound. The results of the experiment are shown in Table 3. Complete removal of Hmim+ and Bmpyr+ was achieved, reaching 54% TOC conversion. The consumption of H_2O_2 occurred mainly during the first 90 min and then, a very slow decay was observed. COD conversion increased up to around 70%. In spite of the complete depletion of the starting compounds, TOC and COD conversion did not reach higher values due mainly, as is well known, to the formation of short-chain organic acids which are refractory to Fenton oxidation. Thus, more than 80% of the measured TOC was identified as short-chain organic acids, mostly formic and acetic acids, being other oxidation by-products the unidentified TOC fraction. Around 40% of the measured TN was measured as nitrate. The nitrogen mass balance was incomplete mainly due to the formation of different nitrogen species in the gas phase, as has been previously reported (Garcia-Segura et al. 2017), such as NOx species, and to a lesser extent by nitrogen species by-products in the liquid phase, which have been included in the proposed pathway (Fig. 3). Finally, the chlorine balance was almost completely closed. Probably, the unidentified fraction could correspond to the formation of chloramines (De Vidales et al. 2016) or other chlorine species. Comparing these results with those described for Fenton oxidation of ionic liquids separately, it can be concluded that the presence of both compounds lead to similar results in terms of IL removal, mineralization of the starting compounds and COD conversion and no synergistic effect,

Table 2 Ecotoxicity (TU), BOD_5/COD, and TOC/COD ratios for effluents from Fenton oxidation at different substoichiometric H_2O_2 doses

H_2O_2 (%)	HmimCl			BmpyrCl		
	TU	BOD_5/ COD	TOC/ COD	TU	BOD_5/ COD	TOC/ COD
0	3.53	0.03	0.55	2.22	0.06	0.40
20	3.78	0.11	0.61	54.9	0.07	0.41
40	3.22	0.21	0.62	7.34	0.24	0.43
60	1.17	0.36	0.55	3.86	0.36	0.43
80	0.75	0.38	0.77	0.87	0.58	0.44
100	0.56	0.40	0.73	0.11	0.59	0.41

Table 3 Conversion of IL, TOC, and COD (%) upon Fenton oxidation of HmimCl and BmpyrCl at stoichiometric H_2O_2 dose. Measured (M) and identified (Id) TOC, TN, and chloride concentration from resulting effluent from Fenton oxidation

	Conversion (%)			TOC ($mg\ L^{-1}$)		TN ($mg\ L^{-1}$)		Cl^- ($mg\ L^{-1}$)	
	IL	TOC	COD	M_{TOC}	Id_{TOC}	M_{TN}	Id_{TN}	M_{Cl-}	Id_{CL-}
HmimCl	> 99	54.1	70.0	625	509	178	71	364	354
BmpyrCl	> 99								

interference or competition between HmimCl and BmpyrCl was observed.

Conclusions

Fenton oxidation at controlled temperature (70 °C) was proved to be an efficient process for the removal of imidazolium (HmimCl)- and pyridinium (BmpyrCl)-based ionic liquids. Using the stoichiometric H_2O_2 dose, the complete conversion of both ILs was achieved at the early stages of the oxidation, observing remaining IL concentrations at substoichiometric H_2O_2 doses below 40%. TOC and COD conversion increased as the H_2O_2 dose increased, reaching values around 40–55% for both ILs. The possible degradation pathway for $Hmim^+$ and $Bmpyr^+$ includes the hydroxylation of the cations by the attack of the ·OH radicals, followed by the ring-opening and the formation of short-chain organic acids, in a considerable concentration in assays with H_2O_2 near stoichiometric dose, which could be partially oxidized up to CO_2 and H_2O. The resulting effluents showed lower ecotoxicity values than the target compounds, with a highly improved biodegradability.

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