

Degradation of imidazolium-based ionic liquids in aqueous solution by Fenton oxidation

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Abstract

BACKGROUND: The breakdown of imidazolium ionic liquids (ILs) by Fenton oxidation has been demonstrated, but using unaffordable doses of hydrogen peroxide (H_2O_2). The literature studies so far do not report on the evolution of total organic carbon (TOC) and ecotoxicity. Therefore, the potential application of the process for the degradation of ILs still remains an open question. This work investigates the feasibility of the Fenton process for the treatment of aqueous effluents containing imidazolium-based ILs of different structures, represented by the length of the alkyl chain and the nature of the anion. Special attention is paid to the evolution of the ecotoxicity and the consumption of H_2O_2 as a critical issue for the economy of the process. The experiments were performed at 70 °C.

RESULTS: With the stoichiometric H_2O_2 dose, the complete conversion of the starting imidazolium-based ILs was achieved in less than 5 min, at 70 °C, with 60% of TOC reduction after 4 h, except in the $[C_4mim][CH_3CO_2]$ case, where iron precipitation was observed, thus inhibiting its catalytic action. Low ecotoxicity effluents were obtained at the stoichiometric H_2O_2 dose, even in the cases of the highly ecotoxic ILs of long alkyl chain with chloride anion.

CONCLUSION: Fenton oxidation is shown to be a promising solution for the degradation of imidazolium-based ILs in water, allowing deep detoxification with the stoichiometric H_2O_2 dose.

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Keywords: Fenton oxidation; ionic liquids; imidazolium; ecotoxicity

INTRODUCTION

Ionic liquids (ILs) are salts with low melting points (<100 °C) consisting of large organic cations and organic or inorganic anions. They have gained considerable attention in the last two decades due to their unique properties, such as great dissolving capacity, non-flammability and thermal, chemical and electrochemical stability. Therefore, these materials have emerged as promising 'green' alternatives to conventional volatile organic solvents.^{1–4} Among them, imidazolium-based ILs have been the most extensively studied because of their availability and unique characteristics, among them their tunable properties. For instance, their solubility in water can be drastically modified by changing the length of the alkyl chain and/or the anion nature, covering a wide range of ILs, from almost immiscible to completely miscible with water. Thus, this IL family is in the spotlight of the scientific and industrial community and it is expected that it will be produced and used at an industrial scale in the near future. This fact obviously poses concerns over their environmental impact, in particular in the aquatic compartment.

The synthetic routes for ILs frequently include aqueous media, especially for the complicated purification.⁵ Also, their industrial application can involve water streams⁷ so that imidazolium-based ILs are expected to contaminate the resulting industrial wastewaters. A number of studies have demonstrated their

toxicity and non-biodegradability in aqueous phase,^{2,8,9} which poses questions regarding the green image of these compounds. As a consequence, the application of ILs must be assessed considering the risk associated with their entire life-cycle,^{8,10,11} which implies that the industrial processes using ILs have to consider their recovery or complete destruction from the residual effluents.

Adsorption with activated carbon or other materials^{5,12–15} and the 'salting-out' of ILs with aluminium salts¹⁶ has been investigated as potential solutions for their recovery or non-destructive removal. However, in the case of the imidazolium-based ILs, important limitations have been found regarding the length of the alkyl chain and the nature of the counter anion, since both issues affect the hydrophobicity of the molecule and consequently, their affinity for the carbon surface.^{5,16} These authors demonstrated

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that the adsorption capacity of the activated carbon was highly reduced when dealing with imidazolium-based ILs of short alkyl chains and/or containing the Cl^- anion (e.g. 1-butyl-3-methylimidazolium chloride, $[\text{C}_4\text{mim}]\text{Cl}$). For those ILs, some other solutions implying their degradation are required.

Advanced oxidation processes (AOPs), based on the action of hydroxyl radicals at near-ambient temperature and pressure, can be regarded as a potential solution for the degradation of persistent imidazolium-based ILs from wastewater. Among these treatments, the Fenton process using hydrogen peroxide (H_2O_2) as oxidant and iron salts as catalyst appears to be the most cost-effective process.^{17–19} So far, there are few works dealing with the destruction of imidazolium-based ILs, such as 1-butyl-3-methylimidazolium conjugated with chloride ($[\text{C}_4\text{mim}]\text{Cl}$),^{20,21} trifluoromethanesulfonate ($[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$) and tricyanmethide ($[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$)²² by the Fenton oxidation process at ambient conditions. The viability of $[\text{C}_4\text{mim}]\text{Cl}$ removal has been demonstrated²⁰, achieving complete conversion after 90 min at 25 °C and $[\text{IL}]_0 = 1 \text{ mmol L}^{-1}$, $[\text{Fe}^{3+}]_0 = 1 \text{ mmol L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 400 \text{ mmol L}^{-1}$, which represents an unaffordable dose of hydrogen peroxide (from 4 to 23 times the stoichiometric dose for the complete oxidation of the IL into CO_2 and H_2O). In spite of the high consumption of H_2O_2 , the species identified in the $[\text{C}_4\text{mim}]\text{Cl}$ oxidation pathway, included mainly imidazolones and hydroxyl-derivatives of higher molecular weight than the initial IL, whereas more oxidized by-products, such as organic acids, commonly found in Fenton effluents, were not detected.²¹

The potential application of the Fenton process to the treatment of IL-bearing wastewaters still remains an open question and its assessment must include not only the optimization of the H_2O_2 consumption, but also the in-depth characterization of the resulting effluents to have a better knowledge and understanding of the evolution of important parameters, namely the total organic carbon (TOC) and ecotoxicity upon oxidation. A temperature above the ambient (70 °C) will be used in order to increase the efficiency of hydrogen peroxide consumption and reduce the reaction time.^{23–26} As recently demonstrated, working at temperatures higher than the ambient do not imply an extra cost since the Fenton process is thermally auto-sustained and even a positive heat balance can result.²⁵

The aim of this study is to investigate the feasibility of the Fenton process for the degradation of imidazolium-based ILs in water. That IL family is described as one of the most promising considering their industrial applications. The conversion of the starting IL as well as the evolution of TOC and ecotoxicity will be followed taking into account the H_2O_2 dose, a critical issue for the feasibility of the process. The effect of the structure characteristics of the ILs, represented by the length of the alkyl chain and the nature of the counter anion, will be analysed by testing different imidazolium-ILs. The ecotoxicity of the effluents derived from the Fenton process will be characterized based on the luminescence response of the marine bacteria *Vibrio fischeri* (Standard Microtox[®] liquid-phase assays, here abbreviated as Microtox[®] test). The Microtox[®] test was selected in this study because it is a quick, simple, cost-effective, sensitive, widely used and accepted method of ecotoxicity assessment.

MATERIALS AND METHODS

Chemicals

Nine different ILs of the imidazolium family were tested. The compounds (name, abbreviation and chemical formula) and the

suppliers are summarized in Table 1. The hydrogen peroxide solution (30 wt%) in a stable form and $\text{Fe}(\text{NO}_3)_3$ salt were purchased from Sigma-Aldrich and Panreac, respectively. Other reagents namely HNO_3 (Sigma-Aldrich), $\text{C}_2\text{H}_3\text{N}$ (Riedel-deHaën), Na_2HPO_4 (Panreac), H_3PO_4 (Panreac), HPO_4 (Fisher), $\text{C}_6\text{H}_4\text{COOHCOOK}$ (Sigma-Aldrich), TiOSO_4 (Riedel-deHaën), NaHSO_3 (Sigma-Aldrich) were also used. All these reagents were of analytical grade and were used without further purification. The solutions were prepared with distilled water, except those used as mobile phases for HPLC and IC, which were prepared with milli-Q water.

Fenton experiments

The Fenton experiments were carried out batch-wise in 100 mL stoppered glass flasks shaken in a constant-temperature bath at an equivalent stirring velocity of 200 rpm. The IL solution (48 mL, 1000 mg L^{-1}) at $\text{pH} = 3$ (HNO_3) was placed in the reactor and heated to 70 °C. When the temperature was equilibrated, 1 mL of the H_2O_2 solution at the appropriate concentration for the desired $\text{H}_2\text{O}_2/\text{IL}$ molar ratio, followed by 1 mL of the $\text{Fe}(\text{NO}_3)_3$ aqueous solution ($C_{\text{Fe}} = 50 \text{ mg L}^{-1}$ in the reactor) were injected. Samples were taken from the reactor at different reaction times with a syringe, diluted with distilled water and immediately analyzed. After 4 h of reaction, the heating was switched-off, the reactor cooled to room temperature and the ecotoxicity of the effluents measured. All the experiments were performed in duplicate, the standard deviation always being less than 5%. Blank experiments in the absence of catalyst for all the ILs tested were carried out achieving negligible IL and TOC conversion values ($X_{\text{IL}} < 5\%$, $X_{\text{TOC}} < 2\%$) after 4 h of reaction time. Thermal decomposition was also checked at 70 °C and discarded.

Analytical methods

The ILs were analyzed by high performance liquid chromatography, HPLC-UV (Varian, Mod. ProStar) using a Synergi[™] 4 μm Polar-RP 80 Å Phenomenex column (15 cm length, 4.6 mm diameter) with a diode array detector (PDA detector) at 218 nm wavelength. A new method has been developed, which allows quantifying properly all the ILs individually tested. For that purpose, different mixtures of phosphate buffer (Na_2HPO_4 , 5 mmol L^{-1} - H_3PO_4 , 7.5 mmol L^{-1}) and acetonitrile aqueous solution at 0.75 mL min^{-1} were used as mobile phase, depending on the polarity of each IL tested. The percentage of acetonitrile (ACN) used in each case is included in Table 1. Total organic carbon (TOC) was measured with a TOC analyzer (Shimadzu TOC V_{SC4}). 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 mmol L^{-1} Na_2CO_3 aqueous solution as the mobile phase. Hydrogen peroxide and iron in solution were determined by colorimetric titration with a UV 2100 Shimadzu UV-VIS spectrophotometer using the titanium sulfate²⁷ and the *o*-phenantroline methods,²⁸ respectively. Elemental analyses of some precipitates were performed in a LECO Model CHNS-932 apparatus.

Ecotoxicity tests

The ecotoxicity of the starting IL solutions and the corresponding reaction samples at 4 h of reaction time was measured by a standard toxicity test conducted with the luminescent bacteria *Vibrio fischeri*, strain NRRL B-11177 (Microtox[®]; Azur Environmental

Table 1. Imidazolium-based ILs tested and the percentage of ACN used for their HPLC/UV analyses

IL name (supplier and purity)	Abbreviation	Chemical formula	ACN (%)*
1-ethyl-3-methylimidazolium Chloride (Iolitec, >98%)	[C ₂ mim]Cl		5
1-butyl-3-methylimidazolium Chloride (Green Solutions, >98%)	[C ₄ mim]Cl		5
1-octyl-3-methylimidazolium Chloride (Solchemar, >98%)	[C ₈ mim]Cl		40
1-dodecyl-3-methylimidazolium Chloride (Iolitec, >98%)	[C ₁₂ mim]Cl		60
1-tetradecyl-3-methylimidazolium Chloride (Iolitec, >98%)	[C ₁₄ mim]Cl		80
1-hexadecyl-3-methylimidazolium Chloride (Iolitec, >98%)	[C ₁₆ mim]Cl		80
1-butyl-3-methylimidazolium Methanesulfonate (Sigma-Aldrich, >95%)	[C ₄ mim][CH ₃ SO ₃]		5
1-butyl-3-methylimidazolium Methylsulfate (Green Solutions, >95%)	[C ₄ mim][CH ₃ SO ₄]		
1-butyl-3-methylimidazolium Acetate (Iolitec, >95%)	[C ₄ mim][CH ₃ CO ₂]		

* Phosphate buffer (volume) = 100%-ACN%.

1998). This bioassay is based on the decrease of the light emission by the bacterium as the result of its exposure to a toxicant at 15 °C for 15 min. The tests were conducted adjusting the osmotic pressure of the samples close to 2% NaCl, the pH between 6 and 8 and assuring the complete removal of the hydrogen peroxide by the addition of NaHSO₃. The IC₅₀ (dilution ratio of the sample that produces 50% of light emission inhibition) values were estimated through the Microtox® Omni™ Software version 4.3.0.1 (Microtox®; Azur Environmental 1998). The toxicity units (TU) are inversely proportional to the IC₅₀ values.

RESULTS AND DISCUSSION

Effect of hydrogen peroxide dose on [C₂mim]Cl oxidation

Figure 1 shows the results obtained upon Fenton oxidation of [C₂mim]Cl at different H₂O₂ doses covering up to 200% of the stoichiometric amount, theoretically needed for complete oxidation to CO₂, H₂O and N₂. As can be seen, the complete conversion of IL was achieved at 50% of the stoichiometric H₂O₂ dose. This was accompanied by somewhat more than 50% mineralization, which reached about 60% with the stoichiometric dose. No further significant reduction of TOC was observed, due to the refractory character of around 40% of the reaction by-products in terms of equivalent C. Only 60% of the remaining TOC corresponded to the

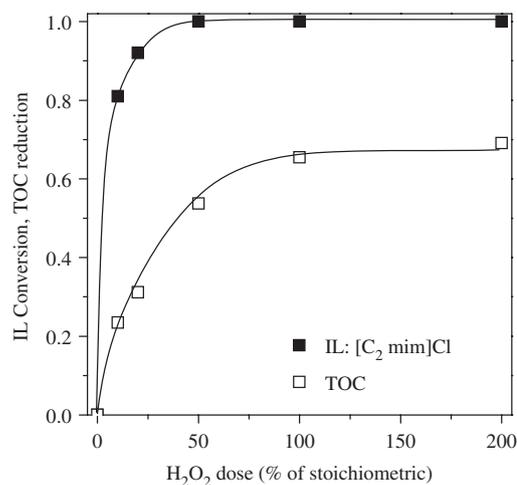


Figure 1. Conversion of [C₂mim]Cl and TOC reduction by Fenton oxidation at different H₂O₂ doses. [IL]₀ = 1000 mg L⁻¹, [Fe]₀ = 50 mg L⁻¹, 70 °C and pH = 3, time of reaction 4 h.

identified compounds, namely acetic, oxalic and formic, which are well-known refractory species to Fenton oxidation, at the operating conditions of this work.^{29,30}

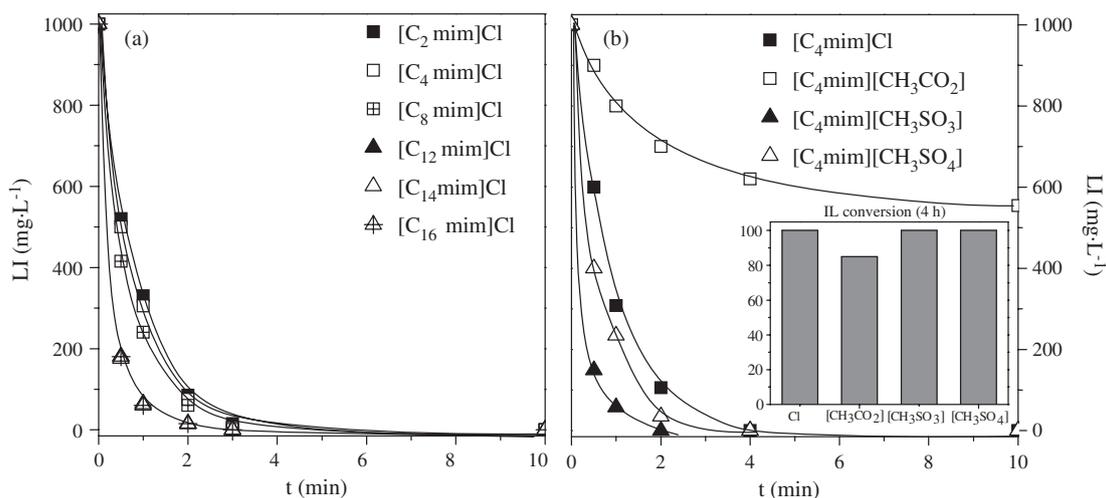


Figure 2. Influence of the alkyl chain length (a) and counter anion (b) on the Fenton oxidation of the imidazolium-based ILs tested. $[IL]_0 = 1000 \text{ mg L}^{-1}$, $[H_2O_2]_0 = \text{stoichiometric dose}$, $[Fe]_0 = 50 \text{ mg L}^{-1}$, 70°C , $\text{pH} = 3$.

Table 2. Ecotoxicity values (TU, 15 min) of $[C_x\text{mim}]\text{Cl}$ initial solutions (1000 mg L^{-1}) and their Fenton effluents (4 h, 70°C and H_2O_2 at the stoichiometric dose)

Cation	Anion	IL solution	Oxidation effluent
$[C_2\text{mim}]^+$	Cl^-	0.2 ± 0.05	non-toxic*
$[C_4\text{mim}]^+$		1.7 ± 0.3	non-toxic*
$[C_8\text{mim}]^+$		385 ± 45	non-toxic*
$[C_{12}\text{mim}]^+$		2857 ± 120	1.2 ± 0.2
$[C_{14}\text{mim}]^+$		3226 ± 200	1.5 ± 0.3
$[C_{16}\text{mim}]^+$		3846 ± 180	1.5 ± 0.3
Non-toxic * $<0.01 \text{ TU}$.			

The starting IL solutions yielded a very low value of ecotoxicity ($0.2 \pm 0.05 \text{ TU}$) and that was also the case of the samples resulting from oxidation, although they gave somewhat higher values (2.4 ± 0.4 the highest one, obtained at 20% of the stoichiometric H_2O_2 dose). A significant peak appeared in the HPLC chromatograms of the Fenton effluents (see Figure S1 in the Supporting Information), which, using CG-MS, was attributed to 1-ethyl-3-methylimidazolone ($m/z = 126$). The increase in H_2O_2 dose decreases the area of the peak and also the ecotoxicity ($1.6 \pm 0.2 \text{ TU}$ at 50% of the stoichiometric). In any case, neither $[C_2\text{mim}]\text{Cl}$ nor the by-products from the Fenton oxidation represent any significant problems in terms of ecotoxicity.

Effect of the alkyl chain length

The increase in the length of the alkyl chain has a dramatic effect on the ecotoxicity of the imidazolium-based ILs, as shown in Table 2. This is consistent with previous ecotoxicity studies based on $[C_n\text{mim}]\text{Cl}$ ILs reported by Ventura *et al.*⁹ The authors explained their findings by suggesting that the long alkyl chains increased the lipophilic nature of the ILs, increasing thus the possibility of their interaction with the cell membrane phospholipids bilayers which are disrupted. Fenton oxidation at the stoichiometric H_2O_2 dose allowed almost complete abatement of that ecotoxicity (Table 2).

Figure 2(a) shows the time-evolution of the concentration of the ILs upon Fenton oxidation with the stoichiometric H_2O_2 dose,

for the different alkyl chain lengths tested. The results show that complete conversion was achieved in all cases in a few minutes. The rate of disappearance of the starting IL increased with the length of the alkyl chain due to the higher number of oxidizable sites. However, a greater and more rapid mineralization was achieved as the length of the alkyl chain of the starting IL decreased, as depicted in Fig. 3(a). This trend consistently agrees with that observed for H_2O_2 decomposition (Fig. 3(b)). In both cases, the differences occur within the range 2 to 8 °C atoms and then, a close behaviour is observed. According to these results, the attack on the imidazolium ring by the oxidizing radicals is favoured when it is linked to a short alkyl chain. Likely, the breakdown of the imidazolium ring would take place by the cleavage of alkyl side chain from the N atom of the ring, which is a less stable bond than the C–C and C–N bonds in the imidazolium ring.⁴

Mineralization accounted for at least 55% after 4 h reaction time (Fig. 3(a)), and the remaining TOC corresponds to species without significance in terms of ecotoxicity.

Effect of the counter anion

Figure 2(b) shows the time-evolution of the concentration of different ILs based on 1-butyl-3-methylimidazolium salts ($[C_4\text{mim}]^+$) conjugated with different anions, namely chloride (Cl^-), acetate ($[\text{CH}_3\text{CO}_2]^-$), methanesulfonate ($[\text{CH}_3\text{SO}_3]^-$) and methylsulfate ($[\text{CH}_3\text{SO}_4]^-$), upon Fenton oxidation with the stoichiometric H_2O_2 dose. The results demonstrate that the degradation of the ILs was affected by the nature of the anion, the oxidation rate following the order: $[\text{CH}_3\text{SO}_3]^- > [\text{CH}_3\text{SO}_4]^- > \text{Cl}^- > [\text{CH}_3\text{CO}_2]^-$. Complete conversions of the ILs was achieved after 5 min, except in the case of $[C_4\text{mim}][\text{CH}_3\text{CO}_2]$ which required 4 h to reach 85%. This remarkably slower oxidation of $[C_4\text{mim}][\text{CH}_3\text{CO}_2]$ can be associated with the precipitation of iron species, with the consequent inhibition of its catalytic action. The dissolved iron in the effluent after 4 h of reaction was only 1.5 mg L^{-1} whereas concentrations ranging from 45 to 50 mg L^{-1} were measured in the experiments with the remaining imidazolium ILs. The final pH in all cases was around 2.5. The brownish orange-colored precipitate was analysed by elemental analysis showing no significant content of carbon (0.69 wt%) but appreciable amounts of hydrogen (9.03 wt%). Therefore, in the case of $[C_4\text{mim}][\text{CH}_3\text{CO}_2]$, an iron sludge is

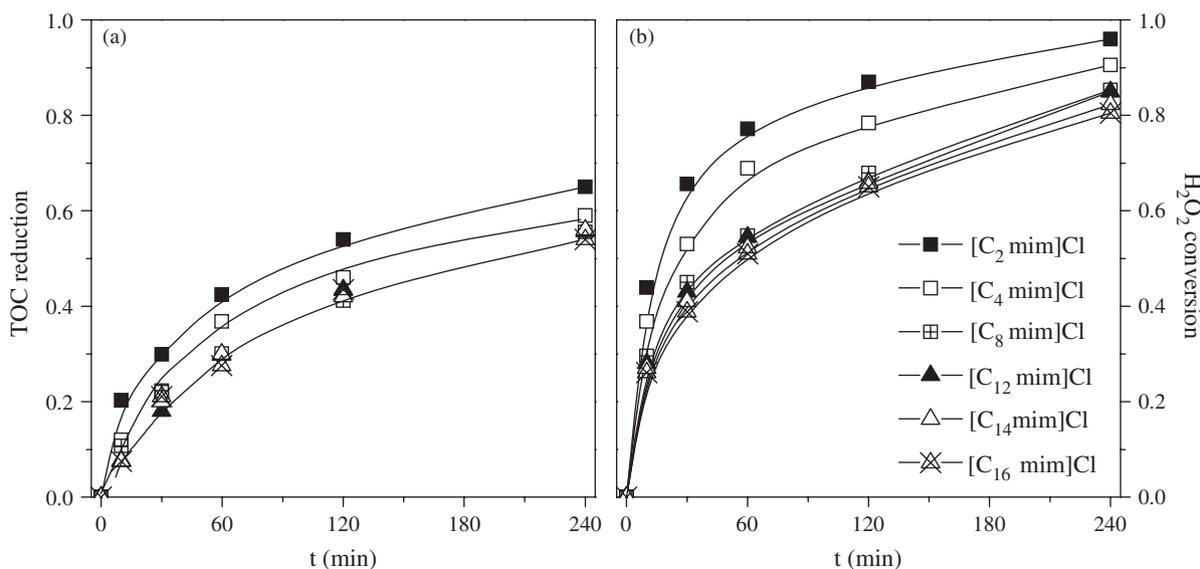


Figure 3. Influence of alkyl chain length on TOC reduction (a) and H_2O_2 decomposition (b) during Fenton oxidation of different Cl-based imidazolium ILs. $[\text{IL}]_0 = 1000 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric dose}$, $[\text{Fe}]_0 = 50 \text{ mg L}^{-1}$, 70°C , $\text{pH} = 3$.

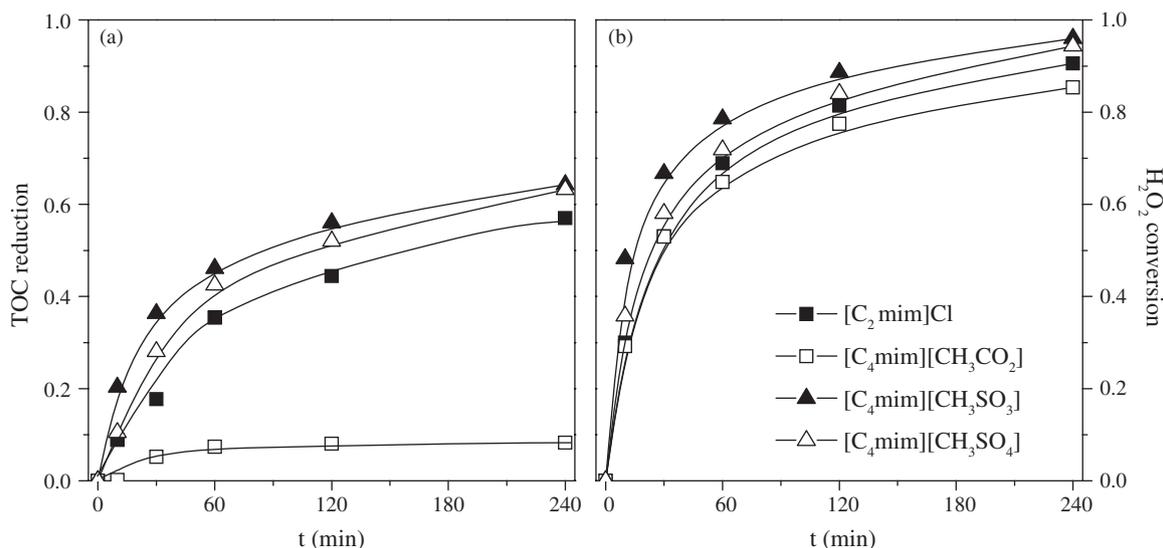


Figure 4. Influence of the anion on TOC reduction (a) and H_2O_2 decomposition (b) during the Fenton oxidation of different $[\text{C}_4\text{mim}]$ -based ILs. $[\text{IL}]_0 = 1000 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric dose}$, $[\text{Fe}]_0 = 50 \text{ mg L}^{-1}$, 70°C , $\text{pH} = 3$.

produced upon oxidation, consisting of ferric and ferrous hydroxo complexes.

The same trend was observed with regard to TOC reduction and H_2O_2 decomposition (Fig. 4(a) and (b), respectively). The mineralization of $[\text{C}_4\text{mim}][\text{CH}_3\text{CO}_2]$ was very poor, remaining below 10% after 4 h reaction time, whereas for the three other ILs, TOC reductions of about 60% were achieved. This much lower mineralization can be related to the competition between the imidazolium cation ($[\text{C}_4\text{mim}]^+$) and the organic anion ($[\text{CH}_3\text{CO}_2]^-$), which can inhibit the breakdown of the imidazolium ring.²²

The ecotoxicity values of the starting 1-butyl-3-methylimidazolium salts conjugated with the aforementioned anions were very low, ranging from 0.8 to 1.7 TU. The anion does not show any significant contribution in that respect. These ecotoxicity values are in good agreement with those reported in literature.³¹ The structure of the cation and, in particular, the

length of the alkyl chain related to the hydrophobicity, is the most important issue affecting the ecotoxicity of these ILs.³¹

CONCLUSIONS

Fenton oxidation is shown to be an efficient technique for the degradation of imidazolium-based ILs in water. At 70°C with the stoichiometric H_2O_2 dose, rapid conversion of the ILs was achieved and the TOC reduction ranged between 55 and 65% after 4 h reaction time with the exception of the acetate-anion IL only.

The rate of mineralization increased with the length of the alkyl chain within the range 2 to 8 carbon atoms and beyond that, the differences were not significant. The nature of the anion also affected the mineralization showing a particularly remarkable effect in the case of acetate, where a very low reduction of TOC was reached.

The ecotoxicity of the ILs is highly dependent on the length of the alkyl chain, increasing dramatically as it increases. Fenton oxidation allowed almost complete abatement of the ecotoxicity in all cases.

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Supporting Information

Supporting information may be found in the online version of this article.

REFERENCES

- Pernak J, Sobaszekiewicz K and Mirska I, Anti-microbial activities of ionic liquids. *Green Chem* **5**:52–56 (2003).
- Bernot RJ, Brueseke MA, Evans-White MA and Lamberty GA, Acute and chronic toxicity of imidazolium-based ionic liquids on daphnia magna. *Environ Toxicol Chem* **1**:87–92 (2005).
- Ventura SPM, Gonçalves AMM, Sintra T, Pereira JL, Gonçalves F and Coutinho JAP, Designing ionic liquids: the chemical structure role in the toxicity. *Ecotoxicology* **22**:1–12 (2013).
- Zhou H, Lv Ping, Shen Y, Wang J and Fan J, Identification of degradation products of ionic liquids in an ultrasound assisted zero-valent iron activated carbon microelectrolysis system and their degradation mechanism. *Water Res* **47**:3514–3522 (2013).
- Palomar J, Lemus J, Gilarranz MA and Rodríguez JJ, Adsorption of ionic liquids from aqueous effluents by activated carbon. *Carbon* **47**:1846–1856 (2009).
- Burrell AK, Del Sesto RE, Baker SN, McCleskey TM and Baker GA, The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids. *ACS Symposium Series* **9**:449–454 (2007).
- Plechova NV and Seddon KR, Applications of ionic liquids in the chemical industry. *Chem Soc Rev* **37**:123–150 (2008).
- Romero A, Santos A, Tojo J and Rodríguez A, Toxicity and biodegradability of imidazolium ionic liquids. *J Hazard Mater* **151**:268–273 (2008).
- Ventura SPM, Marques CS, Rosatella AA, Afonso CAM, Gonçalves F and Coutinho JAP, Toxicity assessment of various ionic liquid families towards *Vibrio fischeri* marine bacteria. *Ecotoxicol Environ Saf* **76**:162–168 (2012).
- Coleman D and Gathergood N, Biodegradation studies of ionic liquids. *Chem Soc Rev* **39**:600–637 (2010).
- Bubalo MC, Radosevic K, Redovnikovic IR, Halambek J and Srcek VG, A brief overview of the potential environmental hazards of ionic liquids. *Ecotoxicol Environ Saf* **99**:1–12 (2014).
- Stepnowski P, Mroziak W and Nithaus J, Adsorption of alkylimidazolium and alkylpyridinium ionic liquids onto natural soils. *Environ Sci Technol* **41**:511–516 (2007).
- Studzinska S, Sprynskyy M and Buszewski B, Study of sorption kinetics of some ionic liquids on different soil types. *Chemosphere* **71**:2121–2128 (2008).
- Stepnowski P and Zaleska A, Comparison of different advanced oxidation processes for the degradation of room temperature ionic liquids. *J Photochem Photobiol A* **170**:45–50 (2005).
- Lemus J, Neves CM, Marques CF, Freire MG, Coutinho JA and Palomar J, Composition and structural effects on the adsorption of ionic liquids onto activated carbon. *Environ Sci Process Impacts* **15**:1752–17529 (2013).
- Neves CM, Freire MG and Coutinho JA, Improved recovery of ionic liquids from contaminated aqueous streams using aluminium-based salts. *RSC Advances* **2**:10882–10890 (2012).
- Beltrán de Heredia J and Domínguez JR, Eliminación de compuestos fenólicos por oxidación avanzada. *Ingeniería Química* **386**:142–146 (2002).
- Esplugas S, Giménez J, Contreras S, Pascual E and Rodríguez M, Comparison of different advanced oxidation processes for phenol degradation. *Water Res* **36**:1034–1042 (2002).
- Cañizares P, Paz R, Sáez C and Rodrigo MA, Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and fenton oxidation processes. *J Environ Manage* **90**:410–420 (2009).
- Siedlecka EM, Mroziak W, Kaczynski Z and Stepnowski P, Degradation of 1-butyl-3-methylimidazolium chloride ionic liquid in a fenton-like system. *J Hazard Mater* **154**:893–900 (2008).
- Siedlecka EM, Gołbiowski M, Kumirska J and Stepnowski P, Identification of 1-butyl-3-methylimidazolium chloride degradation products formed in Fe(III)/H₂O₂ oxidation system. *Chem Anal (Warsaw)* **53**:943–951 (2008).
- Siedlecka EM, Gołbiowski M, Kaczynski Z, Czupryniak J, Ossowski T and Stepnowski P, Degradation of ionic liquids by fenton reaction; the effect of anions as counter and background ions. *Appl Catal B* **91**:573–579 (2009).
- Zazo JA, Pliego G, Blasco S, Casas JA and Rodríguez JJ, Intensification of the Fenton process by increasing the temperature. *Ind Eng Chem Res* **50**:866–870 (2011).
- Pliego G, Zazo J, Casas JA and Rodríguez JJ, Treatment of highly polluted hazardous industrial wastewaters by combined coagulation – adsorption and high-temperature Fenton oxidation. *Ind Eng Chem Res* **51**:2888–2896 (2012).
- Pliego G, Zazo J, Casas JA and Rodríguez JJ, Case study of the application of Fenton process to highly polluted wastewater from power plant. *J Hazard Mater* **253–253**:180–185 (2013).
- Domínguez CM, Quintanilla A, Casas JA and Rodríguez JJ, Treatment of real winery wastewater by wet oxidation at mild temperature. *Sep Purif Technol* Accepted.
- Eisenberg GM, Colorimetric determination of hydrogen peroxide. *Ind Eng Chem Res* **15**:327–328 (1943).
- Sandell EB, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York (1959).
- Carriazo J, Guélou E, Barrault J, Tatibouët JM, Molina R and Moreno S, Catalytic wet peroxide oxidation of phenol by pillared clays containing Al–Ce–Fe. *Water Res* **39**:3891–3899 (2005).
- Zazo JA, Casas JA, Moledano, Gilarranz MA and Rodríguez JJ, Chemical pathway and kinetics of phenol oxidation by Fenton's reagent. *Environ Sci Technol* **39**:9295–9302 (2005).
- Radošević K, Cvjetko M, Kopjar N, Novak R, Dumić J and GaurinaSrček V, *In vitro* cytotoxicity assessment of imidazolium ionic liquids: biological effects in fish channel catfish ovary (CCO) cell line. *Ecotoxicol Environ Safety* **92**:112–118 (2013).