Degradation of imidazolium-based ionic liquids by catalytic wet peroxide oxidation with carbon and magnetic iron catalysts

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1   **Abstract**

2   BACKCGROUND: The "green" image of ionic liquids (ILs) is changing in the last few years

3   since numerous works have evidenced their non-biodegradability, persistence and high

4   ecotoxicity, particularly for the most common imidazolium-based ILs. In this work, the feasibility

5   of catalytic wet peroxide oxidation for the degradation of imidazolium-based ILs of different alkyl

6   chain lengths has been studied under selected operating conditions (1000 mg L^{-1} IL, stoichiometric

7   H_2O_2 dose, 2 g L^{-1} catalyst, pH 3 and 90 ºC temperature) using different catalysts such as

8   magnetic iron (Fe_3O_4) supported on γ-Al_2O_3 and activated carbon (AC) as well as bare carbon

9   materials (graphite, AC). The catalytic activity and stability and the efficiency on H_2O_2

10   consumption have been evaluated.

11   RESULTS: Although both AC-based catalysts led to the conversion of the IL, they yielded a low

12   H_2O_2 consumption efficiency (24% and 45% with AC and Fe_3O_4/AC, respectively) due to the fast

13   decomposition of H_2O_2 and the recombination of radical species into H_2O and O_2, non-reactive

14   species under the operating conditions. In contrast, graphite and Fe_3O_4/γ-Al_2O_3 showed high

15   activity allowing complete conversion and relatively high mineralization degrees of all the ILs

16   tested in 1 h reaction time. Among those catalysts, Fe_3O_4/γ-Al_2O_3 exhibited a considerably greater

17   stability upon 4 successive uses where iron leaching was negligible and the magnetic properties

18   were maintained.

19   CONCLUSIONS: CWPO has proved to be an interesting alternative for the treatment of

20   imidazolium-based ILs in water. The application of Fe_3O_4/γ-Al_2O_3 is particularly promising due to

21   its high activity, remarkable stability and easy magnetic recovery.

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1. Introduction

Ionic liquids (ILs), semi-organic salts that are liquid below 100 ºC, have gained considerable attention in the last two decades due to their unique properties such as high dissolving power, tunable structure, non-flammability and thermal, chemical and electrochemical stability. [1, 2] Accordingly, they have emerged as promising "green" replacements for volatile organic solvents to be used in a wide range of applications, such as separation, coating, chemical synthesis, energy storage and transformation. [1, 3, 4]

Certain amounts of ILs are expected to be present in industrial wastewater since their synthesis routes frequently involve aqueous media and their industrial applications can also produce water streams. [3, 5] This fact represents an environmental concern since, although the low vapor pressure of ILs guarantees the air protection from the emissions of toxic vapors, their stability make them hazardous for water and soil. A number of works have evidenced the non-biodegradability and high ecotoxicity of ILs, particularly for the most common imidazolium-based ILs.[6-11] Bubalo et al. (2014)[10] established that almost none of the commonly used imidazolium-based ILs could be classified as readily biodegradable according to the Organization for Economic Cooperation and Development (OECD) standard tests (OECD, 1992[12]). In addition, those ILs have shown to be more toxic than some conventional hazardous organic compounds like phenol, chloroform or acetonitrile, among others.[8] Their ecotoxicity is mainly related to the alkyl chain length, ranging from negligible toxicity values (EC_{50} >5000 mg L^{-1}) to strongly toxic ones (EC_{50} < 0.3 mg L^{-1}) with increasing the alkyl chain from C_2 to C_{16}.[11]

In this context, the application of imidazolium-based ILs must be assessed considering the risk associated to their entire life-cycle, which implies that the industrial processes using those ILs need to consider their recovery or destruction from the residual effluents.[8, 10, 13] Adsorption onto activated carbon has proved to be an effective method for the recovery of ILs.[14] However, important limitations have been found regarding the length of the alkyl chain and the nature of the counter anion, since both

issues affect the size and hydrophobicity of the molecule.[14, 15] In this sense, the destruction of those ILs from diluted wastewater streams seems to be the most advisable solution. Due to their high stability and resistance to biodegradation, chemical oxidation treatments would represent the best option for their removal. Several advanced oxidation processes have been so far investigated for such purpose.[4, 9, 16-18] Among them, Fenton oxidation is received growing attention and has been so far successfully applied.[19-21] In recent contributions,[11, 22] we reported complete disappearance of imidazolium-based ILs ($[IL]_0 =$ 1000 mg L^{-1}) and more than 50% mineralization under the optimum operating conditions ($[Fe^{3+}] = 50$ mg L^{-1}; stoichiometric dose of H_2O_2; 70-90 ºC). Non-toxic effluents were obtained after 4 h treatment.

An important drawback of the conventional Fenton process is the continuous loss of catalyst which needs to be separated from the effluent to avoid additional water pollution. This has promoted the investigation towards active and stable solid catalysts, giving rise a growing literature on heterogeneous Fenton oxidation or the so-called catalytic wet peroxide oxidation (CWPO).[23-27] Although this technology has been tested with a wide range of industrial wastewaters,[28-30] its application to ILs oxidation has not been reported so far.

The use of magnetic catalysts is attracting increasing attention in the last few years due to their high activity as well as to their easy recovery from the reaction medium by applying an external magnetic field.[31-36] Magnetic activated carbon-based catalysts have proved to be highly active in the oxidation of dyes.[31] In the same line, Munoz et al. (2013)[34] demonstrated the better performance of a magnetic iron on γ-alumina compared to other conventional catalysts in the CWPO of chlorophenols. On the other hand, the interest towards stable catalysts avoiding metal leaching has also promoted the exploration of bare carbon materials, with surface redox properties, allowing the decomposition of hydrogen peroxide into radical species. Promising results have been obtained on the use of activated carbon, graphite and carbon black as CWPO catalysts for the treatment of synthetic phenol-bearing and some real industrial wastewaters.[29, 37, 38]

Here, we study the feasibility of CWPO for the treatment of synthetic wastewater containing different imidazolium-based ILs, the IL family with most industrial applications. The oxidation runs

have been carried out at 90ºC using different catalysts including magnetic iron (Fe_3O_4) on γ-Al_2O_3 and activated carbon (AC) as well as bare carbon materials (graphite (G) and AC). Their activity and stability have been evaluated together with the efficiency of H_2O_2 consumption. The performance of the process has been followed in terms of IL conversion, TOC reduction and H_2O_2 decomposition. The end-reaction organic acids have been analyzed.

2. Materials and methods

2.1. Chemicals

Imidazolium ILs of four different alkyl chain lengths were tested in this work: 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl, >98%), 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl, >98%), 1-octyl-3-methylimidazolium chloride ([C_8mim]Cl, >98%) and 1-hexadecyl-3-methylimidazolium chloride ([C_{16}mim]Cl, >98%). They were purchased from Iolitec, Green Solutions and Solchemar. The $Fe(NO_3)_3$ salt used for the preparation of the Fe-bearing catalysts and the hydrogen peroxide solution (30 wt.%) in a stable form were supplied by Panreac and Sigma-Aldrich, respectively. All the reagents were of analytical grade and were used without further purification.

2.2. Catalysts

The magnetic catalysts (4% wt. Fe), Fe_3O_4/γ-Al_2O_3 and Fe_3O_4/AC, were prepared following the procedures described elsewhere.[31, 34] Briefly, the former were prepared by incipient wetness impregnation followed by calcination in air (300 ºC) (4 h) and reduction in H_2 atmosphere at 350 ºC (2 h) whereas the latter was simply treated at 600 ºC under N_2 (1 h) after the previous impregnation. γ-Al_2O_3 was supplied by Merck (ref.: 1010951000) and the carbon materials, activated carbon (AC) and graphite (G), were purchased from Merck (ref.: 102514) and Sigma-Aldrich (ref.: 282863), respectively. All samples were provided in powder form (<80 μm).

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2.3. Catalyst characterization

The porous structure of the fresh catalysts was characterized from the nitrogen adsorption-desorption isotherms at -196 ºC using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 ºC to a residual pressure of 10^{-3} Torr in order to ensure a dry clean surface. The external or non-microporous surface area (A_{ext}) was calculated by the t-method. The iron content of the catalysts was analyzed by inductively coupled plasma (ICP/MS) Elan 6000 PerkinElmer Sciex. The characterization of the catalysts is summarized in Table 1.

2.4. CWPO experiments

CWPO runs were carried out batch-wise for 4 h in a 100 mL stirred three-necked glass reactor equipped with a reflux condenser and temperature control. The reaction volume was 70 mL and the starting concentrations were 1000 mg L^{-1} IL and the theoretical stoichiometric amount of H_2O_2 for complete oxidation of IL up to CO_2, H_2O, HCl and N_2 (3900, 4500, 5100 and 5800 mg L^{-1} for [C_2min]Cl, [C_4min]Cl, [C_8min]Cl and [C_{16}min]Cl, respectively). In a typical run, an aqueous solution containing the aforementioned concentration of the corresponding IL was placed into the reactor. Once the temperature was equilibrated, 1.5 mL of the hydrogen peroxide solution followed by the catalyst (0.14 g) were added and that was considered the starting time for the reaction. All the experiments were performed at 90 ºC and atmospheric pressure, adjusting the initial pH of the reaction medium to 3 with a nitric acid solution (1 M).

Experiments in absence of H_2O_2 were also conducted in order to check the adsorption of the ILs onto the catalysts tested. Experiments in absence of catalyst were carried out as well and negligible disappearance of IL was always observed (<5%). All the experiments were performed by triplicate being the standard deviation always below 5%.

3   *2.5. Analytical methods*

4   The progress of the reactions was followed by periodically withdrawing and analyzing liquid

5   samples from the reactor. The catalyst was separated by filtration using a PTFE filter (pore size 0.45

6   μm). Imidazolium-based ILs were quantified by means of high performance liquid chromatography,

7   HPLC-UV (Varian, Mod. ProStar), by a Synergi™ 4 μm Polar-RP 80 Å Phenomenex column (15 cm

8   length, 4.6 mm diameter) with a diode array detector (PDA detector) at 218 nm wavelength. The

9   analyses were carried out using different mixtures of phosphate buffer (Na_2HPO_4, 5 mM - H_3PO_4, 7.5

10   mM) aqueous solution and acetonitrile at 0.75 mL min^{-1} as mobile phase, depending on the polarity of

11   the IL tested.[11] Total organic carbon (TOC) was measured with a TOC analyzer (Shimadzu TOC V_{SCH}).

12   Short-chain organic acids were analyzed by ion chromatography with chemical suppression (Metrohm

13   790 IC) using a conductivity detector. A Metrosep A supp 5-250 column (25 cm length, 4 mm internal

14   diameter) was used as stationary phase and a 3.2 mM Na_2CO_3 aqueous solution as the mobile phase.

15   Hydrogen peroxide concentration was determined by colorimetric titration with a UV 2100 Shimadzu

16   UV-VIS spectrophotometer.[39] Fe leached to the reaction medium was measured by the *o*-phenantroline

17   method.[40]

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19   **3.   Results and discussion**

20   *3.1. Catalysts screening: activity and H_2O_2 efficiency*

21   A previous set of experiments in absence of H_2O_2 confirmed that none of the catalysts tested

22   showed significant adsorption of [C_2mim]Cl (<5%), even in the case of AC, with a high BET surface

23   area (1019 m^2 g^{-1}) (Table 1). These results are consistent with those reported by Palomar et al. (2009)[14],

24   where very low adsorption was observed for short-chain imidazolium-based ILs.

Figure 1 shows the time-evolution curves of [C$_2$mim]Cl concentration, H$_2$O$_2$ conversion and TOC upon CWPO with the catalysts tested. As observed, all the catalysts yielded complete conversion of the IL but significant differences were found among them. Whereas the Fe$_3$O$_4$/AC and G catalysts allowed complete disappearance of the IL upon 15 min reaction time, 30 min were required in the case of Fe$_3$O$_4$/γ-Al$_2$O$_3$ and 4 h with the bare AC. The values of the pseudo first-order rate constants were 0.79, 0.59, 0.09 and 0.02 min^{-1}, respectively (see Figure S1 of Supplementary Material).

Although the iron content of the catalysts was highly different (Table 1), almost complete decomposition of H$_2$O$_2$ occurred after 4 h reaction time in all cases (conversion values of 89, 100, 98 and 92% were obtained for Fe$_3$O$_4$/γ-Al$_2$O$_3$, Fe$_3$O$_4$/AC, G and AC, respectively) but fairly different percentages of mineralization were achieved. It is noteworthy to mention that the bare AC (0.04% Fe, Table 1) led to a reduction of TOC around 20% whereas the other three catalysts achieved around 50-60%, equivalent to the mineralization obtained upon conventional homogeneous Fenton oxidation under similar operating conditions.[22] Accordingly, the efficiency of hydrogen peroxide consumption (η_{H2O2}), defined as the amount of TOC converted per unit of hydrogen peroxide consumed, was also significantly influenced by the catalyst used. Efficiencies of 62, 45, 60 and 24% were calculated at the end of the 4h-experiments for the Fe$_3$O$_4$/γ-Al$_2$O$_3$, Fe$_3$O$_4$/AC, G and AC catalysts, respectively. The fairly low efficiency obtained with the bare AC catalyst is directly associated with the high ability of AC for H$_2$O$_2$ decomposition, related to its high surface area (Table 1). The fast decomposition of H$_2$O$_2$ over the carbon surface, which is entirely available due to the negligible adsorption of the IL, promotes parasitic reactions consuming HO· and HOO· radicals to produce O$_2$, a non-effective species under these operating conditions.[37] In the same line, the efficiency obtained with the Fe$_3$O$_4$/AC catalyst is lower than those obtained with G and Fe$_3$O$_4$/γ-Al$_2$O$_3$ catalysts due to the faster decomposition of H$_2$O$_2$, which was completely consumed in 1 h reaction time. These results are again related to the abovementioned rapid decomposition of H$_2$O$_2$ promoted by the AC support as well as to the contribution of homogeneous Fenton reaction since a significant amount of iron was leached from the Fe$_3$O$_4$/AC

1   catalyst (12 mg L^{-1} detected in the liquid phase after 4 h). Although the decomposition of H_2O_2

2   promoted by G was more progressive along the course of the reaction, that catalyst also suffered from

3   iron leaching (3.2 mg L^{-1}), being Fe_3O_4/γ-Al_2O_3 the most stable catalyst, with a leached iron

4   concentration of 0.25 mg L^{-1} at the end of the 4h-experiment. Additional homogeneous Fenton

5   experiments carried out with 0.25 mg L^{-1} Fe^{3+} did not lead to any significant decomposition of H_2O_2 and

6   TOC mineralization after 4 h reaction time. Therefore, the contribution of the homogeneous reaction at

7   that iron concentration can be considered negligible.

8   According to previous works,[11, 22] the final products obtained upon homogeneous Fenton oxidation

9   of [C_2mim]Cl were mainly short-chain organic acids. In this case, those compounds represented around

10   60% of the residual TOC in the cases of the Fe_3O_4/γ-Al_2O_3 and G catalysts, 45% with the Fe_3O_4/AC one

11   and only 20% with the bare AC. The concentration of these compounds is collected in Table S1 of

12   Supplementary Data. In consonance with the low amount of short-chain organic acids obtained and the

13   low TOC reduction achieved with the AC-based catalysts, hydroxylated intermediates of higher

14   molecular weight than the starting IL seem to be formed.[22]

15   The results with Fe_3O_4/γ-Al_2O_3 and G are comparable to those obtained upon homogeneous Fenton

16   oxidation under similar operating conditions,[22] but the heterogeneous process has the advantage that the

17   catalyst can be recovered and further reused. Those two catalysts yielding the best results in terms of

18   H_2O_2 consumption efficiency were selected for the following experiments.

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20   *3.2. Dependence on the alkyl chain length*

21   The length of the alkyl chain determines the potential application of the imidazolium ILs since it

22   shows a significant effect on the melting point and hydrophobicity, among other physicochemical

23   properties.[41] Moreover, it also strongly affects its ecotoxicity.[11] Therefore, the effect of the alkyl chain

24   length of imidazolium-based ILs on their behavior upon CWPO must be analyzed. Figure 2 compares

1   the results obtained with the four ILs tested. As can be seen, regardless the alkyl chain length all of them

2   were completely converted within 60 and 15 min reaction time, with the $Fe_3O_4/\gamma\text{-}Al_2O_3$ and G catalysts,

3   respectively. As observed, the values of the pseudo first-order rate constants, collected in Table 2, are

4   fairly similar. Nevertheless, it should be taken into account that the initial concentration of H_2O_2 used

5   for their removal, which is included in the kinetic constant, can be different depending on their

6   stoichiometry for complete mineralization. In fact, the mineralization of the ILs seems remarkably

7   affected by the alkyl chain length (Table 2, see Figure S2 in the Supporting Information for time-

8   evolution of TOC). In this sense, a decay on the mineralization with increasing the alkyl chain length

9   was observed with both $Fe_3O_4/\gamma\text{-}Al_2O_3$ and G catalysts. Accordingly, the efficiency on H_2O_2

10   consumption with increasing the alkyl chain length was decreased (Table 2).

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12   *3.3. Catalysts stability and reusability*

13   To learn on the stability of $Fe_3O_4/\gamma\text{-}Al_2O_3$ and G catalysts, they were used in the oxidation of

14   [C$_2$mim]Cl upon four successive runs with simply drying at low temperature overnight (60 ºC) after

15   each use. Iron concentration in the liquid phase was analyzed at the end of the 4h-experiments in order

16   to evaluate possible iron leaching from the catalysts. The results obtained are depicted in Figure 3.

17   Although both catalysts allowed achieving complete conversion of [C$_2$mim]Cl upon the four

18   consecutive cycles, G suffered a significant reduction of activity amounting about 70% and almost 50%

19   based on TOC removal and H_2O_2 decomposition after the four consecutive runs, respectively. This loss

20   of activity is directly related to the iron leaching observed upon consecutive uses (Figure 3). In fact, the

21   highest depletion of activity occurred from the first to the second run where 3.2 mg L^{-1} of iron were

22   analyzed in the liquid phase, representing 40 wt.% of the initial amount. Upon further runs, the amount

23   of dissolved iron was considerably lower and the activity was maintained. According to previous

24   works,[24, 42, 43] iron leaching from the catalysts upon CWPO of organic pollutants is directly related to the

1   formation of oxalic acid (27 mg L^{-1} in this work), which leads to the formation of a Fe-oxalate complex.

2   In this respect, carbon-based catalysts have proved to be less resistant than Al_2O_3-based ones.[24, 42, 43] On

3   the other hand, it has to be highlighted that the efficiency on the use of H_2O_2 followed the same trend as

4   the iron leaching, remaining almost unchanged from the second cycle for both catalysts.

5   The Fe_3O_4/γ-Al_2O_3 catalyst was significantly more resistant to iron leaching than G. In this sense,

6   only a slight decrease of H_2O_2 decomposition and TOC removal was observed from the first to the

7   second run, remaining almost unchanged for the next three consecutive uses. Accordingly, lower iron

8   leaching after each run was detected and the hydrogen peroxide efficiency was almost entirely

9   maintained. These results are consistent with previous works where Fe/Al_2O_3 catalysts have proved to

10   be fairly stable in both consecutive and long-term continuous experiments.[43, 44] Moreover, it has to be

11   pointed out that this catalyst, which exhibits magnetic properties ($M_S = 2.24$ emu g^{-1})[34], can be easily

12   separated from the reaction system by applying an external magnetic field after being used.

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4. Conclusions

15   CWPO has proved to be an effective process for the removal of imidazolium-based ILs regardless

16   their alkyl chain length. Among the catalysts tested, those based on AC yielded very low H_2O_2

17   efficiencies due to the recombination of radical species into H_2O and O_2, non-reactive under the

18   operating conditions. Although Fe_3O_4/AC showed higher activity and H_2O_2 consumption efficiency

19   compared to the bare AC, its stability was negatively affected by strong iron leaching. On the opposite,

20   Fe_3O_4/γ-Al_2O_3 and G showed high activities, allowing complete conversion of the ILs regardless their

21   alkyl chain lengths with high H_2O_2 consumption efficiencies in short reaction times. In fact, their

22   performance was similar to that obtained by conventional homogeneous Fenton oxidation with the

23   advantage of avoiding the continuous loss of iron as well as the formation of iron sludge at the end of

24   the process. Regarding the stability, Fe_3O_4/γ-Al_2O_3 exhibited a good performance in a four-run test,

showing negligible iron leaching and maintaining almost unchanged the TOC reduction. Thus, the Fe$_3$O$_4$/γ-Al$_2$O$_3$ represents a promising catalyst for the CWPO of imidazolium-based ILs due to its high activity, remarkable stability and easy recovery from the liquid phase given its magnetic properties.

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2   **Table 1.** Characterization of the catalysts.

Catalyst	S_{BET} (m^2 g^{-1})	A_{ext} (m^2 g^{-1})	Fe (%)
AC	1019	175	0.04
G	12	12	0.4
$Fe_3O_4/\gamma\text{-}Al_2O_3$	136	135	3.8
Fe_3O_4/AC	924	80	3.9

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Table 2. Values of the pseudo first-order rate constant of IL disappearance (k', min^{-1}), TOC removal

(%) and η_{H2O2} (%) in the CWPO of imidazolium-based ILs with the $Fe_3O_4/\gamma\text{-}Al_2O_3$ and G catalysts

($[IL]_0$ = 1000 mg L^{-1}; [catalyst] = 2 g L^{-1}; $[H_2O_2]_0$ = stoichiometric dose; pH_0 = 3; T = 90 ºC; t = 4h).

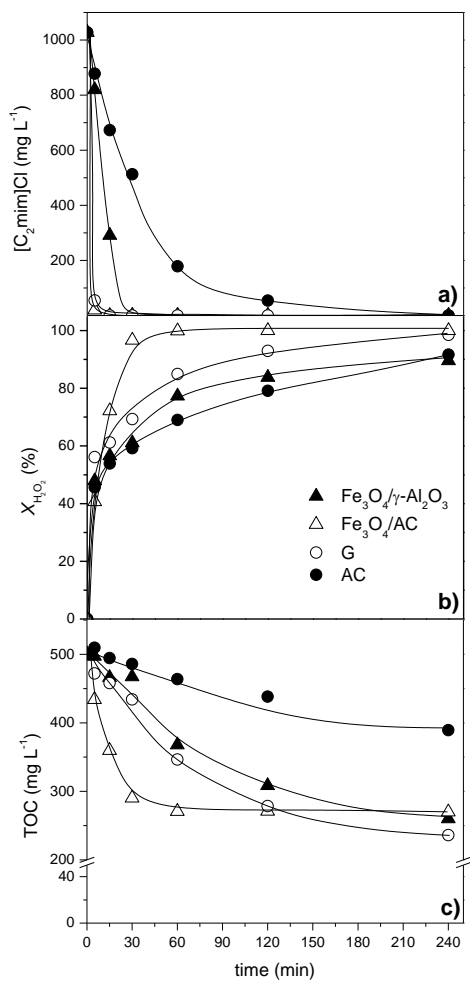| Catalyst	[C$_2$mim]Cl			[C$_4$mim]Cl			[C$_8$mim]Cl			[C$_{16}$mim]Cl		
	k' (r^2)	X_{TOC}	η_{H2O2}	k' (r^2)	X_{TOC}	η_{H2O2}	k' (r^2)	X_{TOC}	η_{H2O2}	k' (r^2)	X_{TOC}	η_{H2O2}
Fe$_3$O$_4$/γ-Al$_2$O$_3$	0.087 ± 0.008 (0.97)	44	62	0.089 ± 0.009 (0.99)	38	49	0.068 ± 0.012 (0.99)	36	42	0.070 ± 0.010 (0.99)	33	38
G	0.587 ± 0.03 (0.97)	53	60	0.533 ± 0.04 (0.99)	47	51	0.560 ± 0.02 (0.99)	45	50	0.635 ± 0.06 (0.99)	37	44

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Figure 1. Evolution of [C$_2$mim]Cl concentration (a), H$_2$O$_2$ conversion (b) and TOC (c) upon CWPO with the catalysts tested ([[C$_2$mim]Cl]$_0$ = 1000 mg L^{-1}; [catalyst] = 2 g L^{-1}; [H$_2$O$_2$]$_0$ = 4300 mg L^{-1}; pH$_0$ = 3; T = 90 ºC).
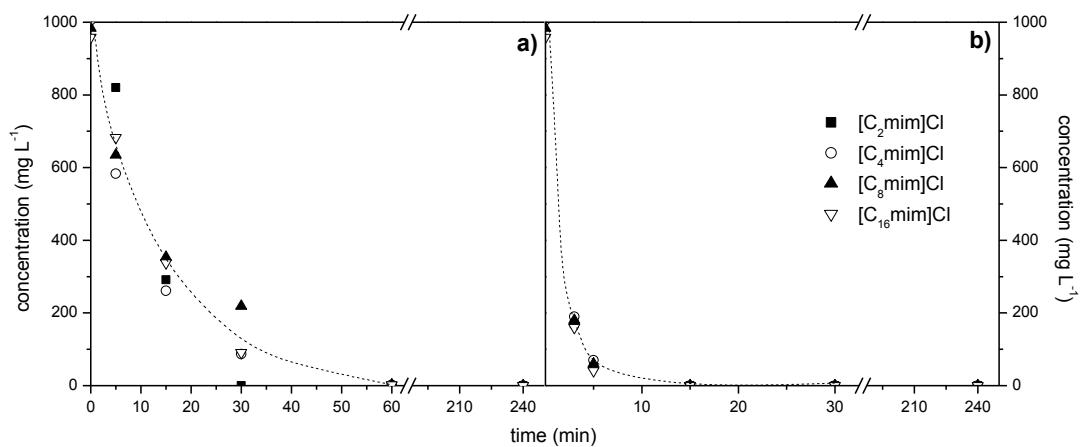
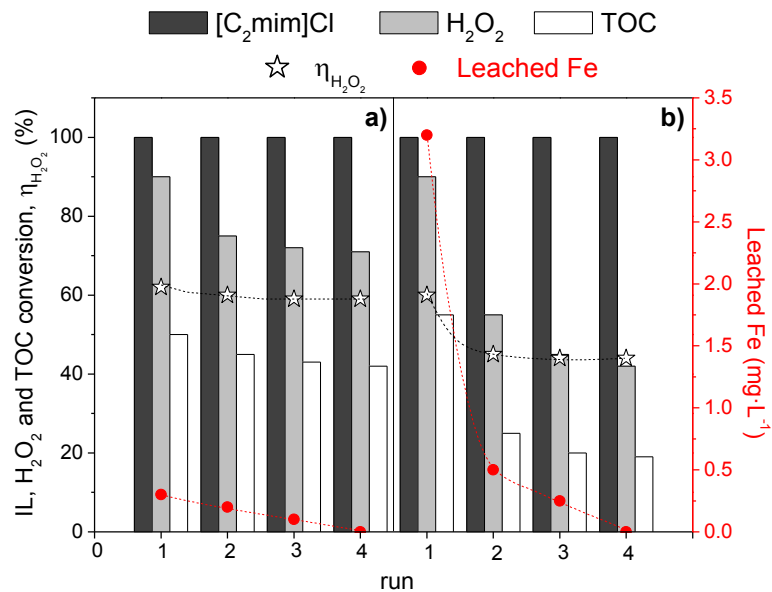**Figure 2.** Effect of the alkyl chain length of imidazolium-based ILs on their degradation upon CWPO with $Fe_3O_4/\gamma\text{-}Al_2O_3$ (a) and G (b) catalysts ($[IL]_0 = 1000$ mg L^{-1}; $[catalyst] = 2$ g L^{-1}; $[H_2O_2]_0 =$ stoichiometric dose; $pH_0 = 3$; T = 90 ºC).

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Figure 3. [C$_2$mim]Cl, TOC, H$_2$O$_2$ conversion, η_{H2O2} and iron leached (4 h) upon CWPO with the Fe$_3$O$_4$/γ-Al$_2$O$_3$ (a) and G (b) catalysts in successive applications ([[C$_2$mim]Cl]$_0$ = 1000 mg L^{-1}; [catalyst] = 2 g L^{-1}; [H$_2$O$_2$]$_0$ = 4300 mg L^{-1}; pH$_0$ = 3; T = 90 ºC, t = 4 h).

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