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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 H_2O_2 consumption, by increasing the temperature is necessary to avoid high reaction times and the need of large excess of H_2O_2. In this work, temperatures within the range of 70-90 ºC have been used, which allowed an effective breakdown of the ILs tested (1 $g \cdot L^{-1}$ initial concentration) with the stoichiometric amount of H_2O_2 and a relatively low Fe^{3+} dose (50 $mg \cdot L^{-1}$). 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.

1. Introduction

Room temperature ionic liquids (ILs) are a novel, broad class of semi-organic salts or salt mixtures that are liquid below 100 ºC. 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. (2008)[11] pointed out that the low vapor pressures of ILs are not enough to justify 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 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 (2006)[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 (Fe^{2+}/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 ($[IL]_0 = 1$ mM; $[Fe^{3+}]_0 = 1$ mM; $[H_2O_2]_0 = 400$ 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-methypyridinium 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 sodium phosphate dibasic heptahydrate (>99.9%) were purchased from Sigma-Aldrich. Iron (III) nitrate nonahydrate (98%), sodium chloride (99.5%), sodium hydroxide (>98%) and phosphoric acid (85%) 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 $g \cdot L^{-1}$ and the theoretical stoichiometric amount of H_2O_2 for complete mineralization was used in all the experiments (3900, 5000, 5500 and 6000 $mg \cdot L^{-1}$ H_2O_2 for [emim][Cl], [bmpyr][Cl], [tbN][Cl] and [tbP][Cl], respectively). The Fe^{3+} dose was varied within the range of 10 to 125 $mg \cdot L^{-1}$ and temperatures between 50 and 90 ºC were tested. The use of temperatures above the ambient is used in order to increase the efficiency of hydrogen peroxide consumption and reduce the reaction time [20]. As recently demonstrated, working at

temperature higher than the ambient do not imply an extra cost since Fenton process is thermally auto-sustained and even a positive heat balance can result [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 chromatoghraphy-mass spectrometry (LC/MS SQ Agilent 6120) equipped with a quadrupole detector using a Synergy 4 mm Polar-RP 80 $\mathring{A}$ 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 ºC. 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 Shimazdu 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 mM Na_2CO_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 bioluminisence was measured in a M500 Microtox Analyzer (Azur Environmental). The toxicity tests were performed using a range of diluted aqueous solutions (from 0 to 100 percent) of each IL solution or Fenton sample. The light output of the luminescent bacteria was measured and compared with the light output 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 ºC, adjusting the osmotic pressure close to 2% NaCl and pH between 6 and 8. The EC_{50} is defined as the effective nominal concentration (mg·L^{-1}) that reduces the intensity of light emission by 50% after 15 min contact time. For complex samples, as Fenton oxidation effluents, IC_{50} is used, defined as the reciprocal of the dilution percentage giving rise to 50% reduction of light emission. The IC_{50} values are inversely proportional to the biological toxicity expressed as toxicity units (TU).

2.5. Biodegradability assays

The biodegradability of the initial IL solutions and the reaction effluents was evaluated by biological batch runs carried out in a liquid static respirometer provided with an air diffuser and a mechanical

stirrer. The specific oxygen uptake rate (SOUR, mg $O_2 \cdot g^{-1}$ VSS$\cdot h^{-1}$) profiles were directly monitored using an oxygen meter (Model 407510, EXTECH). The temperature was controlled by means of a thermostatic bath at 25 °C. An initial biomass (VSS) of 350 mg$\cdot L^{-1}$ was used. The original inoculum was taken from a municipal wastewater treatment plant and was maintained under aeration, with acetate and glucose as carbon sources. The respirometric lasted 48 h and were carried out by triplicate. The data reproducibility was better than ± 5% in all cases.

3. Results and discussion

3.1. Analysis of the operating conditions

Previous works in the literature dealing with Fenton oxidation of ILs have been carried out with large excess of H_2O_2 [21-23]. However, since H_2O_2 consumption is a critical issue for the feasibility of the process it is important to learn more in depth on the true H_2O_2 needs. In this sense, increasing the temperature has demonstrated to allow a more efficient use of the reagent [20, 24, 27].Thus, experiments were performed at different temperatures and catalyst (Fe^{3+}) concentrations maintaining the dose of H_2O_2 at the stoichiometric amount.

Figure 1 shows the results obtained with [emim][Cl] at different temperatures and Fe^{3+} doses, in terms of H_2O_2 conversion (decomposition) and TOC reduction after 4 h reaction time. As observed, the increase of temperature improved the conversion of both H_2O_2 and TOC. This effect is more pronounced when using moderate Fe concentrations (50 mg$\cdot L^{-1}$) which led to practically the same TOC reduction as the highest Fe dose (125 mg$\cdot L^{-1}$) working at temperatures at or above 70 °C. Working at iron doses as low as possible improves the efficiency on the use of H_2O_2 by minimizing competitive scavenging reactions [24, 28, 29]. In addition, it has the obvious benefit of reducing the catalyst consumption, which is lost with the effluent requiring further disposal of the $Fe(OH)_3$ sludge resulting

upon neutralization. However, the use of very low iron concentrations (10 mg·L^{-1}) leads to increased reaction times to achieve acceptable efficiencies. Therefore, we selected 50 mg·L^{-1} as the iron dose for further experiments.

Figure 2 shows the evolution of [emim][Cl], H_2O_2 and TOC upon reaction time, in the oxidation of the IL at different temperatures. It is noteworthy that complete conversion of the IL was reached at all the temperatures tested in very short reaction times (5 min, 3 min and 10 seconds were required at 50, 70 and 90 ºC, respectively), in contrast with the much higher reaction time (90 min) previously reported in the literature at 25 ºC [21]. Similarly, the oxidation rate increased significantly with temperature but beyond 70 ºC the residual TOC became quite similar. The efficiency on the use of H_2O_2, namely the TOC reduction per unit of H_2O_2 consumption (X_{TOC}/X_{H2O2}, %) was considerably improved from 39% at 50 ºC to 57% at 70ºC. No further improvement of that ratio was observed beyond 70 ºC (55% at 90 ºC). Therefore, the temperature for further experiments was set at 70 ºC. Nevertheless, that complete conversion of the starting IL did not imply more than about 60% mineralization, as can be seen in Figure 2.

3.2. Fenton oxidation of ILs from different families

Four ILs were tested corresponding to different families, whose cations were imidazolium, pyridinium, ammonium and phosphonium with chloride as anion in all the cases. Complete conversion of all the ILs was achieved in less than 10 min in the operating conditions of Figure 3. That figure depicts the results obtained after 4 h reaction time, in terms of H_2O_2 conversion, COD and TOC reduction, where significant differences can be seen among the four ILs tested. Although almost complete decomposition of H_2O_2 occurred in all the cases except for the oxidation of [tbP][Cl] ($X_{H2O2} =$ 77%), fairly different percentages of mineralization were achieved, varying from almost 65% for the imidazolium IL to less than 30% for the phosphonium one.

3.2.1. Reaction pathways

To the best of our knowledge, so far the only work dealing with the identification of the by-products from Fenton oxidation of ILs was carried out by Siedlecka et al. (2008b)[22] who studied the oxidation of [bmim][Cl]. These authors reported the formation of different hydroxylated by-products upon the early stages of the process. In the current work, the reaction samples from the experiments performed at all the temperatures tested were analyzed by LC/MS. From the results obtained, the reaction pathways depicted in Figure 4 are proposed on the basis of the *m/z* of the detected compounds. In all the cases, the first step of the oxidation process consisted in the hydroxylation of the IL giving rise to different hydroxylated by-products of higher molecular weight than the starting ILs. Then, ring opening of the imidazolium and pyridinium ILs and breakdown of the ammonium and phosphonium ones took place leading to partially oxidized fragments. Further attack of ·OH radicals to the aforementioned by-products resulted in the formation of organic acids, primarily maleic and fumaric which evolved into malonic, acetic, oxalic and formic. In fact, these are the compounds typically found as final reaction products upon Fenton oxidation of most organic species. These acids are partially oxidized up to CO_2 and H_2O at slow rate, being oxalic and acetic the most resistant [30-32]. It has to be highlighted that all of the aforementioned by-products with the exception of short-chain organic acids were completely degraded upon 4 h at 70 ℃ and 90 ℃. The organic acids represented 60% of the remaining TOC. Their concentrations are collected in Table S1 of Supplementary Data.

3.2.2. Evolution of ecotoxicity

None of the four ILs tested showed high ecotoxicity. In fact, the measured EC_{50} values were fairly high: 4000, 294, 476 and 172 mg·L^{-1} for the imidazolium, pyridinium, ammonium and phosphonium ILs, respectively. The differences on the ecotoxicity values observed between the ring ILs, imidazolium

and pyridinium, are consistent with the results reported by Docherty et al., (2005)[33], who established that the toxicities of imidazolium and pyrinidium were not directly comparable, being [bmim][Br] one order of magnitude less toxic than [bmpyr][Br] upon *Vibrio fischeri* ecotoxicity test. On the other hand, the higher ecotoxicity value displayed by the phosphonium IL is in agreement with the results obtained by Ventura et al. (2012)[34] who established that phosphonium-based ILs are more toxic than the analog imidazolium-based ILs (with the same anion and equivalent alkyl chains).

Oxidation at 50 ℃ led to a moderate increase of the ecotoxicity but at 70 and 90 ℃, negligible values (<0.01 TU) were measured.

3.2.3. Biodegradability

Figure 5 collects the respirometric profiles and the TOC evolution in the biological tests with the starting IL solutions and the corresponding effluents from Fenton oxidation. None of the four ILs tested were degraded upon 48 h biodegradation runs (<5% TOC reduction in all cases). On the opposite, the Fenton effluents (4 h) showed highly susceptible to biodegradation in the cases of the imidazolium and pyridinium ILs and moderately in the two other cases. Docherty et al., (2007)[17] studied the biodegradability of six imidazolium and pyridinium ILs by an activated sludge microbial community, concluding that imidazolium and pyridinium rings are not biodegradable and cannot be mineralized. They observed partial degradation of the side chain but the rings remained intact and were not used as carbon source by the microbial community. Thus, the ring opening accomplished upon Fenton oxidation must be determining for the observed high biodegradability of the resulting effluents.

The higher resistance to biodegradation of the effluents from the oxidation of aliphatic ILs must be associated to the lower COD and TOC removal achieved as well as to the nature of the reaction by-products.

4. Conclusions

Fenton oxidation at 70 °C has proved to be efficient for the breakdown of ILs of four different families, *viz.* imidazolium, pyridinium, ammonium and phosphonium. At that temperature, using the stoichiometric amount of H_2O_2 and a Fe^{3+} dose of 50 mg·L^{-1} allows complete conversion of the starting ILs in fairly short reaction time (> 10 min) with more than 60% TOC reduction after 4 h, except for the phosphonium IL. The resulting effluents showed negligible ecotoxicity values. The scarce biodegradability of the ILs (>5%) was highly improved in the cases of the imidazolium and pyridinium ILs and moderately for the ammonium and phosphonium ones. Reaction pathways have been proposed from the identification of the by-products from Fenton oxidation.

Figure captions

Figure 1. Effect of temperature on H_2O_2 conversion and TOC reduction in Fenton oxidation of [emim][Cl] (1000 mg·L^{-1}) at different Fe^{3+} doses. ($[H_2O_2]_0$ = stoichiometric dose: 4000 mg·L^{-1}; pH_0 = 3; t = 4 h).

Figure 2. Evolution of [emim][Cl] (a), H_2O_2 and TOC (b) upon Fenton oxidation at different temperatures. ($[Fe^{3+}]_0$ = 50 mg·L^{-1}; $[H_2O_2]_0$ = stoichiometric dose: 4000 mg·L^{-1}).

Figure 3. H_2O_2 conversion, COD and TOC reduction upon Fenton oxidation of the ILs tested after 4 h reaction time ($[IL]_0$ = 1000 mg·L^{-1}; $[Fe^{3+}]_0$ = 50 mg·L^{-1}; $[H_2O_2]_0$ = stoichimetric dose; pH_0 = 3; T = 70 ºC).

Figure 4. Proposed reaction pathways for Fenton oxidation of the ILs tested.

Figure 5. Respirometric profiles (circles) and evolution of TOC (squares) in the biological batch runs with the starting ILs solutions (solid symbols) and the effluents from Fenton oxidation in the conditions of Figure 3 (open symbols).

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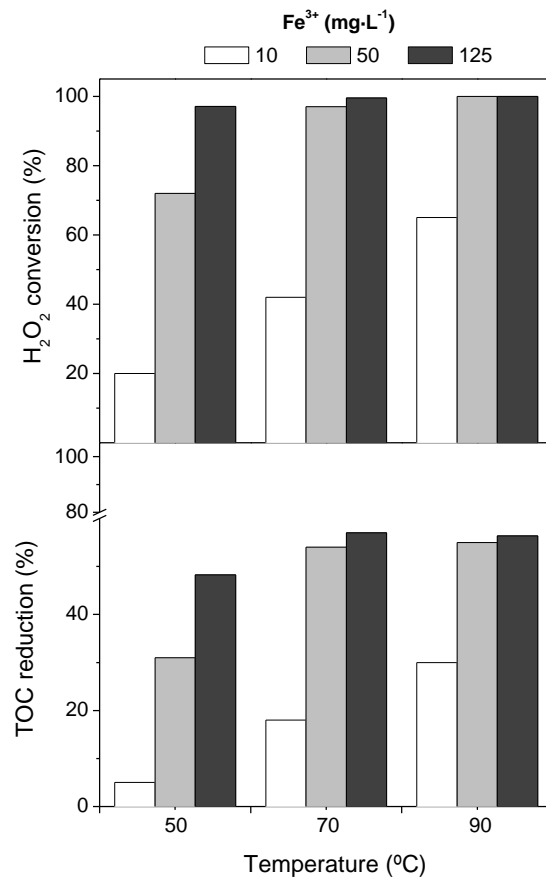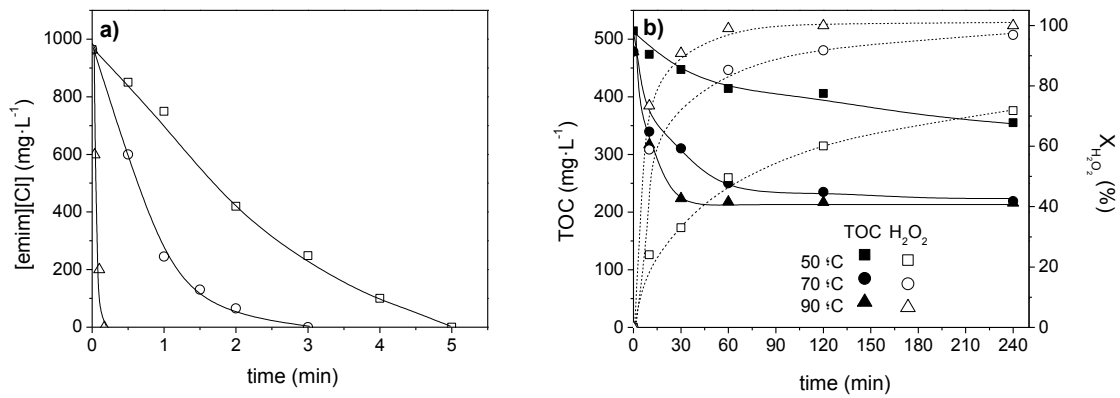
Figure 1

Figure 2

Figure 3
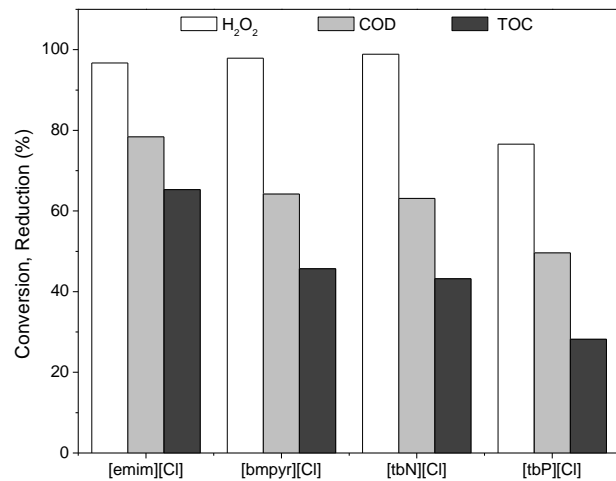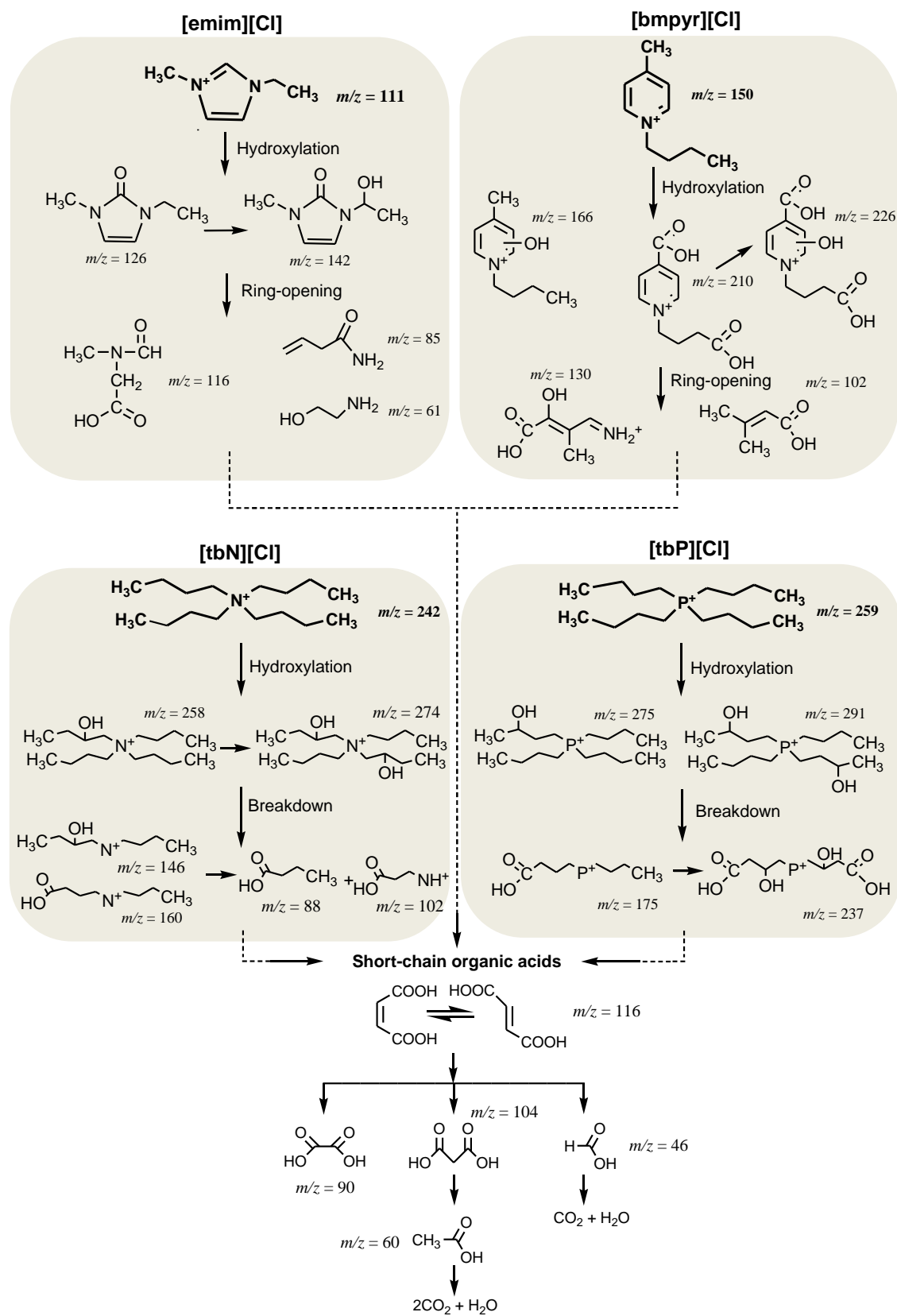
Figure 4

Figure 5