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1 **Removal of imidazolium-based ionic liquid by coupling Fenton and biological**
2 **oxidation**

3

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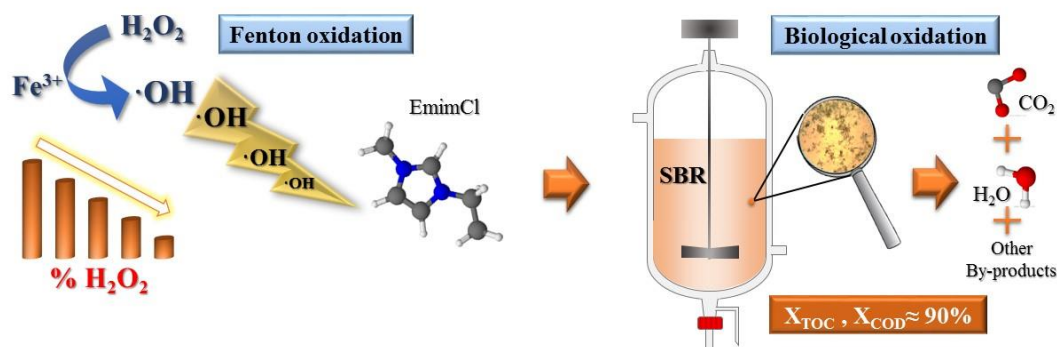
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Abstract

In this work, we assessed the potential of combining Fenton's reagent and biological oxidation for removing the imidazolium-based ionic liquid 1-Ethyl-3-methylimidazolium chloride (EmimCl). Fenton-like oxidation was conducted at variable H_2O_2 doses from 20 to 100% the stoichiometric value as calculated from the theoretical chemical oxygen demand (COD). The stoichiometric H_2O_2 dose afforded Total Organic Carbon (TOC) conversion and COD removal of 50 and 62%, respectively. Identifying the reaction by-products formed at low hydrogen peroxide doses allowed a plausible pathway for EmimCl oxidation to be proposed. The effluents from Fenton-like oxidation at substoichiometric H_2O_2 doses were less ecotoxic and more biodegradable than was the parent ionic liquid. The effluent from Fenton-like oxidation with the 60% H_2O_2 dose (TOC conversion \cong 41%, COD removal \cong 31%) was subsequently subjected to an effective biological treatment that allowed complete removal of the starting compound, increased its ecotoxicity to a low-moderate level and rendered it acceptably biodegradable. Biological oxidation was performed in 8-h and 12-h cycles in a sequencing batch reactor. Combining Fenton and biological oxidation of EmimCl afforded TOC conversion and COD removal of around 90%.

27 Graphical abstract



28 Keywords

29 Biodegradability, biological treatment, ecotoxicity, Fenton-like oxidation, ionic liquid.

30

31 Highlights

32 Fenton-like oxidation was performed at variable H_2O_2 doses.

33 A pathway for the oxidation of EmimCl by Fenton's reagent is proposed.

34 Stoichiometric H_2O_2 doses led to TOC conversion by 50% and COD removal by 62%.

35 Using a H_2O_2 dose 60% provided an effluent amenable to biological treatment.

36 The combined treatment ensured high TOC conversion - COD removal efficiency (>

37 90%).

1. Introduction

Ionic liquids (ILs) are a novel class of room-temperature salts consisting of large organic cations and organic or inorganic anions. In recent years, ILs have aroused increasing attention by virtue of their physicochemical properties, which include non-flammability, high dissolving capacity, extremely low vapor pressure, and thermal and chemical stability [1, 2]. In fact, these compounds are environmentally friendly and widely deemed “green” [3], and hence promising alternatives to volatile organic solvents.

Using a suitable combination of cation and anion cores, and an appropriate alkyl chain length, allows ILs to be converted into “designer solvents” for altering the properties of some compounds [4] (particularly polarity, solubility and hydrophobicity) in order to render them useful for industrial use. Although their low vapor pressure avoids atmospheric contamination, ILs are highly soluble in water and thus pose environmental risks for aquatic media. The efficiency of available biological treatments for IL removal is limited by the poor biodegradability, high stability and, in some cases, toxicity of the liquids [5]. Some authors have examined the ecotoxicity and biodegradability of various IL families, and concluded that their green image is largely unrealistic [6, 7]. For example, only the alkyl side chain of imidazolium-based ILs is biodegradable and not completely [8].

Advanced oxidation processes (AOPs) based on hydroxyl radicals may be an effective choice for removing ILs [9]. One such process, and probably the easiest and most cost-effective, is Fenton oxidation, which uses H_2O_2 and iron salts ($\text{Fe}^{2+}/\text{Fe}^{3+}$) [10], and has proved highly efficient in removing imidazolium, pyridinium, phosphonium and ammonium ILs [11, 12]. Other AOPs including heterogeneous Fenton [13, 14], electrolysis [15, 16, 17], photoelectrolysis [9, 18], photocatalysis [19], electro-Fenton [15, 20] and heterogeneous electro-Fenton [21, 22] have also been successfully used for this purpose.

Imidazolium-based ionic liquids are probably the most widely studied family of ILs. These substances are used as solvents in major chemical processes such as catalysis, synthetic chemistry and separation [23, 24]. So far, the degradation of imidazolium-based

ILs by Fenton oxidation has focused on complete mineralization with a large excess of hydrogen peroxide at room temperature for a long time [25, 26]. Some authors have examined the kinetics of the process, and the influence of operating conditions including the reaction temperature, catalyst load and hydrogen peroxide dose on the oxidation reaction [12, 27, 28].

Various combinations of AOPs and activated sludge treatments have been used in the last decade to reduce the operational cost of removing hazardous pollutants [29, 30, 31]. Sequencing batch reactors (SBRs) are fill-and-draw activated sludge systems widely used to treat municipal and industrial wastewater. SBRs are probably the most suitable choice in this context by virtue of their low room and energy requirements, and also of the ability to process variable organic loads and to alter operational and control strategies [32, 33, 34].

The aim of this work was to assess the potential of a two-step oxidation process (Fenton-like and biological oxidation) for removing the imidazolium-based ionic liquid 1-ethyl-3-methylimidazolium chloride (EmimCl). The optimum hydrogen peroxide dose was established in order to minimize the toxicity and maximize the biodegradability of the effluents from the Fenton-like reaction. A plausible pathway for EmimCl degradation based on the nature of the resulting by-products is proposed. The proposed biological treatment, which is conducted in a sequencing batch reactor, provided effluents of acceptable toxicity and biodegradability.

2. Materials and Methods

2.1. Chemicals

EmimCl (98%) was purchased from Sigma–Aldrich®. Hydrogen peroxide (33 wt.%), hydrochloric acid (37%), iron (III) nitrate nonahydrate (98%) and sodium hydroxide (98%) were purchased from Panreac, all in analytical grade.

2.2. Fenton-like oxidation

Fenton-like runs were performed in 1 L glass reactor at 70 °C, using a stirring rate of 200 rpm for 4 h. The IL, at a concentration of 1 g L⁻¹, was placed in the heated reactor together with variable H₂O₂ doses ranging from the stoichiometric value (viz., the theoretical concentration needed for complete mineralization of the IL, which is 3.9 g L⁻¹ for EmimCl) to 20% that value. Hydrogen peroxide and the iron salt were added simultaneously at the beginning of the oxidation reaction. Adding HCl to the Fe³⁺ solution decreased the pH to about 3, which is the optimum value for Fenton oxidation [35]. As in previous work [12], an Fe³⁺/H₂O₂ ratio of 1/10 (M/M) was used in all assays. Samples were periodically withdrawn, neutralized with NaOH to precipitate Fe³⁺ as Fe(OH)₃ and passed through glass microfiber filters (45 µm, Albert FV-C). Changes in Emim⁺, TOC and H₂O₂ at each H₂O₂ dose used were monitored, and COD, BOD₅ and reaction byproducts present in the effluents after 4 h reaction were determined.

2.3. Inoculum source

The inoculum used to assess biodegradability and feed the SBR was collected from a municipal sewage plant. The activated sludge was placed in an SBR at 25 °C and supplied with sodium acetate and glucose as carbon sources. The medium was supplemented with ammonium sulfate, phosphoric acid and mineral salts as nitrogen and phosphorous sources and micronutrients, respectively. The COD:N:P:micronutrient proportion used was 100:5:1:0.05 (w/w).

2.4. Ecotoxicity tests

The ecotoxicity of the starting IL solutions and the effluents from **Fenton-like** oxidation was assessed with the standard toxicity test based on the luminescent bacterium *Vibrio fischeri* (ISO 11348-3 1998), using a Microtox[®] analyzer from SDI. Ecotoxic effects decreased light emission by the bacterium after incubation at 15 °C for 15 min. Ecotoxicity was defined as the effective concentration or dilution ratio of a sample reducing the initial bioluminescence by 50% and evaluated in terms of EC₅₀ for the starting IL and IC₅₀ for the effluents from **Fenton-like** oxidation.

2.5. Biodegradability tests

The biodegradability of the effluents from Fenton-like oxidation was assessed via the fast biodegradability test [36]. Runs were performed in a 1 L LSS respirometer where the effluents were mixed with biomass (350 mg VSS L⁻¹), stirred and aerated throughout (24 h) [37]. The vessels were placed in a thermostatic bath for temperature control (25 °C). The specific oxygen uptake rate (SOUR, mg O₂ g⁻¹ VSS h⁻¹) was determined by using an oximeter to measure the decrease in dissolved oxygen concentration between two sets of values. TOC was also measured during the experiment.

2.6. Biological treatment

Selected effluents from Fenton-like oxidation were treated by using a 3 L SBR at a controlled temperature (30 °C) at 200 rpm. The SBR was equipped with an air diffuser, peristaltic pumps to feed and unload the reactor, and a dissolved oxygen probe. Each sequence involved the following steps: filling and anoxic stage (0.75–1 h), aeration (6.5–10 h), settling (0.5 h) and drawing (0.25–0.5 h) for cycles of 8–12 h. The biomass concentration was kept at ca. 3.5 g VSS L⁻¹ in order to ensure an organic load rate of 0.18–0.2 kg COD kg⁻¹ VSS d⁻¹. Each selected effluent was used as the sole carbon source, and was supplied with nitrogen, phosphorous and mineral salts for microbial growth. TOC, COD, organic by-products and inorganic nitrogen species were determined in samples withdrawn at the end of the biological treatment and during a whole aerobic step in the biological oxidation process.

2.7. Analytical methods

COD and biomass concentration were determined in accordance with APHA 5220A and 2540E [38], respectively. Biological oxygen demand (BOD₅) was measured with a Velp Scientifica instrument, using the standard procedure APHA 5210 (APHA, 1992), a sample volume of 500 mL and a biomass concentration of 135 mg VSS L⁻¹. Residual hydrogen peroxide was determined by colorimetric titration with titanium

sulfate [39] on a Shimadzu UV-1603 spectrophotometer. Total organic carbon (TOC) and total nitrogen (TN) were measured with a Shimadzu TOC-Vcsh instrument. The ionic liquid was quantified by HPLC at 218 nm on a Varian Prostar 325 instrument equipped with a UV-Vis detector, a Synergy 4 mm Polar-RP 80 A column (15 cm length, 4.6 mm diameter, Phenomenex) as stationary phase and phosphate buffer at a constant flow rate of 0.75 mL min⁻¹ as mobile phase. Short-chain organic acids, nitrate and nitrite were determined by ion chromatography with chemical suppression on a Metrohm 790 IC, using a Metrosep A suppp 2-250 column (25 cm length, 4 m i.d.) as stationary phase and an aqueous solution containing 1 mM NaHCO₃ and 3.2 mM Na₂CO₃ at a constant flow rate of 0.7 mL min⁻¹ as mobile phase. Reaction by-products were detected by HPLC/MS on an Agilent Quadrupole LC/MS using an ACE Excel 3 C-18-amide column (15 cm length, 4.6 mm diameter) as stationary phase and an aqueous solution of formic acid (0.1%) at a constant flow rate of 0.5 mL min⁻¹ as mobile phase for Emim⁺ samples. Mass spectrometry in the ESI⁺ ionization mode was used at a drying gas flow rate of 9 L min⁻¹.

3. Results and discussion

3.1. *Fenton-like* oxidation

Table 1 shows the percent removal of Emim⁺, COD, TOC and TN after 4 h of *Fenton-like* oxidation at different H₂O₂ dose. Complete H₂O₂ removal was achieved for all the experiments, even for the run performed with the stoichiometric dose. As can be seen, complete removal of Emim⁺ was accomplished with H₂O₂ doses above 60% the stoichiometric value. TOC conversion and COD removal barely reached 50% and 62%, respectively, at the stoichiometric H₂O₂ dose despite complete decomposition of H₂O₂. This was a result of some by-products, mainly short-chain organic acids resisting mineralization and constituting a refractory TOC fraction. The neutralization of the effluents from EmimCl oxidation formed iron flocs (Fe(OH)₃) which were removed by filtration. A slightly organic matter removal by coagulation/adsorption was observed (less than 3% for the run performed with the stoichiometric H₂O₂ dose). COD, TOC and TN

conversion decreased with decreasing concentration of H_2O_2 from 100% to 20% the stoichiometric value. Using overstoichiometric doses of H_2O_2 led to no improvement in TOC removal [26] or oxidation efficiency [35] in previous studies. Gomez-Herrero et al. [11] examined Fenton-like oxidation in other imidazolium- and pyridinium-based ILs and obtained similar conversion values. The results provided by substoichiometric H_2O_2 doses confirm the presence of recalcitrant by-products that could not be removed and constituted the refractory TOC fraction. Also, using low substoichiometric doses of H_2O_2 in the chemical oxidation can cause the formation of by-products even more toxic and recalcitrant than the parent IL. By contrast, using medium H_2O_2 substoichiometric doses produces highly oxidized by-products and effluents that are more biodegradable and less ecotoxic while saving reagents and obtaining effluents amenable to biological treatment.

Figure 1 shows a potential pathway for EmimCl degradation by Fenton-like oxidation. HPLC/MS analysis of effluents obtained at low H_2O_2 doses revealed the presence of hydroxylated compounds of greater molecular weights than the starting IL. Hydroxylation of the IL was thus assumed to be the first oxidation step. By-products formed in this step were identified in a supplementary test with an H_2O_2 dose 10% the stoichiometric value. The test revealed the presence of another compound with $m/z = 154$ and a hydroxylated one with $m/z = 155$ that was detected at low H_2O_2 doses. Based on this result, hydroxyl radicals were not selective for the target pollutant. As the H_2O_2 dose was raised, attack by hydroxyl radicals led to partially oxidized by-products with different breaks in the alkyl-chain at m/z values of 98, 97 and 82. The last oxidation steps involved cleavage of the imidazolium ring (peaks at $m/z = 87$, $m/z = 73$ and $m/z = 59$) and the formation of short-chain organic acids. These by-products were oxidized to products such as CO_2 and H_2O , together with NO_x species such as NO and NO_2 [15].

The by-products formed by imidazolium-based ILs in advanced oxidation processes (AOPs) have been studied in some detail. Thus, Siedlecka et al. [40] found electrocatalytic oxidation of 1-butyl-3-methylimidazolium chloride to give intermediates with $m/z = 82$ and $m/z = 154$. Also, Pieczyska et al. [41] detected further compounds at

$m/z = 155$ in the electrochemical decomposition of imidazolium and pyridinium ILs. Garcia-Segura et al. [15] also identified a compound at $m/z = 97$ in the photoelectron-Fenton and anoxic oxidation of EmimCl, and Calza et al. [42] proposed a novel pathway for the photocatalytic transformation of imidazolium-based ILs. The presence of previously unidentified compounds (**Fig. 1**), and the wide variety of compounds found by other authors, have improved existing knowledge about advanced oxidation processes involved in the degradation of imidazolium ILs.

Figure 2 shows the concentration of short-chain organic acids in the effluents from Fenton-like oxidation of EmimCl with variable H_2O_2 doses. The concentration of formic acid, which was the main short-chain organic acid detected, peaked at 300 mg L^{-1} with a 40% H_2O_2 dose. By contrast, that of malonic acid was virtually negligible at H_2O_2 doses below 60% the stoichiometric value but increased with increasing oxidant dose, and that of fumaric acid was almost zero whichever the dose. The concentrations of acetic and oxalic acid were constant at H_2O_2 doses above 60% the stoichiometric value. Oxalic acid, which was previously deemed recalcitrant to Fenton oxidation [43], exhibited no substantial changes in concentration with increasing H_2O_2 dose.

Figure 3 shows the TOC and TN values obtained as short-chain organic acids and inorganic nitrogen species, respectively. The effluent from Fenton-like experiment with a stoichiometric H_2O_2 dose exhibited about 40% TN removal. The nitrogen balance was invariably incomplete, possibly because of the formation of NO_x species in the gas phase [44, 45] and of chloramines in the liquid phase [44]. TOC conversion was related to H_2O_2 dose and amounted to 50% with the stoichiometric value. As can be seen in **Fig. 3**, the unidentified fraction of TOC and TN decreased as the H_2O_2 dose was raised. To the best of our knowledge, knowing the structure of the compounds present in the effluents allows the C:N ratio to be estimated by comparing the starting compound and the oxidation effluents. The estimated C:N ratio for EmimCl was 3. Therefore, the C:N ratio for the effluent obtained at the stoichiometric H_2O_2 dose was ca. 2, which suggests easy degradation of the alkyl-chain and greater resistance of the imidazolium ring [8].

Figure 3 also shows the variation of the biodegradability index (BOD_5/COD). Increasing the H_2O_2 dose led to more biodegradable effluents. This result was ascribed to a decrease in COD since BOD_5 requirements were only slightly increased at low H_2O_2 doses. However, the index levelled off at an H_2O_2 dose 60% the stoichiometric value as a result of a similar increase in BOD_5 and COD. Therefore, the most biodegradable effluent was that from **Fenton-like** oxidation with an H_2O_2 dose of 60%, which had a higher BOD_5 value than the other effluents.

Ecotoxicity, measured as IC_{50} , decreased with increasing degree of oxidation. In fact, the highest ecotoxicity values (7.81 and 14.35%) were obtained at low H_2O_2 doses (viz., 20% and 40%, respectively, the stoichiometric value). These results suggest that the oxidation by-products were more ecotoxic than the starting compound ($EC_{50} = 1860 \text{ mg L}^{-1}$ versus an insubstantial value), which is consistent with previous results of Munoz et al. [12]. However, the effluents from **Fenton-like** oxidation with H_2O_2 doses exceeding 60% the stoichiometric value reached IC_{50} levels close to 100% as a result of the presence of more biodegradable intermediates that were not toxic enough for further biological treatment. Gomez-Herrero et al. [11] also found more ecotoxic effluents at lower reactant doses and non-ecotoxic effluents with the stoichiometric H_2O_2 dose in other imidazolium (HmimCl) and pyridinium ILs (BmpyrCl) subjected to Fenton oxidation ($EC_{50} = 50.2 \text{ mg L}^{-1}$ for the former and 35 mg L^{-1} for the latter). These results are consistent with the widely accepted assumption that ecotoxicity increases with increasing length of the alkyl chain [46, 47].

Figure 4 compares the time course of SOUR and TOC/TOC_0 in the effluents with a high biodegradability index (i.e., a high BOD_5/COD ratio), which were those obtained with an H_2O_2 dose of 60 or 100% the stoichiometric value, and in that from **Fenton-like** oxidation with 40% the stoichiometric dose, which had a low BOD_5/COD ratio. TOC decay was consistent with the respirometric profiles, with an initial maximum due to activation of the sludge by oxidation of easily biodegraded compounds (short-chain organic acids) present in all effluents. The additional slight increase in SOUR from the middle of the test with the 60 and 100% doses was ascribed to need of the biomass to

acclimate to partially biodegraded compounds in the effluents since their removal decreased TOC. In contrast, the effluent from **Fenton-like** oxidation with the 40% dose exhibited no significant decrease in TOC after the first few hours owing to the scarcity of short-chain organic acids.

The effluent from **Fenton-like** oxidation with the 60% H_2O_2 dose was thus selected for subsequent biological treatment because it allowed exhibited complete removal of the starting IL and efficient enough TOC removal as confirmed by its moderate ecotoxicity and acceptable biodegradability. Using the 60% H_2O_2 dose substantially reduced consumption of Fenton reactants and improved the oxidation efficiency relative to the stoichiometric value.

3.2. Biological oxidation

Figure 5a shows the variation of TOC and COD during the biological treatment of **Fenton-like** effluent in an SBR, as well as the corresponding conversions over several cycles. Sludge acclimation for 10–15 days was needed for organic matter to be degraded to an acceptable extent. Using 8-h cycles led to accumulation of by-products in the SBR, and also to TOC and COD values up to 355 mg L^{-1} and $654 \text{ mg O}_2 \text{ L}^{-1}$, respectively, in the reactor. Once the sludge acclimated to the reactor, new organic matter fed was efficiently degraded in each 8-h cycle and previously accumulated matter for the first 15 days of operation was gradually reduced. Once biological oxidation reached a steady state after 30 days, cycle length was increased to 12 h in order to improve the efficiency of the process while keeping the organic load rate at $0.18\text{--}0.2 \text{ kg COD kg}^{-1} \text{ VSS d}^{-1}$. The longer cycles led to increased TOC conversion and COD removal (52 mg L^{-1} and $124 \text{ mg O}_2 \text{ L}^{-1}$, respectively). Coupling a chemical oxidation reaction and a biological treatment thus led to increased overall TOC and COD conversions in the region of 90%. Residual TOC and COD were assigned to the presence of non-biodegradable by-products and refractory microbial products released by cell lysis of active sludge [33].

An additional experiment performed with the effluent from **Fenton-like** oxidation of EmimCl with an H_2O_2 dose 40% the stoichiometric value was conducted in order to

examine the response of the active sludge to more ecotoxic and less biodegradable effluents. As can be seen in **Fig. 5b**, no TOC or COD conversion was observed during the acclimation stage, which suggests the absence of biodegradation in the effluent. Subsequently, TOC and COD conversion increased more gradually, which suggests degradation of organic matter in the SBR, albeit to an inadequate extent for acceptable performance. The sludge may have had an inhibitory effect involving no breakage of cell walls since no increase in carbon content in the reactor was observed.

TOC, COD, and the concentrations of nitrogen inorganic species and short-chain organic acids, during the 12-h cycle were measured after SBR operation reached a steady state with the effluent from **Fenton-like** oxidation at the 60% H₂O₂ dose. As can be seen in **Fig. 6a**, TOC and COD decreased very markedly in the first hour of the cycle (viz., at the anoxic stage, which extended to the start of the aerobic stage). An identical trend was observed with short-chain organic acids, with especially pronounced removal of acetic and formic acid that resulted in substantial biomass activity (**Fig. 6b**). The nitrate and nitrite concentrations decreased in the anoxic stage of the SBR cycle, and then increased during the aerobic reaction (**Fig. 6c**). Hence, removal of the organic matter in this stage may have resulted from heterotrophic denitrification, where organic compounds are used as electron donors to reduce nitrate [32]. Biological oxidation successfully removed all ammonium present in the influent, which came from the nitrogen supply used to maintain the sludge. Nitrate and nitrite were produced during the aerobic reaction through the uptake of oxygen by nitrifying bacteria, which can oxidize ammonium to NO₃⁻ and NO₂⁻ ions. Alternately using anaerobic and aerobic conditions is a major advantage of SBR over other, conventional biological systems [48]. This is specifically the case with wastewater containing oxalic acid, which is poorly biodegradable [49]. Acclimation of the active sludge to biological oxidation in the SBR cycles facilitated the removal of by-products such as short-chain organic acids present in the effluents from **Fenton-like** oxidation of EmimCl.

4. Conclusions

Coupling **Fenton-like** and biological oxidation of EmimCl was found to provide substantial advantages. Thus, **Fenton-like** oxidation produced effluents containing substantial concentrations of short-chain organic acids, as well as aromatic and unidentified compounds of lower ecotoxicity and significantly higher biodegradability than the parent compound. Biodegradability and toxicity tests proved useful to select the optimum dose of H₂O₂ for the chemical oxidation step. Using a H₂O₂ dose 60% of the stoichiometric value in the **Fenton-like** oxidation of EmimCl provided an effluent amenable to the combined treatment. Aerobic oxidation of effluents from **Fenton-like** oxidation of EmimCl resulted in COD and TOC conversions around 90% with the combined treatment, and also in decreased concentrations of aromatic by-products and short-chain organic acids present in the effluents.

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504 **Table 1.** Percent Emim⁺, COD, TOC and TN conversion by Fenton-like oxidation at
 505 different substoichiometric H₂O₂ doses.

H ₂ O ₂ (% stoic.)	Emim ⁺	COD	TOC	TN
20	92	23	15	7
40	96	29	22	19
60	> 99	41	31	29
80	> 99	57	43	34
100	> 99	62	50	41

506

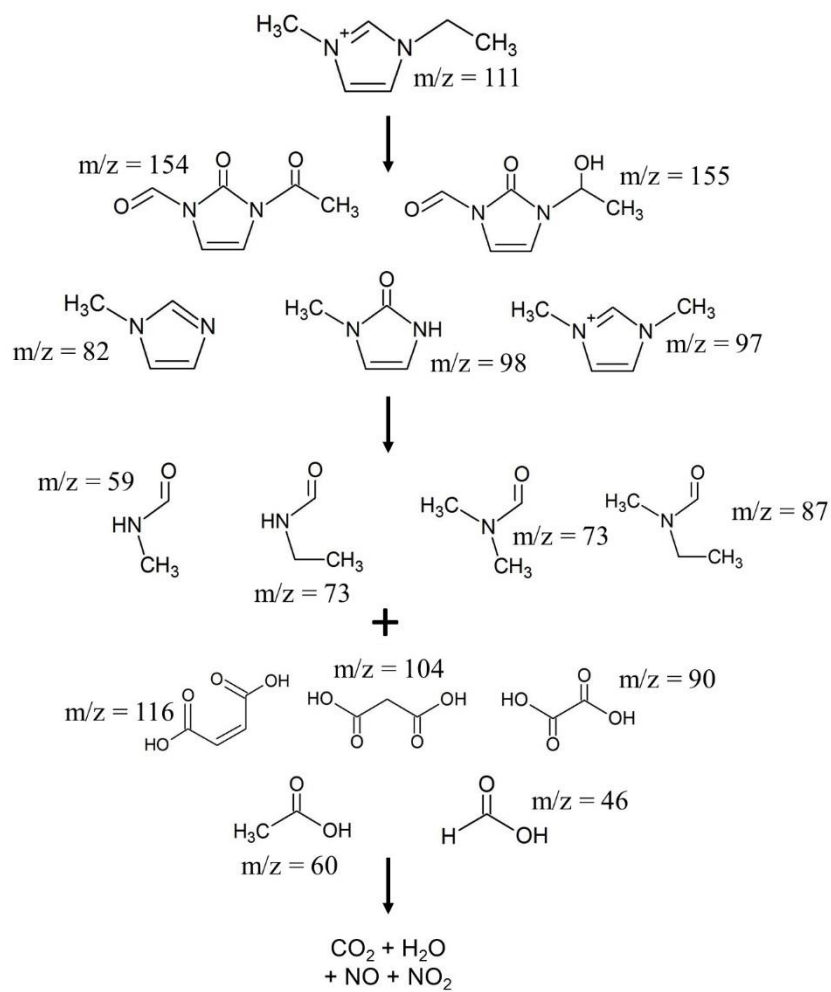
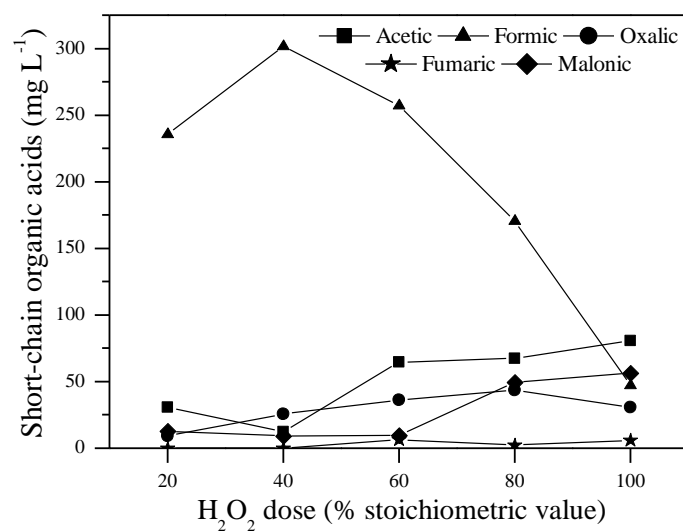
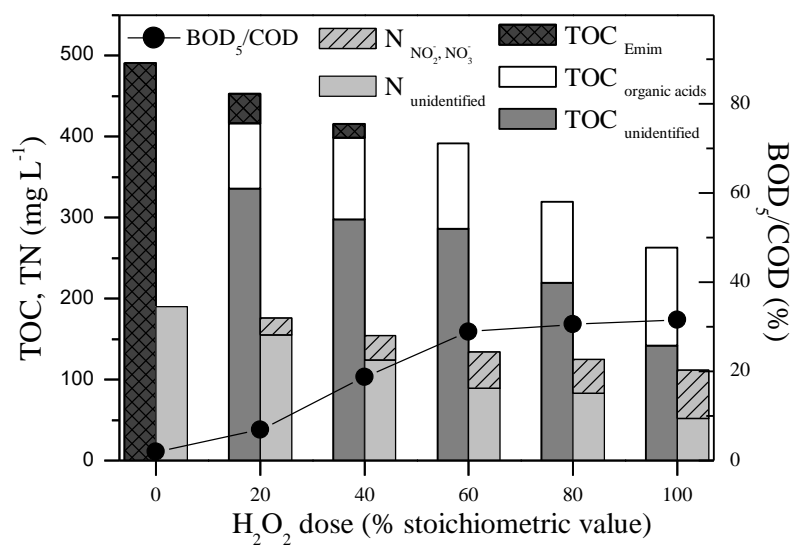


Fig. 1. Proposed pathway for EmimCl oxidation by Fenton's reagent.



509

510 **Fig. 2.** Concentrations of short-chain organic acids in the effluents from [Fenton-like](#)
 511 oxidation at different substoichiometric doses of H₂O₂.



512

513 **Fig. 3.** BOD₅/COD ratio, and measured and unidentified TN and TOC balance closure,
 514 in effluents from Fenton-like oxidation at different substoichiometric H₂O₂ doses.

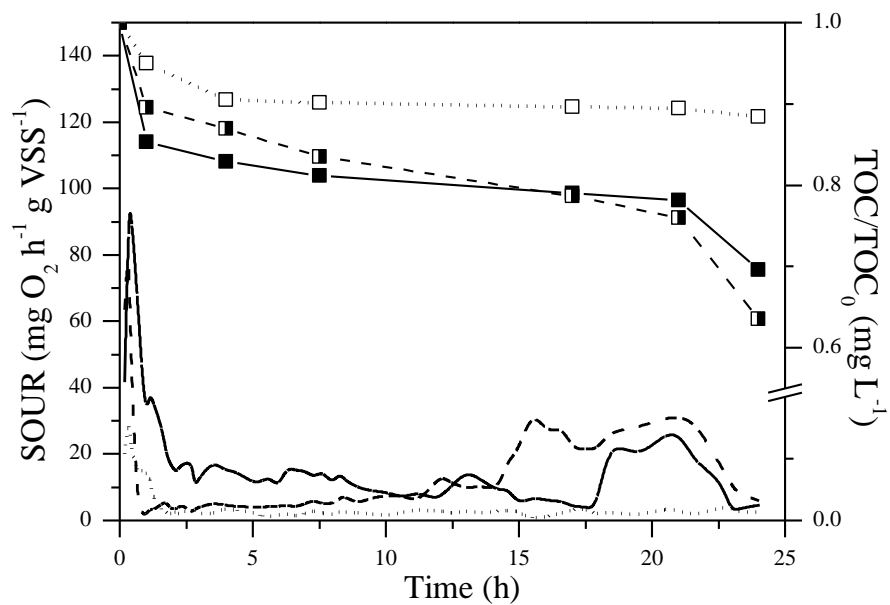


Fig. 4. Variation of SOUR (solid lines) and TOC (symbol lines) during the respirometric test of effluents from Fenton-like oxidation at different H₂O₂ doses: 100% (solid lines), 60% (dashed lines) and 40% (dotted lines).

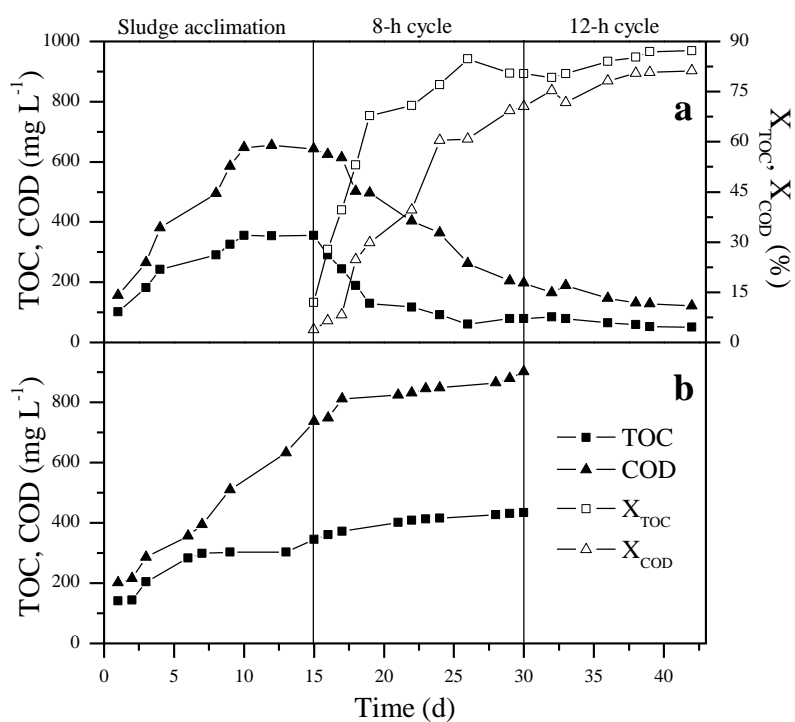


Fig. 5. Time course of organic matter (as TOC and COD) upon biological oxidation in SBR cycles of 8-h (days 15 to 30) and 12-h (days 31 to 42) for the effluents from Fenton-like oxidation at an H₂O₂ dose of 60 % (a) and 40 % the stoichiometric value (b).

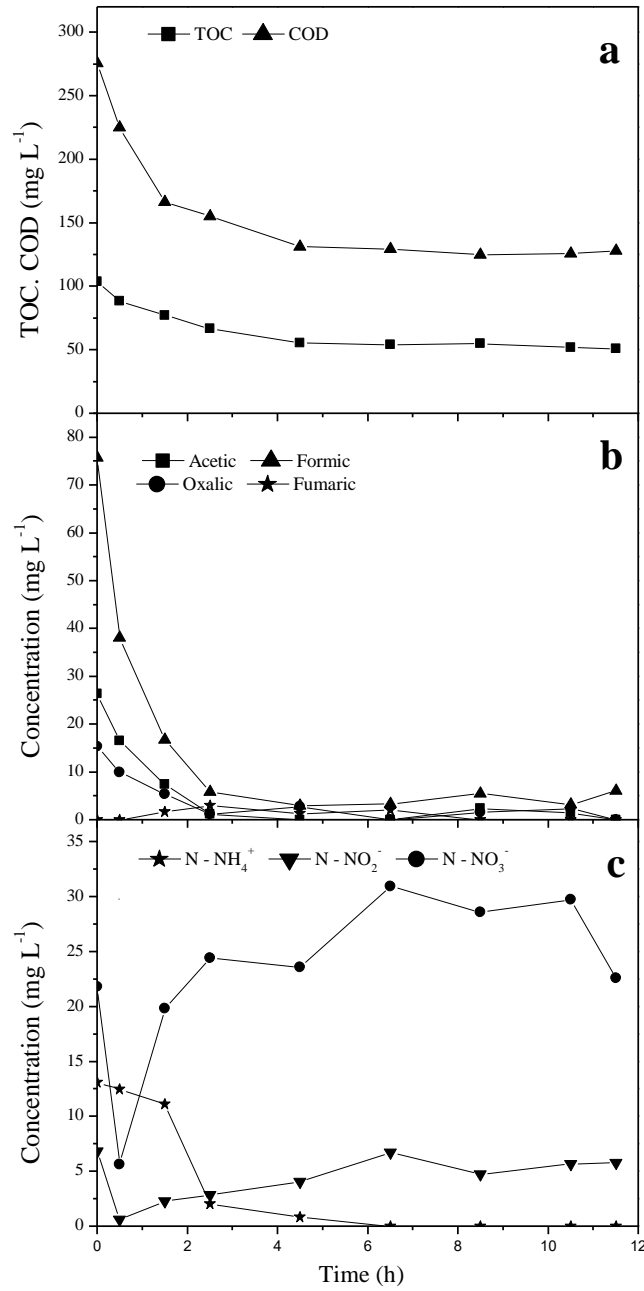


Fig. 6. Time course of TOC, COD (a), short-chain organic acids (b) and nitrogen inorganic species (c) over a 12-h SBR cycle with the effluents from Fenton-like oxidation using an H₂O₂ dose of 60% the stoichiometric value.