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Factors that influence the degradation of 1-ethyl-3-methylimidazolium hexafluorophosphate by Fenton oxidation†

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Stable and anti-biological ionic liquids are difficult to degrade in wastewater. Classical Fenton oxidation has been proved to be an efficient treatment for the degradation of various toxic organic pollutants in aqueous solution. However, its oxidizing ability to degrade short-chain and hydrophilic ionic liquid has not been carefully evaluated. In this work, batch experiments were carried out to investigate systemically the role of pH, temperature, substrate concentration, hydrogen peroxide and ferrous levels, as well as coexisting halogen anions and small molecular organic acids in the degradation of 1-ethyl-3-methylimidazolium hexafluorophosphate ([C_2mim][PF_6]). Optimum condition occurred at starting conditions of pH 3.0, 5 mmol L^{-1} Fe(II) dosage and 20 mmol L^{-1} H_2O_2 concentration at 313 K. Under such conditions, the degradation efficiency of 2 mmol L^{-1} [C_2mim][PF_6] concentration is up to 89.4%. Coexisting halogen anions (F^-, Cl^- and Br^-) and organic acids (acetic, oxalic and citric acids) significantly inhibited the degradation efficiency of Fenton oxidation. The influence of counter anions was also investigated. Finally, the mineralization of [C_2mim][PF_6] after 120 min in Fenton system was detected and some possible intermediates were deduced.

1. Introduction

Ionic liquids (ILs), are a series of ionic chemicals with the structure of large-volume organic cations together with small-volume inorganic anions, which have a melting point near room temperature. Their extended liquid-state temperature range provides high thermochemical stability and solvent miscibility. These properties make ILs useful for organic synthesis, green catalysis, electrochemistry, extraction and separation processes.[1,2] Large-scale industrial application will inevitably cause the release of ILs-containing water into the environment, thereby threatening the surrounding ecosystems.[3,4]

ILs exhibit weak adsorption to soil particles and the poor biodegradability in the environment.[5–8] They are also resistant to direct photodegradation, especially for the long alkyl substituent imidazolium species, whose degradation rate is less than 15% after 360 min of UV irradiation.[1] Electrochemical degradation is an effective way to remove the ILs and the mineralization efficiency of imidazolium cations can be high up to 97%.[9] However, the high energy consumption and operating expenses prohibit industrial application. Therefore, it is necessary to develop economic ways to effectively remove the ILs contaminants from the environment.

Fenton is a mature advanced oxidation process, which has been successfully applied in aqueous solution for degrading various organic pollutants such as acetaminophen,[10] azo dye,[11] *p*-nitroaniline,[12] 2-chlorophenol,[13] cosmetic[14] as well as waste activated sludge containing steroid estrogens.[15] The classical Fenton reagent is comprised of aqueous mixtures of ferrous iron as catalyst and hydrogen peroxide as oxidant. It can produce powerful and non-selective oxidizing agent-hydroxyl radicals ($^{\bullet}OH$) at normal temperature and atmospheric pressure. The hydroxyl radical has a high electrode potential (2.80 V) and exhibits high reaction rates compare with other conventional oxidants such as Cl_2, O_2, O_3, hydrogen peroxide or $KMnO_4$.[16] The hydroxyl radical can rapidly decompose the organic pollutants into harmless inorganic materials, such as carbon dioxide and water. The mechanism of classical Fenton process is generally explained as follows[12,17]

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \ (k_1 \approx 76\ M^{-1}\ s^{-1}) \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \ (k_2 \approx 0.01\text{–}0.02\ M^{-1}\ s^{-1}) \quad (2)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^- + Fe^{3+} \ (k_3 = 4.3 \times 10^8\ M^{-1}\ s^{-1}) \quad (3)$$

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$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \ (k_4 = 3.3 \times 10^7\ M^{-1}\ s^{-1}) \quad (4)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \ (k_5 = 5.3 \times 10^9\ M^{-1}\ s^{-1}) \quad (5)$$

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow \text{further oxidation} \quad (6)$$

Recently, Fenton technologies have been applied to degrade ILs. It was found that the oxidation efficiency of ILs was structure-dependent and related to the *n*-alkyl chain length substituted on imidazolium ring.[18] In addition, imidazolium-based ILs with different counter ions showed different degradation efficiencies. For example, the observed degradation rates of 1-butyl-3-methylimidazolium ranked as $CF_3SO_3^- > C(CN)_3^- > Cl^-$ (ref. 19) and $[CH_3SO_3]^- > [CH_3SO_4]^- > Cl^- \gg [CH_3CO_2]^-$.[20] Moreover, the operation conditions and aqueous chemical parameters may also influence on ILs degradation by Fenton process. The dose of H_2O_2 and Fe(II)/Fe(III) affected the rate and efficiency of ILs degradation.[21] At the stoichiometric H_2O_2 ratio, 60% mineralization of ILs was achieved.[20] A high degradation rate constant was observed in weak acid solution but was inhibited at a very low pH.[21] Additionally, increased temperature accelerates the degradation conversion of TOC.[22] To date, most of studies focused on the degradation of long alkyl chain imidazolium-based ILs ($n \geq 4$), the optimal condition parameters for short-chain imidazolium-based ILs ($n = 2$) was not fully investigated.

In this work, the degradation of 1-ethyl-3-methylimidazolium hexafluorophosphate ($[C_2mim][PF_6]$), a hydrophilic IL with short side alkyl chain, was performed under different environmental conditions, such as different H_2O_2/Fe(II) ratios, substrate concentrations, solution pH, temperatures, in presence of different ions/organic acids and different counter anions. The goal of this work is to comprehensively explore factors affecting degradation of short-chain ILs by Fenton oxidation in aqueous solution, to optimize the Fenton degradation process, and then to realize a rapid and economic Fenton degradation for highly soluble short-chain ILs.

2. Materials and methods

2.1 Chemicals

The five tested ILs: 1-ethyl-3-methylimidazolium hexafluorophosphate ($[C_2mim][PF_6]$, purity > 98%), 1-ethyl-3-methylimidazolium acetate ($[C_2mim][CH_3COO]$, purity > 98%), 1-ethyl-3-methylimidazolium trifluoroacetate ($[C_2mim][CF_3COO]$, purity > 98%), 1-ethyl-3-methylimidazolium methanesulfonate ($[C_2mim][CH_3SO_3]$, purity > 98%), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[C_2mim][CF_3SO_3]$, purity > 98%) were purchased from Shanghai Chengjie Chemical Co. Ltd. (China). Hydrogen peroxide (30%, w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), isopropyl alcohol, sulfuric acid, sodium hydroxide, sodium sulfite anhydrous, sodium chloride, sodium fluoride, sodium bromide, acetic acid, oxalic acid and citric acid were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All chemicals used were of analytical grade without any further purification. Deionized water was used throughout this study.

2.2 Experimental procedures

The $[C_2mim][PF_6]$ solution of different concentrations were prepared with deionized water and homogenized by stirring until completely dissolving. The pH of the reaction mixture was adjusted by adding 25% (v/v) sulfuric acid or 1 mmol L^{-1} sodium hydroxide. The reaction began with the addition of necessary quantities of Fe(II) and H_2O_2 in the $[C_2mim][PF_6]$ solution. The Fenton oxidation experiments were carried out using a thermostated batch reactor at an equivalent stirring velocity of 500 rpm. All experiments were conducted at atmosphere pressure and in the dark condition (wrapped with tinfoil). Samples were collected at different reaction times and immediately quenched with isopropyl alcohol (for HPLC analysis)[23] or 0.1 mmol L^{-1} sodium sulfite solutions (for mineralization analysis).

2.3 Analytical methods

The ILs were analyzed by high performance liquid chromatography (Agilent, USA 1200) using a Sepax Mixed-Mode HP-SCX column (4.6 × 150 mm, 5 μm) with a diode array detector (DAD detector) at 218 nm wavelength. The analyses were performed at 30 °C at a flow rate of 0.5 mL min^{-1}, and the separation column was equilibrated with mobile phase until baseline stabilization, at which point the sample injections (10 μL) were made. The mobile phase was acetonitrile (50% v/v) mixed with phosphate buffer (KH_2PO_4/H_3PO_4) and adjusted to pH 3.0.

The measurement of total organic carbon (TOC) and total nitrogen (TN) of samples were carried out by a TC/TN analyzer (TOC-VCPN, Shimadzu, Japan). Each samples were filtered (0.22 μm) and acidified by sulfuric acid before the analysis.

The samples of degradation reaction mixture were extracted with a mixture of benzene/ethyl acetate/ether (2 : 2 : 1),[24] concentrated by rotary evaporator and then analyzed by GCMS-QP2010SE (Shimadzu, Japan) for identification of degradation products under the following conditions: capillary column: HP-5 ms (30 m × 0.25 mm × 0.25 μm); carrier gas: He (1 mL min^{-1}); column oven temperature: 40 °C (2 isotherm); heating rate: 10 °C min^{-1}; final temperature: 250 °C (2 isotherm); injection temperature: 250 °C; injection model: splitless; ionization mode: EI (70 eV); scan mode: full scan (14–310*m*/*z*); interface temperature: 270 °C; ion source temperature: 230 °C; injected volume: 2 μL.

3. Results and discussion

3.1 Effect of initial pH

The effect of solution pH in the wide range of 1.5 to 11.5 on the degradation of $[C_2mim][PF_6]$ is shown in Fig. 1. The optimal degradation efficiency was pH 2.5–3.0. As the solution pH increased from 3.0 to 11.0, the degradation efficiency decreased gradually. This occurred because that the hydrolysis of Fe(II) at alkaline or neutral pH resulted in the precipitation of ferrous and ferric oxyhydroxides. Additionally, the decreased degradation efficiency was also observed at lower pH (<2.5). For example, when pH decreased from 2.5 to 1.4, the degradation

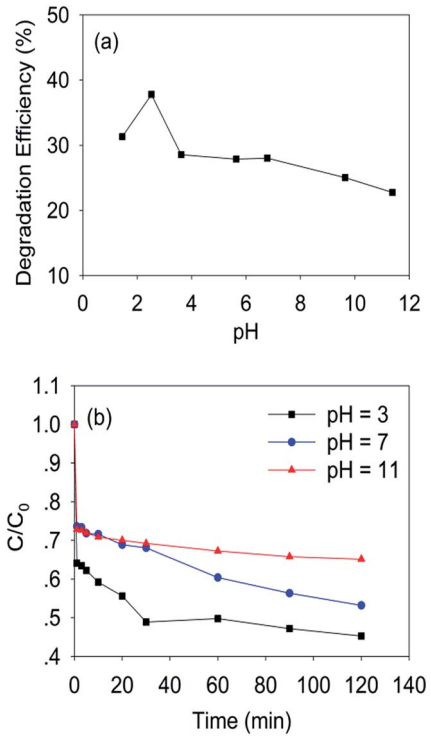

Fig. 1 Effect of pH on (a) the Fenton degradation efficiency of [C_2mim][PF_6] ([H_2O_2] = 20 mmol L^{-1}, [Fe(II)] = 1 mmol L^{-1}, $[IL]_0$ = 2 mmol L^{-1}, 298 K) and (b) the conversion of [C_2mim][PF_6] at different pH. ([Fe(II)] = 2 mmol L^{-1}, [H_2O_2] = 20 mmol L^{-1}, $[IL]_0$ = 2 mmol L^{-1}, 313 K).

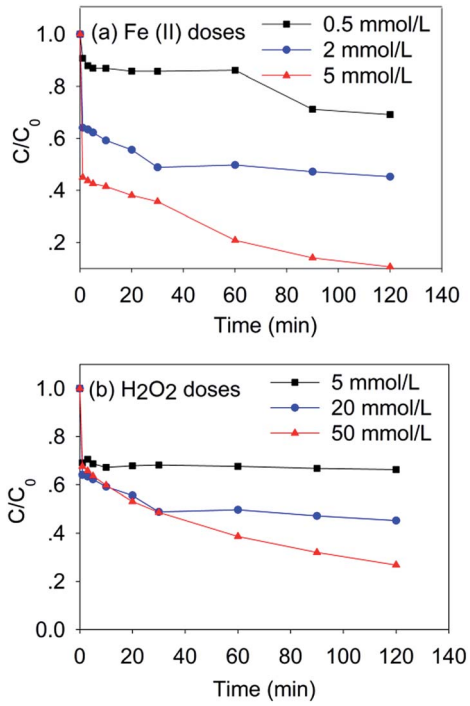

Fig. 2 Conversion of [C_2mim][PF_6] by Fenton oxidation at (a) different Fe(II) doses and (b) different H_2O_2 doses. ($[IL]_0$ = 2 mmol L^{-1}, 313 K, pH = 3).

efficiency of [C_2mim][PF_6] decreased from 37.8% to 31.3%. It was presumably due to the formation of the oxonium ion (*i.e.* $H_3O_2^+$) and complex species of $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$, which are less reactive.[21] Additionally, excessive hydrogen ions in highly acidic solution increase the chance to scavenge hydroxyl radical (˙OH) according to the eqn (7).[12,25]

$$H^+ + OH^{\cdot} + e^- \rightarrow H_2O \quad (7)$$

This result is consistent with many previous studies, where the optimum pH for Fenton oxidation of Reactive blue 19,[26] Direct Blue 71,[11] *p*-nitronaniline,[12] methyl *tert*-butyl ether[27] and 1-butyl-3-methylimidazolium chloride[21] was approximately 3.0. It seems that the pH-dependent Fenton degradation is independent of the substrate types. High degradation efficiencies for a variety of different structure compounds were all achieved at acidic pHs.

3.2 Effect of the initial concentrations of Fe(II), H_2O_2 and [C_2mim][PF_6]

In the Fenton process, the oxidation efficiency of organics is strongly dependent on the addition dosage of both the catalyst [Fe(II)] and the oxidant (H_2O_2). Generally, the more [Fe(II)] and [H_2O_2] added, the faster the degradation rate.[28] Similar observations are found in this experiments. As the Fe(II) concentration increased from 0.5 to 5 mmol L^{-1} (Fig. 2a), the degradation efficiency of [C_2mim][PF_6] increased from 31% to 89% because the increasing concentration of Fe(II) accelerates the decomposition of H_2O_2 and consequently induces higher availability of ˙OH.[13] When the H_2O_2 concentration increased from 5 to 50 mmol L^{-1} (Fig. 2b), the decomposition efficiency increased from 34% to 73%. In general, the more Fe(II) and H_2O_2 doses were added, the more reactive hydroxyl radicals were produced (eqn (1)). However, excess Fe(II) and H_2O_2 will also consume the ˙OH radicals (eqn (3) and (4)) and increase the chance of ˙OH recombination (eqn (5)). In addition, the excess consumption of Fe(II) would cause the formation of large quantities ferric-based sludge, thereby increasing the disposal cost. Munter *et al.*[29] found that the consumption of H_2O_2 contributed 91% of the total cost of Fenton process. Therefore, optimizing the H_2O_2- : Fe(II) ratio is needed to improve the Fenton efficiency and to reduce the total costs.

Different substrate systems showed the different optimal [H_2O_2]/[Fe(II)] ratios (abbr. H_2O_2/Fe). Table 1S† shows the significant difference in H_2O_2/Fe values. For example, the ratio for degrading formic acid is only 1, while the ratio needed to degrade carpet dyeing wastewater is as large as 470 (Table 1S†). The higher value of H_2O_2/Fe is required for the more resistant compounds and produces higher reagent cost. Considering overall removal efficiency and the operation cost, the optimal H_2O_2/Fe molar ratio in this work was chosen as 4, where the concentration of H_2O_2 and Fe(II) are 20 mmol L^{-1} and 5 mmol L^{-1}, respectively.

It was also found that the degradation efficiency of [C_2mim][PF_6] is correlated with its initial concentration (Fig. 3). Fenton oxidation over 2 h contact can degrade 97.1% and 89.4%

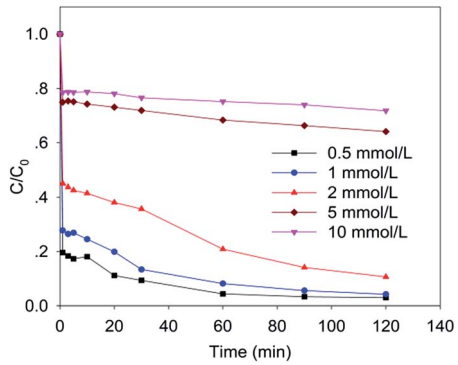

Fig. 3 Fenton oxidation of different concentration $[C_2mim][PF_6]$. ($[Fe(II)] = 5$ mmol L^{-1}, $[H_2O_2] = 20$ mmol L^{-1}, $[IL]_0 = 2$ mmol L^{-1}, 313 K, pH = 3).

low-concentration $[C_2mim][PF_6]$ (0.5 and 2.0 mmol L^{-1}, respectively). As the substrate concentration increased to 5.0 or 10.0 mmol L^{-1}, the degradation efficiencies decreased steeply to 35.9% or 28.2%, respectively. It was concluded that the amount of the hydroxyl radical was insufficient for oxidizing the high concentration substrates. The result is consistent with previous studies.[10,11] Obviously, for lower molar ratio of contaminants to Fe(II) and H_2O_2, greater degradation efficiency is achieved. The result is in agreement with Burbano *et al.*[30] who has showed that the value of Fenton reagents to MTBE molar ratio is an important controlling parameter of the overall MTBE degradation/mineralization efficiency.

3.3 Effect of temperature

The Fenton degradation is strongly affected by the solution temperature. Within 3 min reaction time, the degradation efficiency of $[C_2mim][PF_6]$ is 18%, 37%, 64% and 50% at 298 K, 313 K, 328 K and 343 K, respectively (Fig. 4a). After oxidizing for 60 min, the degradation efficiency reaches to 26%, 50%, 81% and 93%, respectively. The first-order degradation reaction rate constant at 343 K is 18 times greater than that at 298 K (Table 1). It seems that high temperature can increase the efficiency of hydrogen peroxide consumption and reduce the reaction time.

The thermodynamic parameters, Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated to better understand the temperature effect on the degradation of $[C_2mim][PF_6]$ (eqn (8), (9) and Fig. 4b). The activation energy (E) is also calculated according to Arrhenius expression (eqn (10) and Fig. 1S†).

$$\Delta G = -RT \ln K \tag{8}$$

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \text{(Van't Hoff equation)} \tag{9}$$

$$K = A \exp\left(-\frac{E}{RT}\right) \text{or } \ln K = -\frac{E}{RT} + \ln A \tag{10}$$

where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}); T is the reaction solution temperature (K); A is the pre-exponential factor and the K is the equilibrium constant, which is defined

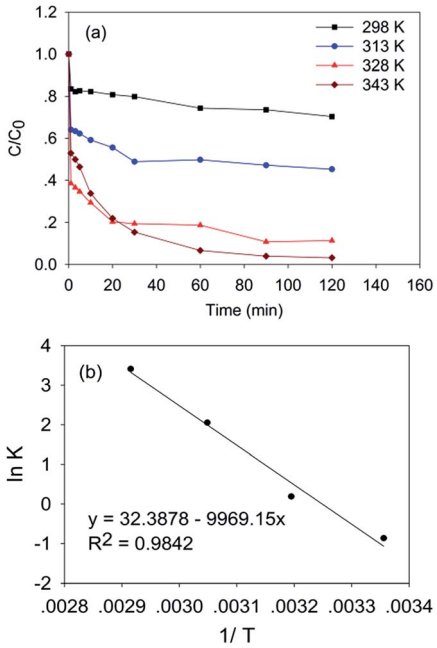

Fig. 4 Conversion of $[C_2mim][PF_6]$ by Fenton oxidation (a) at different temperature and (b) the plot of ln K *vs.* $1/T$ in Van't Hoff equation. ($[Fe(II)] = 2$ mmol L^{-1}, $[H_2O_2] = 20$ mmol L^{-1}, $[IL]_0 = 2$ mmol L^{-1}, pH = 3).

as the ratio of the degraded $[C_2mim][PF_6]$ concentration to the final $[C_2mim][PF_6]$ concentration at equilibrium. As observed in Table 1, the positive ΔG value at 298 K indicates that energy must be supplied to imitate the decomposition reaction. As the temperature increased, the ΔG turns to negative, showing that the oxidation process is spontaneous. The positive ΔH value indicates that the degradation of $[C_2mim][PF_6]$ is endothermic. The positive ΔS value reveals that the increase of randomness during the degradation process, indicating $[C_2mim][PF_6]$ decompose to many small molecular substances. The high activation energy of 56.1 kJ mol^{-1} suggests that Fenton reaction of $[C_2mim][PF_6]$ cannot be initiated easily.

3.4 Effect of coexistence of halogen anions and organic acids

Many inorganic anions existing in water have great influence on the Fenton oxidation of target contaminants. Siedlecka *et al.*[31] studied the inhibition of chloride, phosphate, sulfates and perchlorates to MTBE decomposition in the Fenton process following the sequence of: $ClO_4^- < SO_4^{2-} < Cl^- < H_2PO_4^-$. The adverse effects of chloride and sulfate ions were also found for decolorization of RB19.[26] In this study, the effects of series halogen anions (F^-, Cl^- and Br^-) were examined. After separately introducing 1 mmol L^{-1} F^-, Cl^- and Br^- into solutions and with reaction for 120 min, the Fenton degradation efficiency of $[C_2mim][PF_6]$ fell from 89.4% to 62.7%, 66.4% and 43.4% (Fig. 5a), respectively. It shows that the halogen anions suppress the Fenton process in the sequence of $Br^- > F^- > Cl^-$. The negative effect of coexisting chloride anions results from two aspects (Table 2). One is to form a less powerful oxidizing species in solution by reacting with $^{\bullet}OH$ (*e.g.* $X^- + {}^{\bullet}OH \rightarrow XOH^{-\bullet}$). Another effect is to form complexes with ferric or

Table 1 Thermodynamic parameters for Fenton oxidation of $[C_2mim][PF_6]$. ($[H_2O_2]$ = 20 mmol L^{-1}, [Fe(II)] = 2 mmol L^{-1}, $[IL]_0$ = 2 mmol L^{-1}, pH = 3)

Temp. (K)	Equilibrium constant	Kinetic rate (min^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	E (J mol^{-1})
298	0.4217	0.0014	2.1395	82.88	0.2693	5.61×10^4
313	1.2109	0.0029	−0.4980			
328	7.7796	0.0104	−5.5944			
343	30.25	0.025	−9.7229			

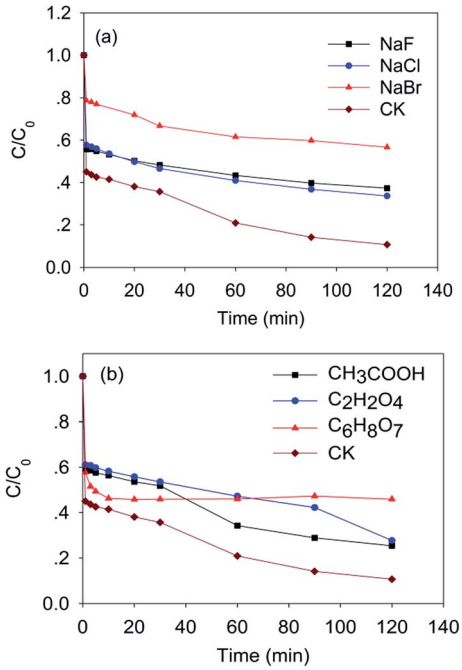

Fig. 5 Conversion of $[C_2mim][PF_6]$ by Fenton oxidation in the presence of (a) halogen anions and (b) organic acids. ($[H_2O_2]$ = 20 mmol L^{-1}, [Fe(II)] = 5 mmol L^{-1}, $[IL]_0$ = 2 mmol L^{-1}, 313 K, pH = 3 [halogen anion] = 1 mmol L^{-1} and [organic acids] = 1 mmol L^{-1}).

Table 2 Additional complex reactions in the presence of some other ions in the Fenton system[a]

Reaction	Constant	Reference
$Fe^{3+} + F^- \leftrightarrow FeF^{2+}/FeF_2^+/FeF_3$	$\sim 10^5/10^5/10^3$ M^{-1}	33
$Fe^{2+} + Cl^- \leftrightarrow FeCl^+$	2.88 M^{-1}	34
$Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+}$	6.61 M^{-1}	34
$Fe^{3+} + Br^- \leftrightarrow$ no complexes	—	35
$Cl^- + OH^\bullet \rightarrow ClOH^{\bullet -}$	4.2×10^9 M^{-1} s^{-1}	34
$ClOH^{\bullet -} \rightarrow Cl^- + OH^\bullet$	6.0×10^9 M^{-1} s^{-1}	34
$Br^- + OH^\bullet \rightarrow BrOH^{\bullet -}$	10^{10} M^{-1} s^{-1}	36
$BrOH^{\bullet -} \rightarrow Br^- + OH^\bullet$	4.2×10^6 M^{-1} s^{-1}	36
$F^- + OH^\bullet \rightarrow FOH^{\bullet -}$	Poor scavengers	33
Oxalate + $Fe^{3+} \leftrightarrow$ Fe(III)(oxalate)	$\beta_1\beta_2\beta_3$: $10^{9.5}$, 10^{16}, 10^{20}	35
Oxalate + $Fe^{2+} \leftrightarrow$ Fe(II)(oxalate)	$\beta_1\beta_2$: $10^{4.5}$, $10^{5.2}$	35
Citric + $Fe^{3+} \leftrightarrow$ Fe(III)(citric)	β_1: 10^{25}	37
Oxalate + $OH^\bullet \rightarrow$ products	3.2×10^8 M^{-1} s^{-1}	38
Citric + $OH^\bullet \rightarrow$ products	1.4×10^6 M^{-1} s^{-1}	38

[a] M^{-1} is the unit of equilibrium constant; M^{-1} s^{-1} is the unit of rate constant; β_n means the stability constant of Fe complexes.

ferrous ions thereby changing the distribution of the iron species and affecting their reactivity with H_2O_2. With the increase of Cl^- in solution, the yield of $^\bullet OH$ declines. When the initial concentration of Cl^- is larger than 200 mM, $Cl_2^{\bullet -}$ instead of $^\bullet OH$ becomes the predominant species in Fenton system.[32] The influence of fluoride ions may be due to their affinity to ferric ion, these ferric–fluoride complexes are catalytically inactive.[33] Although bromide anions do not form complexes with Fe(II)/Fe(III),[35] they have the greatest inhibitory effect, almost halving the degradation efficiency, which is primarily due to the much greater ability of scavenging $OH^\bullet$ (Table 2).

The effect of low-molecular acids on $[C_2mim][PF_6]$ degradation is shown in Fig. 5b. After oxidation for 2 h, acetic, oxalic and citric acids reduced the degradation efficiency of $[C_2mim][PF_6]$ from 89.4% to 74.7%, 72.3% and 54.1% respectively. The inhibitory effect is mainly due to the fast complex formation of ferric and ferrous with organic acids and the competition for hydroxyl radicals with $[C_2mim][PF_6]$ (Table 2). The adverse influence of organic acids is in the sequence of citric > oxalic > acetic. It may be related to the number of carboxyl group in acidic molecules. The strongest inhibition by citric acid is approximately due to the largest stability constant of Fe–citric complex (10^{25})[37] and the much high reaction rate constant with hydroxyl radical (1.4×10^6 M^{-1} s^{-1}).[38]

3.5 Effect of counter anion

The influence of counter anion on Fenton oxidation was conducted by changing PF_6^- with $CH_3SO_3^-$, $CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$. Fig. 6 demonstrates that the degradation efficiency of

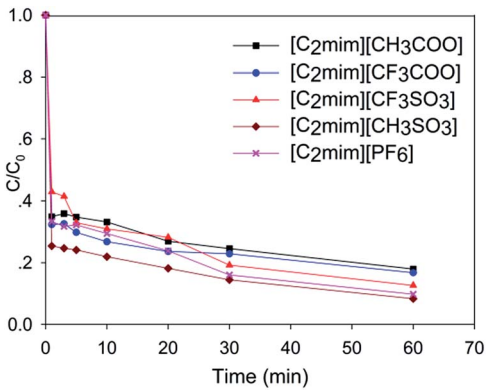

Fig. 6 Influence of the counter anion on the Fenton oxidation of the $[C_2mim]^+$. ($[H_2O_2]$ = 20 mmol L^{-1}, [Fe(II)] = 5 mmol L^{-1}, $[IL]_0$ = 1 mmol L^{-1}, 313 K, pH = 3).

$[C_2mim]^+$ with different counter anions at 60 min fluctuated from −9% to 1.6%, compared with Fenton degradation of $[C_2mim][PF_6]$. It suggests that the general influence of counter anion is not strong. Their degradation efficiencies are sequenced as follows: $CH_3SO_3^- \approx PF_6^- > CF_3SO_3^- > CF_3CO_2^- \approx CH_3CO_2^-$. The acetate and trifluoroacetate anions presented the lowest degradation efficiency, which was 82.1% and 83.2% at 60 min, respectively. It is presumably due to the coordination interactions between iron species and the acetate/trifluoroacetate anions. However, $CH_3SO_3^-$ and $CF_3SO_3^-$ show the negligible effect on Fenton degradation, owing to their poor coordination with iron species.[19]

3.6 Mineralization analysis and preliminary degradation products of $[C_2mim][PF_6]$

The mineralization of $[C_2mim][PF_6]$ is investigated by the TOC and TN measurements. Fig. 7 showed that 51.5%, 38.1%, 32.8% removal of TOC and 50.3%, 51.5%, 48.7% removal of TN after 120 min with the initial IL concentration of 0.5, 1 and 2 mmol L^{-1}, respectively. The removal efficiency of TOC is dependant of the initial substrate dose of $[C_2mim][PF_6]$. With the increase of initial $[C_2mim][PF_6]$ concentration, the removal efficiency of TOC decreases. The result is different from the TN removal experiment, in which TN removal remains stable. It possibly means that the easier oxidation on the substituted alkyl chain of ILs than the N-containing imidazolium ring of ILs. The result of ILs mineralization indicates that hydroxyl radical generated by Fenton reagents can oxidize the organic carbon and the organic nitrogen of ILs to CO_2 and NO_x. The TN removal suggest a state of imidazole-ring-open for the degradation of $[C_2mim][PF_6]$ during Fenton process. However, the ILs mineralization efficiency is lower than the ILs degradation efficiency.

Siedlecka *et al.*[39] found that imidazolones and hydroxyl groups substitute derivatives occurred in the first stage (10 min) of Fenton-like oxidation of $[C_4mim]Cl$. These intermediates would further decompose by ring opening or cleavage of the N–C bond in the *N*-alkyl side chain. But they did not identify these small molecular chemicals. In this work, some Fenton degradation products after 2 h oxidation of $[C_2mim][PF_6]$ are identified *via* the preliminary GC-MS experiment. The possible degradation products includes (a) *N*-methylformamide, (b) *N*-ethylformamide, (c) diethylamine and (d) 1-ethyl-3-methyl-2,4,5-trioxoimidazolidine (Fig. 2S†). The first three products may be the results of the imidazolium ring opening. And the last one is commonly regarded as the first oxidized intermediate of 1-alkyl-3-methyl-imidazolium by plasma electrolysis,[40] H_2O_2/CH_3COOH with ultrasonic irradiation[41] and electro-Fenton treatment.[42] However, not all intermediates were identified due to the poor extraction efficiency and the loss in evaporation. Therefore, the pathways are not deduced in the present study. The further investigation of the degradation products and pathways will be carried on in the next experiments.

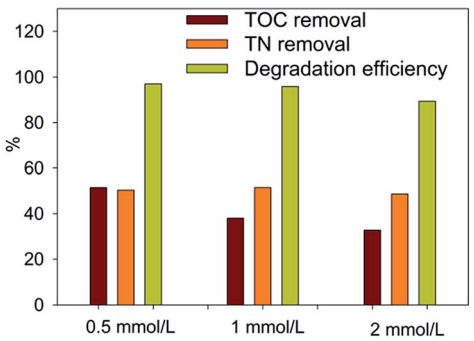

Fig. 7 TOC, TN removal and degradation efficiency with different initial $[C_2mim][PF_6]$ concentration by Fenton oxidation at 120 min. ($[H_2O_2]$ = 20 mmol L^{-1}, [Fe(II)] = 5 mmol L^{-1}, 313 K, pH = 3).

4. Conclusions

Parametric studies were carried out to evaluate $[C_2mim][PF_6]$ degradation in aqueous solution by Fenton oxidation process. The effects of pHs, temperature, dosages of H_2O_2 and Fe(II), initial substrate concentration were assessed by IL removal efficiencies. The optimal reaction conditions were recommended as follows: initial concentration of $[C_2mim][PF_6]$ = 1 mmol L^{-1}, pH = 3.0, temperature = 313 K, Fe(II) dosage = 5 mmol L^{-1}, H_2O_2 dosage = 20 mmol L^{-1}, H_2O_2 to Fe(II) molar ratio = 4. Under these conditions, the degradation efficiency of $[C_2mim][PF_6]$ was larger than 95.8% but only 38.1% TOC removal and 51.5% TN removal achieved. There is a cleavage of imidazolium ring during the Fenton system. The presence of halides (F^-, Cl^- and Br^-) and polycarboxylic acids (acetic, oxalic and citric acids) had a negative impact on the degradation efficiency of Fenton oxidation. The inhibition order is in the sequence of Br^- > citric > F^- > Cl^- > oxalic > acetic. The degradation efficiency of ionic liquid with different counter anions is insignificant. The thermodynamic results implied that the oxidation process was feasible, spontaneous, and endothermic.

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