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Heterogeneous electro-Fenton as plausible technology for the degradation of imidazolinium-based ionic liquids

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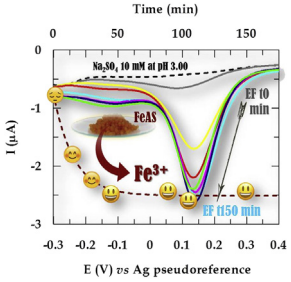
HIGHLIGHTS

- Ionic liquid successfully degraded by electro-Fenton using iron alginate spheres.
- Heterogeneous electro-Fenton (HEF) optimized by Box-Behnken experimental design.
- Current is a crucial parameter in HEF and high catalyst dosage is required.
- Iron and its complexes were monitored by DPV on screen-printed electrodes.
- DPV allowed elucidating the main degradation pathway of [IMes.HCl].

GRAPHICAL ABSTRACT



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ABSTRACT

Conventional water treatments are generally inadequate for degradation of emerging pollutants such as ionic liquids (ILs). The use of heterogeneous electro-Fenton (HEF) has attracted great interest, due to its ability to efficiently oxidize a wide range of organic pollutants operating in cycles or in continuous mode. In this study, the removal of a complex IL from the imidazolinium family (1,3-Bis(2,4,6-trimethylphenyl) imidazolinium chloride), by means of HEF using iron alginate spheres as catalyst has been investigated, resulting in significant TOC decay after 6 h. The optimization of the key process parameters (current, IL concentration and catalyst dosage) has been performed using a Box-Behnken experimental design and achieving 76.98% of TOC abatement in 2 h of treatment. Current proved to be a crucial parameter and high catalyst dosage is required to achieve the maximum removal. In addition, an insight about the availability of iron into the reactor and the evolution of several intermediates has been carried out by employing differential pulse voltammetry on screen-printed carbon electrodes. The evolution of the different voltammetric peaks confirmed the influence of iron release, and the generation of several iron complexes has permitted the comprehension of the degradation pathway, which has been validated by chromatographic techniques.

1. Introduction

Ionic liquids (ILs) are organic salts with low vapor pressure, melting point and flammability that have attracted attention, in

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recent years, as 'green' replacements for industrial volatile compounds in applications such as catalysts, biocatalysts, biotechnology, synthetic chemistry and electrochemistry (Dai et al., 2017). Although they are considered as green solvents due to their low volatility, they are highly water-soluble and chemically and thermally stable. This fact, together with their complex chemical structure, that involves a cationic or anionic polar head group with accompanying alkyl side chains, creates the potential for entry and persistence in the environment (Deive et al., 2011). Kalcikova et al. (2012) compared the ecotoxicity of 1-butyl-3-methylpyridinium dicyanamide to other commonly used solvents, and found it to be toxic to all organisms tested and even more toxic than common solvents. Current data highlights this problem and shows that ILs are toxic in nature and that their toxicities vary considerably across organisms and trophic levels (Egorova and Ananikov, 2014). Therefore, they are considered as "Contaminants on the Horizon" (Richardson and Kimura, 2017).

In this context, processes that could be effective are required to deal with these non-readily biodegradable and toxic pollutants (Pęziak-Kowalska et al., 2017). Several processes as photodegradation, ultrasonic, electrochemical or Fenton (Muñoz et al., 2015; Morandeira et al., 2017; Mena et al., 2018) have been tested in order to degrade different families of ILs contained in water. Table 1 summarizes some recent research on this topic. Among all the degradation techniques, electro-Fenton (EF) process is one of the most known and popular (Sirés et al., 2014). Recently, this process has been evaluated for the removal of ILs; however, to our knowledge, there are only few studies reported in the literature about this issue (Bocos et al., 2016; Garcia-Segura et al., 2016). In EF, the degradation reaction of the anodic oxidation is enhanced by the generation of the hydroxyl radical from the reaction of electrogenerated H_2O_2 with Fe^{2+}, which can be considered as catalyst. Due to the application of electric field, the Fe^{3+} generated in the process is regenerated to Fe^{2+}.

Heterogeneous iron catalyst has a number of benefits, such as it can be easily and effectively recovered from a reaction mixture in a straightforward manner and reused in other cycles or permits the operation in continuous mode, which is an important consideration for industrial manufacturing processes. Nowadays, to perform heterogeneous iron catalyst processes several strategies are leading such as use of iron-based solid particles (pyrite, magnetite, wustite, chalcopyrite) (Barhoumi et al., 2015, 2017; Ouiriemmi et al., 2017) or by hosting on different supports (alginate, sepiolite, kaolinite) (Iglesias et al., 2013; Bocos et al., 2014). In several of these heterogeneous processes, the catalyst is used as iron reservoir for constant dosing of homogenous iron catalyst avoiding the negative effect of the use of high iron concentration. To understand the mechanisms that take place in these heterogeneous processes and

Table 1
Recent research on ILs degradation.

IL	Proc[a]	IL elimination (%)	Mineralization[b]	Ref.
a) 1-Ethyl-3-methylimidazolium chloride (1 g L^{-1}) b) 1-Butyl-4-methypyridinium chloride (1 g L^{-1}) c) Tetrabutylammonium chloride (1 g L^{-1}) d) Tetrabutylphosphonium chloride (1 g L^{-1})	F	100 (<10 min)	TOC/COD decay (4 h): a) 65%/78% b) 45%/64% c) 43%/63% d) 28%/50%	Muñoz et al. (2015)
a) 1-Hexyl-3-methylimidazolium dicyanamide (0.5 g L^{-1}) b) 1-Butyl-3-methylimidazolium dicyanamide (0.5 g L^{-1}) c) 1-Ethyl-3-methylimidazolium dicyanamide (0.5 g L^{-1}) d) 1-Ethyl-3-methylimidazolium acetate (0.5 g L^{-1}) e) 1-Ethyl-3-methylimidazolium methylsulfate (0.5 g L^{-1})	HEF	100 (2 h)	TOC decay (8 h): a) 80% b) 85% c) 100% (6 h) d) 100% e) 100%	Bocos et al. (2016)
a) 1-Butyl-4-methylpyridinium chloride (0.83 mM) b) 1-Ethyl-3-methylimidazolium chloride (1.39 mM)	E-H_2O_2 EF PEF	–	DOC decay (6 h): a) 97% (E- H_2O_2), 91% (EF), 97% (PEF) b) 94% (E- H_2O_2), 93% (EF), 94% (PEF)	Garcia-Segura et al. (2016)
a) 1-Ethyl-3-methylimidazolium chloride (1 g L^{-1}) b) 1-Butyl-3-methylimidazolium chloride (1 g L^{-1}) c) 1-Octyl-3-methylimidazolium chloride (1 g L^{-1}) d) 1-Hexadecyl-3-methylimidazolium chloride (1 g L^{-1})	HF	100 (1 h)	TOC decay (4 h): a) 44% b) 38% c) 36% d) 33%	Muñoz et al. (2016)
1-Butyl-3-methylimidazolium triflate (0.5 g L^{-1})	EF	100 (45 min)	100% TOC decay (45 min)	Bocos et al. (2017)
(2-Hydroxyethyl)trimethylammonium chloride (Choline chloride, 1 mM)	B	100 (<24 h)	–	Morandeira et al. (2017)
Didecyldimethylammonium (4-chloro-2-methylphenoxy) acetate (0.05 g L^{-1})	EF E	100 (15 min)	TOC/COD decay (6 h): 80%/95% (EF) 30%/50% (E)	Pęziak-Kowalska et al. (2017)
a) 1-Hexyl-3-methylimidazolium chloride (1 g L^{-1}) b) 1-Butyl-4-methylpyridinium chloride (1 g L^{-1})	F	a) 100 (30 min) b) 100 (2 h)	TOC decay (4 h): a) 54% b) 44%	Gomez-Herrero et al. (2018)
1-Butylpyridinium chloride (0.5 g L^{-1})	HEF	100 (2 h)	TOC/COD decay (8 h): 94%/95%	Meijide et al. (2018)
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (0.419 g L^{-1})	E E-H_2SO_4 SE PE	–	TOC decay (8 h): 68% (E) 81% (E-H_2SO_4) 78% (SE) 76% (PE)	Mena et al. (2018)

[a] **B**: biotechnology; **E**: electrolysis; **EF**: electro-Fenton; **F**: Fenton; **HEF**: heterogeneous electro-Fenton; **HF**: heterogeneous Fenton; **PE**: photoelectrolysis; **PEF**: photoelectro-Fenton; **SE**: sonoelectrolysis.
[b] **COD**: chemical oxygen demand; **DOC**: dissolved organic carbon; **TOC**: total organic carbon.