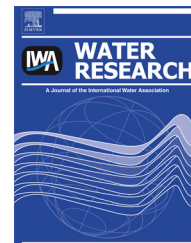


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# Identification of degradation products of ionic liquids in an ultrasound assisted zero-valent iron activated carbon micro-electrolysis system and their degradation mechanism

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## ARTICLE INFO

### Article history:

Received 3 December 2012

Received in revised form

28 March 2013

Accepted 29 March 2013

Available online 8 April 2013

### Keywords:

Ionic liquid

Degradation product

Ultrasonic irradiation

ZVI/AC micro-electrolysis

Degradation mechanism

## ABSTRACT

Ionic liquids (ILs) have potential applications in many areas of chemical industry because of their unique properties. However, it has been shown that the ILs commonly used to date are toxic and not biodegradable in nature, thus development of efficient chemical methods for the degradation of ILs is imperative. In this work, degradation of imidazolium, piperidinium, pyrrolidinium and morpholinium based ILs in an ultrasound and zero-valent iron activated carbon (ZVI/AC) micro-electrolysis system was investigated, and some intermediates generated during the degradation were identified. It was found that more than 90% of 1-alkyl-3-methylimidazolium bromide ( $[C_n\text{mim}]\text{Br}$ ,  $n = 2, 4, 6, 8, 10$ ) could be degraded within 110 min, and three intermediates 1-alkyl-3-methyl-2,4,5-trioxoimidazolidine, 1-alkyl-3-methylurea and N-alkylformamide were detected. On the other hand, 1-butyl-1-methylpiperidinium bromide ( $[C_4\text{mpip}]\text{Br}$ ), 1-butyl-1-methylpyrrolidinium bromide ( $[C_4\text{mpyr}]\text{Br}$ ) and N-butyl-N-methylmorpholinium bromide ( $[C_4\text{mmor}]\text{Br}$ ) were also effectively degraded through the sequential oxidization into hydroxyl, carbonyl and carboxyl groups in different positions of the butyl side chain, and then the N-butyl side chain was broken to form the final products of N-methylpiperidinium, N-methylpyrrolidinium and N-methylmorpholinium, respectively. Based on these intermediate products, degradation pathways of these ILs were suggested. These findings may provide fundamental information on the assessment of the factors related to the environmental fate and environmental behavior of these commonly used ILs.

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## 1. Introduction

Ionic liquids (ILs) are low melting organic salts. They have negligible vapor pressure under ordinary conditions, extended liquid-state temperature range, high thermal and chemical

stability, wide electrochemical window and tunable structures and properties. Therefore, these materials have emerged as promising “green” replacements for volatile organic solvents to be used in a wide range of applications, such as separation process, chemical synthesis, energy storage and

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<http://dx.doi.org/10.1016/j.watres.2013.03.057>

transformation, coating and biotechnologies (Bermudez, 2010; Grätzel, 2003; Pham et al., 2010; Zhu et al., 2006).

Due to the negligible vapor pressure, the use of ILs can avoid the risk of air pollution. This is the main reason why ILs were regarded as green materials. However, it was shown that ILs are commonly toxic in nature, and their toxicity varies considerably across organisms and trophic levels (Matzke et al., 2007; Pham et al., 2010; Ranke et al., 2007; Stolte et al., 2007). Owing to their solubility in water, the environmental impact of these ILs could be a significant concern when they come into the environment via wastewater effluents during large-scale applications. Therefore, it is imperative to develop efficient and economic methods for the removal of ILs from aqueous solutions, and to understand their degradation mechanism.

Because ILs are highly stable and resistant to biodegradation (Coleman and Gathergood, 2010; Quijano et al., 2011; Stolte et al., 2008), chemical treatment would be the main method for the removal of ILs. In this context, chemical processes such as advanced oxidation, electrochemical and thermal degradation of ILs in aqueous media have been reported, in which photo-degradation (Stepnowski and Zaleska, 2005), ozonation (Pernak and Biernacka, 2004), Fenton and “Fenton-like” oxidation (Siedlecka et al., 2008, 2009),  $\text{TiO}_2/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{UV}$  (Czerwicka et al., 2009; Stepnowski and Zaleska, 2005), and  $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ /sonication process (Li et al., 2007) have been used with success. Three advanced oxidation processes (UV,  $\text{UV}/\text{H}_2\text{O}_2$  and  $\text{UV}/\text{TiO}_2$ ) were investigated by Stepnowski and Zaleska (2005) for the degradation of imidazolium ILs in aqueous solution. Their results showed that the greatest degradation efficiency was achieved in  $\text{UV}/\text{H}_2\text{O}_2$  system, and the degradation depends on the alkyl chain length of the 1-alkyl-3-methylimidazolium cations. Siedlecka and Stepnowski (2009) evaluated the effect of hydrogen peroxide concentration on degradation rate of imidazolium and pyridinium ILs in a Fenton-like system and found that the oxidation rate of the imidazolium ILs was structure-related, and the level of degradation was dependent on the alkyl chain length, but no oxidation products and degradation mechanism were investigated. Li et al. (2007) reported the degradation of 1,3-dialkylimidazolium ILs in  $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  system assisted by ultrasonic irradiation. They indicated that more than 93% of the tested imidazolium ILs (2.5 mmol/L) could be degraded within 12 h, and alkyl chain length of the cations and type of the anions do not affect the degradation efficiency. A tentative mechanism was proposed in which three H atoms in the imidazolium ring were firstly oxidized, followed by cleavage of the alkyl groups attached to the N atoms. Then, selective fragmentation of C–N bonds of the imidazolium ring leads to ring opening, and acetoxyacetic acid and biurea are the ultimate degradation products. Kroon et al. (2006) predicted the possible electrochemical degradation products of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_4\text{mpyr}][\text{NTf}_2]$ ) using quantum chemical calculations and validated them by experiments. It was shown that when an electron was added to the  $[\text{C}_4\text{mpyr}]^+$  cation, 1,1-butylmethylpyrrolidinium radical was produced and then decomposed in three reaction pathways, and methylpyrrolidine, dibutylmethylamine and butylpyrrolidine were detected to be the decomposition products.

Zero-valent iron activated carbon (ZVI/AC) micro-electrolysis, developed as a wastewater treatment technology during the 1970s, has been widely used in the treatment of pesticide, pharmacy and dye wastewaters (Dou et al., 2010; Ghauch, 2008; Keum and Li, 2004; Liu et al., 2007) because of its advantages of easy operation, low cost and good treatment efficiency. Our preliminary study showed that ZVI/AC assisted by ultrasonic irradiation is effective for  $[\text{C}_4\text{mim}]\text{Cl}$  degradation (Zhou et al., 2013). Therefore, the aim of the present work is to assess the performance of ZVI/AC micro-electrolysis assisted by ultrasonic irradiation for the degradation of ILs residues in water and to investigate the degradation mechanism of ILs in such systems. For this purpose, eight kinds of ILs are selected including 1-alkyl-3-methylimidazolium bromide ( $[\text{C}_n\text{mim}]\text{Br}$ ,  $n = 2, 4, 6, 8, 10$ ), 1-butyl-1-methylpyrrolidinium bromide ( $[\text{C}_4\text{mpyr}]\text{Br}$ ), 1-butyl-1-methylpiperidinium bromide ( $[\text{C}_4\text{mpip}]\text{Br}$ ) and N-butyl-N-methylmorpholinium bromide ( $[\text{C}_4\text{mmor}]\text{Br}$ ). This allows us to investigate the effects of cationic structure and alkyl chain length on the degradation efficiency and degradation rate of the ILs. The degradation processes were probed by HPLC, gas chromatography-mass spectrometry (GC–MS) and HPLC coupled to electrospray mass spectrometry (HPLC–ESI–MS), and some main intermediates were detected. Based on these observations, pathway of degradation was suggested for the ILs under study.

## 2. Experimental

### 2.1. Chemicals and reagents

The ILs with purity greater than 99% were obtained from Chengjie Chem. Co. Ltd. (Shanghai, China) and used without further purification. Stock solutions of these ILs at a concentration of 25 mmol/L were prepared in purified water from a Milli-Q apparatus (Millipore, Co., USA) and then stored at 4 °C before use. The name, chemical structure and HPLC detection wavelength of the ILs were listed in Table 1.

ZVI powders (325 mesh) and activated carbon (35–50 mesh) were from Beijing Chem. Co., Ltd. Acetonitrile and methanol (LC grade) were from Kernal Chemical Reagents Development Center (Tianjin, China). All other reagents were of analytical grade from Beijing Chemical Factory (Beijing, China).

### 2.2. Degradation experiments of the ILs

The ultrasonic irradiation was conducted with a KQ-300GVDV ultrasonic cleaner (45 kHz, 300 W, Kunshan Ultrasonic Instruments Co. Ltd, China) in a temperature controlled container filled with water. Degradation reactions were carried out in a reaction flask at 30 °C with an ultrasonic irradiation at a frequency of 45 KHz. To eliminate the effect of the ILs adsorbed by activated carbon, the activated carbon used in this work was soaked in the aqueous IL solutions (8 mmol/L) three times (each time 12 h) to ensure the saturation adsorption of the ILs in advance. Then the activated carbon was dried at 40 °C. Before the degradation reaction, a certain amount of such activated carbon was added in the reaction flask (1 mmol/L of the IL) and soaked for another 12 h to make sure that during the degradation process, the decrease in ILs

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