



Degradation of imidazolium-based ionic liquids in aqueous solution using plasma electrolysis



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HIGHLIGHTS

- More than 95% of imidazolium-based ILs was degraded within 120 min by means of PE.
- The removal efficiency decreased as the order $[Cl]^- > [Br]^- > [Ac]^- \approx [BF_4]^-$.
- $[C_2mim]Cl$ was the most stable compared to $[C_4mim]Cl$ and $[C_6mim]Cl$.
- The initial concentration of ILs was found to affect the degradation efficiency.
- The imidazole ring was oxidized and then broken to form small molecular compounds.

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ABSTRACT

A novel method of degrading imidazolium-based ionic liquids (ILs) in wastewater using plasma electrolysis (PE) was proposed. The advantage of the PE method was that the ILs acted as both pollutant and electrolyte in the system. Results indicated that ILs with initial concentrations of 1.0–4.0 g/100 mL readily decomposed under an applied voltage of 600 V within 120 min. The anion and alkyl chain lengths of the ILs, discharge time, and post-treatment time were also found to be significant, and the degradation could be described by pseudo-first-order kinetics. Moreover, the energy efficiency of PE for degradation was calculated. The energy yield was generally higher than 2.0 g/kWh, which is approximately 100 times that of the degradation of methyl orange. The oxygen atom, hydroxyl radicals, and hydrogen peroxide produced by PE were important in the oxidation and cleavage of the ILs, and the degradation pathway of the imidazolium-based ILs was investigated using IC, FT-IR, NMR, and GC-MS techniques.

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1. Introduction

Ionic liquids (ILs) are regarded as a potential “green” alternative to volatile organic compounds because of their advantages of negligible vapor pressure, low-flammability, high thermal stability, and chemical stability. ILs are widely used in the areas of biotechnologies [1–4], catalysis [5,6], biocatalysis [7–9], synthetic chemistry [10,11], and electrochemistry [12–14] over the past decade. However, toxicity studies on aquatic organisms suggest the potential environmental risk of ILs [15–18]. *Pseudokirchneriella subcapitata* in water was sensitive to the anion moieties of ILs [19]. A stronger toxic effect was found for ILs containing $[Cl]^-$ compared with those containing $[PF_6]^-$ [20,21]. Meanwhile, the length of the alkyl side chain, which alters the lipophilicity of ILs, was also reported to have a pronounced effect on toxicity [22,23]. Although several methods for recovering and recycling ILs have been developed to avoid the

release of ILs into the environment through wastewaters [24–27], the potential of ILs to break through classical treatment systems into natural waters and become persistent pollutants requires the development of further strategies to improve the IL degradability.

Primary biodegradation is an alteration in the chemical structure of a substance, brought about by biological action, thus resulting in the loss of a specific property of that substance [19]. The introduction of ester or amide groups into the cation side chain was demonstrated to increase the biodegradation of imidazolium-based ILs [28–30]. However, the few studies conducted so far to investigate the degradability of ILs has shown these materials to be highly resistant to microbial degradation, particularly the most common imidazolium-based compounds [19,29]. In contrast to biodegradation, chemical degradation offers an efficient method to overcome the chemical and thermal stability of ILs. A Fenton-like system with Fe^{3+} and H_2O_2 was found to improve the degradation of ILs [31,32]. Meanwhile, Stolte et al. [33] reported for the first time that 1-butyl-3-methylimidazolium cation was completely destroyed within 4 h using an electrochemical method. Consequently, a combination of UV irradiation and zero-valence

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iron activated carbon micro-electrolysis system was developed [34].

Discharge plasmas have been widely used over the last decade for their advantages, such as direct in situ production of multiple types of high-reactive chemical species and enhancement and facilitation of degradation reactions without secondary pollution [35]. Compared with other plasma technologies, plasma electrolysis (PE) is sustained by DC or DC-pulsed glow discharges between an electrode and the electrolyte. A remarkable feature of PE is its high deviation of the chemical yields that are expected based on Faraday's law. Such yields include new products for conventional electrolysis. Meanwhile, PE generates active radicals, such as HO• radicals, H• radicals, H₂O₂, and hydrated electrons. Therefore, PE has been explored in the treatment of wastewater containing harmful organics [36,37].

In this work, the degradation of imidazolium-based ILs was performed for the first time by means of PE. The effect of anion, alkyl chain length and initial concentration of the ILs, applied voltage, discharge time, and post-treatment on degradation efficiency was evaluated. The energy efficiency of PE for the degradation process was also calculated. Moreover, the major intermediate products and residual ILs were analyzed using FT-IR, ¹H NMR, and GC-MS to explore the degradation mechanism.

2. Experimental

2.1. IL solutions

The ILs used in this work were the following: 1-ethyl-3-methylimidazolium chloride, [C₂mim]Cl; 1-butyl-3-methylimidazolium chloride, [C₄mim]Cl; 1-hexyl-3-methylimidazolium chloride, [C₆mim]Cl; 1-ethyl-3-methylimidazolium acetate ([C₂mim]Ac); 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]BF₄); 1-ethyl-3-methylimidazolium bromide ([C₂mim]Br); 1-butyl-3-methylimidazolium bromide ([C₄mim]Br); 1-amyl-3-methylimidazolium bromide ([C₅mim]Br); and 1-heptyl-3-methylimidazolium bromide ([C₇mim]Br). All ILs possessed greater than 99% purity and were supplied by the Center of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics. Then, 100 mL of each sample was prepared by adding ILs to deionized water at the designed concentrations.

2.2. Procedure

The experimental apparatus consisted of a DC high-voltage power supply and a reactor, as shown in Fig. 1. The reactor was made of two glass tubes with an inner diameter of 2.0 cm, outer diameter of 4.0 cm, and height of 14.0 cm. The two tubes were connected to a cylindrical tube with an inner diameter of 2.0 cm and length of 2 cm. The cathode was a wolfram stick (purity ≥ 99.9%, ρ ≥ 18.0 g/cm³, Φ = 0.3 cm) sealed into one glass tube, and the anode was a stainless steel plate (area = 10.0 cm²) placed in the other tube. The reaction vessel was coated with a water jacket, where the solution was maintained below 70 °C by circulating water. DC voltage of 400–700 V with power from 250 W to 700 W was applied across the electrodes to initiate treatment.

2.3. Analytical method

The degradation yields of ILs were monitored using high-performance liquid chromatography (HPLC, Agilent 1200, USA) consisting of a chromatographic interface, binary pump, UV/VIS variable wavelength detector, vacuum degasser, and rheodyne injection valve. The IL was separated by a symmetry C-18 column (250 mm × 4.6 mm, 5 μm). The analyses were performed at a flow rate of 0.8 mL min⁻¹ at 30 °C, and the elution profiles were

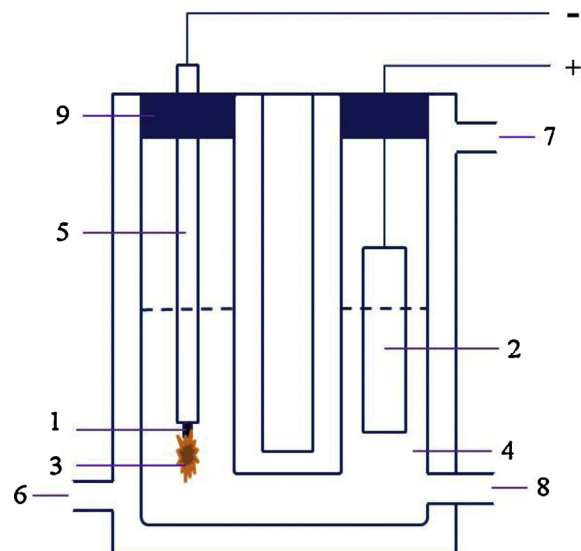


Fig. 1. Schematic of PE reactor: (1) cathode; (2) anode; (3) glow discharge; (4) IL wastewater; (5) alumina ceramic tube; (6) cooling water in; (7) cooling water out; (8) degradation product out; (9) rubber plug.

monitored at 212 nm. The mixture of methanol (35%, v/v) with 25 mmol/L phosphate buffer (KH₂PO₄/H₃PO₄) in 0.5% triethylamine at pH 3 was used as mobile phase [38,39]. The degradation efficiency η can be calculated as

$$\eta_{IL}(\%) = 100 \times \frac{C_0 - C}{C_0} \quad (1)$$

where C_0 and C are the initial and the final molar concentrations of IL, respectively. The energy yields were calculated in terms of G_{50} yield value expressing the amount of pollutant converted, divided by the energy input required at 50% conversion of the IL [40]:

$$G_{50} = 1.8 \times \frac{10^6 C_0 V_0 M}{Pt_{50}} \quad (2)$$

where C_0 is the molar concentration of the IL at $t=0$, V_0 is the volume of treated solution in liters, M is the molecular weight of the IL, P is power of the reactor in watts, and t_{50} is the time in seconds required for 50% conversion. G_{50} is expressed in grams/kilowatt-hour (g/kWh).

The concentration of anions in the liquids was tested using ion chromatography (Basic IC 792, Methohm, Switzerland). Throughout the study, a flow rate of 1 mL min⁻¹ and a sample size of 10 μL were applied. For the eluent solution, 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃ were used as a mixture. The pH of the solutions was tested by a PHS-25 pH meter. Conductivity measurement was performed using a DDS-11A conductometer (Jingke, Shanghai, China). The active plasma species of the glow discharge formed during the degradation process were observed by means of a QE 65000 OES with a spectral resolution of 1 nm according to our previous work [41]. The detector is a Hamamatsu S7031-1006 and the slit is SLIT-200. The emitted light was collected by an optical fiber close to the quartz glass vessel wall of the reactor in a dark room to avoid external light interference. The integration time of the spectral peak intensity of each specific light-emitting species was auto-recorded at an interval of 100 ms.

Residual ionic liquids were vacuum dried to remove moisture for analysis using FT-IR and ¹H NMR. The samples were mixed with anhydrous KBr and then compressed into thin disk-shaped pellets. The FT-IR spectra were obtained using a Vector 33 spectrometer (Bruker, German). The samples of the residual ILs were dissolved in 0.6 mL of 99.8% D₂O (Norell, Landisville, USA), and ¹H NMR spectra were recorded on an Avance 400 MHz spectrometer (Bruker,

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