



Removal of hydrophilic ionic liquids from aqueous solutions by adsorption onto high surface area oxygenated carbonaceous material



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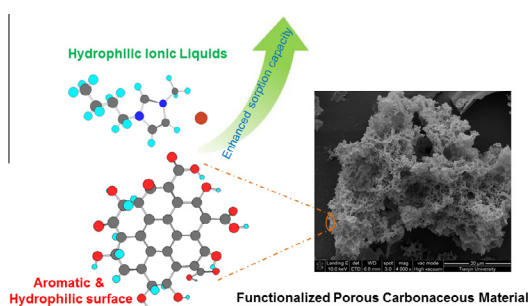
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HIGHLIGHTS

- Carbonaceous material with a large hydrophilic surface area was prepared.
- Enhanced sorption of hydrophilic ionic liquids from aqueous solution was achieved.
- The effect of ionic liquid chemical structure on *a*-CM sorption was investigated.
- Ionic liquid can be efficiently removed by tailoring adsorbent surface chemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

A carbonaceous material having a large surface area and high number of oxygenated groups was prepared by hydrothermal carbonization of cellulose and chemical activation with KOH with the goal to develop an adsorbent for hydrophilic ionic liquids. The as-prepared carbonaceous material (*a*-CM) was used to study the adsorption of representative imidazolium-based hydrophilic ionic liquids and exhibited adsorption capacity that was almost three times higher than that of commercial activated carbon (CAC) adsorbent. The large adsorption capacity of *a*-CM adsorbent for hydrophilic ionic liquids is attributed to its polar oxygenated surface groups (C–OH, C=O and –COOH). The effect of ionic liquid chemical structure on *a*-CM adsorption was investigated in which it was found that adsorption capacity increased with increasing hydrophobicity of the anions and increasing alkyl chain length of the imidazolium cation. Hydrophilic ionic liquids were favorably adsorbed onto the highly-oxygenated *a*-CM adsorbent whereas hydrophobic ionic liquids were favorably adsorbed onto CAC adsorbent. The as-prepared adsorbent could be characterized by the point of zero charge (pH_{PZC}) derived from zeta potential. The results of this work demonstrate that ionic liquids can be efficiently removed from aqueous wastewater by tailoring adsorbent surface chemistry to the chemical characteristics of the ionic liquid.

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1. Introduction

Ionic liquids (ILs) are organic salts that have low melting points (ca. 373 K) and have become one of the hottest research topics in

chemistry and engineering, due to their ability to solvate many problematic compounds such as cellulose [1,2]. Ionic liquids are generally considered as viable substitutes for volatile organic compounds, because of their negligible vapor pressure. However, while

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ionic liquids have many favorable properties, reports on their risk to the environment indicate a wide range of toxicities on bacteria, duckweed, algae, daphnia, and zebrafish [3]. Since the application of ionic liquids on an industrial scale will lead to contaminated wastewater streams, the removal or recovery of ionic liquids has to be considered as an important topic to prevent their release into the environment [4,5].

Treatment techniques such as advanced oxidation [6,7], biodegradation [8], and adsorption [9,10] have been evaluated for the removal of ionic liquids from aqueous streams with adsorption being favored due to it being eco-friendly, cost-effective and non-destructive. Although adsorption behavior of ILs in environmental systems such as natural soils [11,12], aquatic sediments [13], bacterial and mineral surfaces [14] has been investigated, more research is required to develop suitable adsorbents for the treatment of IL-containing waste streams. In the past years, adsorbents such as montmorillonite [15], ion-exchange resin [16], and activated carbon [10] have been proposed for the adsorption of ionic liquids from aqueous streams. Activated carbon is the most commonly used adsorbent and it has been demonstrated to be effective for ionic liquid removal due to its high surface area and its ease of use in chemical operations [9,10,17,18]. Palomar et al. [10] studied the adsorption of imidazolium-based ionic liquids from aqueous solutions with a commercial activated carbon adsorbent, and demonstrated that adsorption capacity strongly depends on the surface chemistry of the activated carbon as well as on the hydrophobic nature of both cation and anion of the ILs. Palomar et al. [10] concluded that the mechanism of IL adsorption onto activated carbons is mainly controlled by mass transfer into the pores so that the relatively low adsorption rate of the IL onto carbon materials can be promoted by decreasing the adsorbent particle size [17]. Commercial activated carbons show sufficient adsorption capacity for hydrophobic ionic liquids such as those with $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$ anions, but exhibit low adsorption capacity for hydrophilic ionic liquids such as those with Br^- , Cl^- anions [10,18,19]. Removal of ionic liquids that contain hydrophilic cations or anions from waste streams requires the development of new types of adsorbents.

In previous work, a carbonaceous material rich in carboxyl functional groups was prepared by hydrothermal carbonization of cellulose in the presence of acrylic acid and was evaluated as an adsorbent for a hydrophilic ionic liquid [20]. Although the prepared functional carbonaceous material (FCM) had a much lower surface area than commercial activated carbon, it exhibited comparable adsorption capacity [20]. In this work, it was hypothesized that the adsorption capacity of a carbonaceous material could be enhanced by increasing its surface area and maintaining the density of its functional groups.

Over a certain temperature range, increasing the surface area of an activated carbon by thermal treatment normally leads to a decrease in its oxygen content [21]. The chemical oxidation of carbon precursors, such as activated carbon and carbon nanotubes by HNO_3 , H_2O_2 and ammonium persulfate can increase the oxygen content of carbon materials [22,23]. To obtain carbon materials that have both large surface area and high oxygenated groups, carbonaceous microsphere materials with high oxygen content that were prepared from hydrothermal carbonization of cellulose was further chemically modified to increase its porosity, surface area, and to improve its oxygen content. The obtained porous carbon material was investigated in detail with adsorption experiments of a representative hydrophilic ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br) from aqueous solution and compared with the adsorption of other imidazolium-based ionic liquids.

2. Materials and methods

2.1. Materials

Ionic liquids (purity 99%) (1-ethyl-3-methylimidazolium bromide ([EMIM]Br), 1-butyl-3-methylimidazolium bromide ([BMIM]Br), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-hexyl-3-methylimidazolium bromide ([HMIM]Br), 1-octyl-3-methylimidazolium bromide ([OMIM]Br), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), and 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][MeSO₃])) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academic of Sciences (Lanzhou). Microcrystalline cellulose (pharmaceutical grade, particle size 50 μm , DP_v 219) was received from Boya Company (Tianjin). Commercial powder activated carbon was supplied by Hengtai Co., Ltd. (Gongyi). Potassium hydroxide and ethanol were used as received from Guangfu fine chemicals research institute (Tianjin).

2.2. Fabrication and characterization of cellulose-derived porous carbon material adsorbents

Cellulose-derived porous carbon material was prepared with a two-step process. Carbonaceous material (CM) was prepared by incomplete hydrothermal carbonization of cellulose. An aqueous dispersion of 19.2 g of cellulose in 60 ml of water was placed in a 100 mL stainless steel autoclave and heated up to 523 K and maintained at this temperature for 10 h at the autogenous pressure. The resulting crude solid product, denoted as CM, was recovered by centrifugation, washed repeatedly with distilled water and ethanol several times, and oven-dried at 353 K for 12 h.

The above prepared carbon material was chemically activated with potassium hydroxide (KOH) by thoroughly mixing the CM with KOH at a weight ratio (KOH/CM = 4), and then heat-treating the mixture at 873 K under flowing nitrogen gas for 2 h. Samples were thoroughly washed repeatedly with 1 mol/L HCl aqueous solution to remove inorganic salts and washed with distilled water until a neutral pH of the leachate was obtained. The wet solid was dried at 353 K for 12 h. The dried solid thus obtained is denoted as activated CM adsorbent (*a*-CM).

For comparison, a functional carbon material (FCM) adsorbent studied in our previous work was prepared with the method as described in Ref. [20]. Briefly, a mixture of 19.2 g of cellulose and 1.92 g of acrylic acid in 60 ml of water was loaded into a 100 mL stainless steel autoclave and heated at 523 K for 10 h. The crude solid products were isolated by centrifugation and washed repeatedly with distilled water and ethanol several times, and oven-dried at 80 °C for 12 h. The obtained carbonaceous solid materials are denoted as FCM.

Morphology of the samples was examined by Scanning Electron Microscopy (SEM) using a HITACHI S4800 microscope. FT-IR spectra (FTS 6000, Bio-Rad) were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} . BET surface area of samples was determined on the basis of nitrogen adsorption-desorption isotherms at 77 K by a multi-point BET method using a conventional volumetric technique (ASAP2020, Micromeritics Instrument Corp., USA). Elemental analysis was carried out with Elementar Vario EL cube (Germany). Zeta potential was measured five times at each pH using a Zeta-potential-analyzer (Zetapals/BI-200SM, Brookhaven, USA) and the average was adopted. The pH at the point of zero charge (pH_{ZPC}) of the carbonaceous material was determined by plotting zeta potential versus pH. Dissociation pH of $-\text{COOH}$ and $-\text{COH}$ groups of the carbon material was derived from the zeta potential curves as a function of solution pH.

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