Applied Surface Science 440 (2018) 821–829

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Oxidized template-synthesized mesoporous carbon with pH-dependent adsorption activity: A promising adsorbent for removal of hydrophilic ionic liquid

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ARTICLE INFO

Article history:
Received 3 November 2017
Revised 13 January 2018
Accepted 24 January 2018
Available online 31 January 2018

Keywords:
Ordered mesoporous carbon
Activated carbon
Adsorption
Surface modification
Ionic liquid removal

ABSTRACT

Aiming to remove ionic liquid pollutants from water, an ordered mesoporous carbon CMK-3 (OMC) was prepared and modified by oxidation with nitric acid. A commercial microporous activated carbon adsorbent, Filtrasorb-300 (AC), was used as benchmark. Boehm titration showed that oxidized OMC had a substantially higher oxygen content than oxidized AC. Adsorption of the hydrophilic imidazolium-based ionic liquid 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) on OMC and AC was well-described by the Freundlich isotherm model. Surface oxidation markedly enhanced [Bmim]Cl adsorption by both OMC and AC. Nevertheless, [Bmim]Cl adsorption was much higher on oxidized OMC than on oxidized AC. Increasing pH had negligible influence on [Bmim]Cl adsorption on pristine OMC, but enhanced adsorption on oxidized OMC. Regeneration tests showed stable performance of oxidized OMC over five adsorption-desorption cycles. Thus, oxidized OMC can be a highly effective adsorbent for the removal of hydrophilic ionic liquids from water.

1. Introduction

Imidazolium-based ionic liquids (ILs) have found wide industrial applications due to their chemical and thermal stability, non-flammability, tunable physicochemical properties and immeasurably low vapor pressure [1–3]. The large production of ILs will inevitably lead to their release into the aquatic environment. ILs are highly mobile and persistence in natural environment, owing to their high miscibility with water and recalcitrance to biodegradation [4–6]. Although ILs are traditionally considered as environmentally friendly, recent toxicity studies reveal that many ILs are similarly or more toxic than traditional solvents to cells, bacteria, algae, fungi, plants, invertebrates and vertebrates [7–9]. Hence, it is important to develop effective treatment methods to remove ILs from contaminated water before discharge to the environment.

Sorption is generally a simple and cost-effective approach to remove pollutants from water. A variety of sorbents including soils, resins, clay minerals and carbonaceous materials have been previously explored for removal of ILs [10–12], among which carbonaceous sorbents were most frequently studied. However, their adsorption capacities were limited due to a mismatch between their nonpolar surface and the highly hydrophilic nature of ILs [12–14]. Surface modification of carbonaceous sorbents by nitric acid oxidation can introduce oxygen-containing functional groups and change the surface hydrophobic/hydrophilic balance [15,16], which is expected to enhance ILs adsorption. For example, Palomar et al. found that nitric acid treatment of activated carbon AC-MkU improved adsorption of hydrophilic IL 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) [12]. However, chemical modification of activated carbons (ACs) is likely less efficient owing to their disordered and closed microporous structure, which limits this enhancement of ILs adsorption.

Since first synthesized by Ryoo et al. in 1999 [17], ordered mesoporous carbon (OMC) with regular frameworks and narrow pore size distributions were found to be promising adsorbents for the removal of dyes [18], surfactants [19], humid acid [20] and pharmaceutics [21]. Aiming to enhance adsorption of hydrophilic compounds, modification of OMCs by oxidative treatment

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https://doi.org/10.1016/j.apsusc.2018.01.211

has been carried out to introduce oxygen-containing groups to their hydrophobic surface [22]. Compared with ACs, OMCs' regular-shaped and open mesoporous framework allows oxidation to take place in the large internal surface of the pores, which generates a large number of oxygen-containing groups [23,24]. Therefore, it is plausible that surface-oxidized OMCs would have a more hydrophilic surfaces and exhibit superior adsorption of ILs. However, quantitative systematic studies of how such surface modifications of OMCs affect the adsorption of ILs have not been reported.

This study compares the adsorption of a representative ionic liquid, [Bmim]Cl, by OMC versus a commercial activated carbon, and evaluates the effect of surface oxidation of both adsorbents by nitric acid treatment. The structural properties of the materials were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption isotherms, transmission electron microscopy (TEM), potentiometric mass titrations, X-ray photoelectron spectroscopy (XPS) and Boehm titration. Adsorption isotherms and possible interactions between the adsorbents and the adsorbate were also considered to advance mechanistic understanding of IL adsorption.

2. Materials and methods

2.1. Adsorbate

Ionic liquid 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) was purchased from Aldrich.

2.2. Material preparation

Ordered mesoporous carbon CMK-3 was synthesized using mesoporous silica SBA-15 as the hard template [25]. Mesoporous SiO_2 template (SBA-15) was prepared according to the method reported by Zhao et al. using tetraethoxysilane (TEOS, Shanghai Chemical) as the silica source and triblock copolymer EO20PO70EO20 (Pluronic P123, Aldrich) as the organic structure-directing agent [26]. A detailed experimental procedure is given in Supplementary Information (SI).

A coal-based commercial activated carbon (AC), Filtrasorb-300 (Calgon Carbon Co., U.S.), was selected as a microporous adsorbent for comparison. Prior to adsorption and characterization, AC was ground into powder to pass through a 300-mesh sieve. To obtain a rational comparison with OMC, AC was subjected to similar thermal treatment to that for OMC at 850 °C for 5 h in nitrogen atmosphere.

The OMC and AC sorbents were modified by mild and strong oxidation treatments using nitric acid with varied concentrations. Briefly, 1 g of sample was suspended in 150 mL of 0.5 mol/L or 6 mol/L nitric acid solution at 75 °C under refluxing for 4 h. The sample was recovered by filtration and washed with distilled water until pH around 7, and finally dried at 120 °C under vacuum for 4 h. The spent nitric acid solutions were carefully collected and stored in polytetrafluoroethylene (PTFE) waste containers, kept away from organic solvents, and then transferred to the waste recycling, treatment and disposal service.

The modified samples were denoted as OMC-X and AC-X, respectively, where X was the concentration of nitric acid solution applied for oxidation treatment.

2.3. Characterization techniques

The small-angle X-ray powder diffraction (XRD) patterns were recorded in 2θ range of 0.6–5° by a Rigaku D/max-RA powder diffraction-meter (Rigaku, Tokyo, Japan) with a Cu Kα radiation. The pore volume and surface area of the samples were measured on a Micrometrics ASAP 2020 (Micromeritics Instrument Co., Norcross, GA) apparatus at −196 °C (77 K). Transmission electron microscopy (TEM) was carried out in a JEM-200CX electron microscope (JEOL Co., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 VersaProbe instrument (ULVAC-PHI, Japan) with a monochromatic Al Kα excitation source ($h\nu = 1486.6$ eV). The points of zero charge (pH_{pzc}) of the samples were determined by the potentiometric mass titrations method [27]. The oxygen-containing functional groups of the samples were quantified using Boehm titration [16,28]. Detailed experimental procedures are given in SI.

2.4. Adsorption experiments

Adsorption isotherms of [Bmim]Cl on different carbon materials were determined by batch adsorption tests. A weighed amount of adsorbent was added to glass vials containing 40 mL of [Bmim]Cl solution with initial concentration varying from 0.05 to 1.25 mmol/L. The vials were then kept in an rotary shaker at different temperatures (25, 35 or 45 °C) for 48 h. Preliminary kinetic experiments (data not shown) revealed that the adsorption time (48 h) was long enough to reach the apparent adsorption equilibrium. After removal of the adsorbent by filtration using a PTFE filter membrane with a pore size of 0.45 μm, the residual concentration of [Bmim]Cl was measured by high-performance liquid chromatography (HPLC) using a detecting wavelength of 212 nm with a mobile phase consisting of 40/60 (v/v) acetonitrile/10 mmol/L $NaPF_6$ mixture. The pH value of the filtrate measured at the end of adsorption was approximate 6.5. The batch adsorption tests were conducted in duplicate.

To investigate the effect of pH on [Bmim]Cl adsorption, the initial pH was adjusted by 0.1 mol/L HCl or 0.1 mol/L NaOH, and the final pH of the samples was measured after adsorption for 48 h. To determinate the concentration of H^+ released during the adsorption process, the adsorption system was continuously bubbled with a N_2 stream, and the initial and final pH values were recorded. The influence of ionic strength on the adsorption of [Bmim]Cl was tested in the presence of NaCl, KCl, $CaCl_2$ or $MgCl_2$ solutions with different concentrations (0.01, 0.02, 0.05, 0.1 and 0.2 mol/L).

To test the reusability of the adsorbents, [Bmim]Cl adsorption and regeneration of saturated adsorbents under acidic conditions were performed in five consecutive cycles. In the first cycle, a weighed amount of OMC (or OMC-6) was suspended in 0.17 mmol/L (0.34 mmol/L for OMC-6) [Bmim]Cl solution with a fixed solid/liquid ratio of 0.75 (0.25 for OMC-6) g/L under stirring for 48 h. After adsorption experiment, the saturated adsorbent was recovered by filtration and then regenerated by mixing with 100 mL of 0.01 mol/L HCl solution for 12 h, separated by filtration and followed by washing with distilled water and drying at 45 °C in vacuum overnight. Afterwards, triplicates of 10 mg regenerated adsorbent was weighed and placed into glass vials for the subsequent adsorption experiment. The residual regenerated adsorbent was used for the next adsorption-desorption cycle conducted with the same procedure as described in the first cycle. After five cycles, the regenerated adsorbents OMC or OMC-6 deriving from each cycle were reused for adsorption of [Bmim]Cl to evaluate the reusability of the adsorbents.

3. Results and discussion

3.1. Characterization of OMCs

The small-angle XRD profiles of mesoporous SiO_2 template SBA-15 and OMC samples are presented in Fig. 1a. The XRD pattern of SBA-15 displayed three well-resolved diffraction peaks with 2θ at 0.90°, 1.55° and 1.8° respectively, characteristics of (100), (110)