



Biosorbents based on agricultural wastes for ionic liquid removal: An approach to agricultural wastes management



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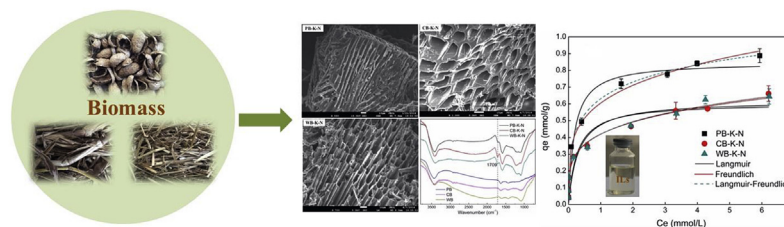
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HIGHLIGHTS

- Modified biochars derived from renewable agricultural wastes were prepared.
- The modified approach improved micropores and polar group quantities of biochars.
- Modified biochars showed superior sorption capacities for [BMIM][Cl].
- The modification method could be applied in other biomass materials treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Modified biochars produced from different agricultural wastes were used as low-cost biosorbents to remove hydrophilic ionic liquid, 1-butyl-3-methyl-imidazolium chloride ([BMIM][Cl]). Herein, the biosorbents based on peanut shell, corn stalk and wheat straw (denoted as PB-K-N, CB-K-N and WB-K-N) all exhibited higher [BMIM][Cl] removal than many other carbonaceous adsorbents and the adsorption capacities were as the following: PB-K-N > CB-K-N > WB-K-N. The characterizations of biosorbents indicated that they had great deal of similarity in morphological, textural and surface chemical properties such as possessing simultaneously accessible microporous structure and abundant oxygen-containing functional groups. Additionally, adsorption of [BMIM][Cl] onto PB-K-N, CB-K-N and WB-K-N prepared from the modified process, which was better described by pseudo-second order kinetic and Freundlich isotherm models. Therefore, the viable approach could also be applied in other biomass materials treatment for the efficient removal of ILs from aqueous solutions, as well as recycling agricultural wastes to ease their disposal pressure.

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1. Introduction

Ionic liquids (ILs) are molten salts with negligible vapor pressure, high solvent capacity, non-flammability and chemical stability that are being proposed as green replacements for volatile solvents

(Zhang et al., 2006). Due to their above specific properties, ILs have been widely used in industrial applications, such as fields of synthesis, electrochemistry and catalysis (Plechova and Seddon, 2008; Zhang et al., 2011; Huie et al., 2015; Shen et al., 2015). Although the air impact of ILs is very low owing to their low volatility, they may enter into the environment through transport, storage and industrial wastewater. However, the environmental hazards of ILs have been frequently reported in literature (Pham et al., 2010; Amde et al., 2015). Toxicity studies of ILs to enzymes

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(Fan et al., 2016), cell lines (Radosevic et al., 2013) and different trophic levels including bacteria (Docherty and Kulpa, 2005), invertebrates (Guo et al., 2016) and plants (Cho et al., 2008a; Bubalo et al., 2014), revealed that some of ILs are the same as, or even more toxic, than traditional organic solvents (Cho et al., 2008b). A wide range of physical-chemical, biological and oxidative technologies for the removal of ILs from aqueous effluents have been proposed (Mai et al., 2014). Among these approaches, adsorption is a simple, effective, and economical method for ILs removal and recovery from aqueous solution.

Biochar has been widely used as adsorbent for the removal of environmental pollutants (Tan et al., 2015). Their feedstocks derived from biomass materials including food waste, sewage sludge, peanut shell, corn stalk, sawdust, and other agricultural wastes, which are considered as worthless waste. Particularly, modified biochars have large surface area, fine porous structure and abundant functional groups, which were widely reported as the effective environmental remediation agent for contaminants in polluted soil or wastewater (Zhou et al., 2014; Morales et al., 2015; Rajapaksha et al., 2016; Xu et al., 2016). Recently, microporous/narrow mesoporous carbonaceous materials have high adsorption capacities for ILs, because they can provide appropriate pore space for the ILs uptake (Lemus et al., 2012, 2013). Furthermore, the polar groups on the surface of the carbonaceous materials through chemical modification also show strong binding to ILs (Palomar et al., 2009; Farooq et al., 2012; Qi et al., 2014). Nevertheless, preparation of targeted adsorbent possessing simultaneously accessible microporous structure and abundant functional groups to efficiently remove ILs is rarely taken into account. To the authors' best knowledge, comparative ability of modified biochars produced from different agricultural wastes to remove ILs from aqueous solution has not been explored.

The objectives of the study were to ascertain the abilities of modified biochars produced from three agricultural wastes (peanut shell, corn stalk and wheat straw) as alternative low-cost biosorbents toward the removal of [BMIM][Cl]. The specific goals were as follows: (1) prepare and characterize three biosorbents derived from agricultural wastes, (2) evaluate their adsorption potentials to remove [BMIM][Cl] from aqueous solutions, (3) determine the sorption characteristics and mechanisms of [BMIM][Cl] on modified biochars, and (4) assess preparation approach of modified biochars for the efficient removal of ILs.

2. Materials and methods

2.1. Materials

The plant material feedstocks were obtained from a rural area in Henan, China. All chemical reagents used in this study were of analytical grade. The [BMIM][Cl] was purchased from Henan Lihua pharmaceutical Co., Ltd.

2.2. Preparation of biochars

The collected feedstocks (peanut shell, corn stalk and wheat straw) were washed, dried and crushed, which of particle sizes were approximately 0.5–1.0 mm. The raw biochars were prepared by pyrolyzing the feedstocks in a tubular furnace at 700 °C for 2 h with a heating rate of 5 °C min⁻¹ under flowing N₂ atmosphere, which were labelled as PB, CB and WB. The raw biochars were activated with KOH (mass ratio of 1: 2) under flowing N₂ at 700 °C for 2 h, and then activated products were washed with 1.0 mol/L HCl and DI water until the pH values were close to neutral. Subsequently, the activated products were oxidized for 8 h with a saturated solution of (NH₄)₂S₂O₈ in 1.0 mol/L H₂SO₄ at room

temperature. The samples were washed by DI water until absence of sulphates in the washing water with barium chloride detection and were dried at 60 °C overnight to obtain the final modified biochars, which were designated as PB-K-N, CB-K-N and WB-K-N.

2.3. Characterization of biochars

Surface morphology was studied by a scanning electron microscopy (SEM) (Nova NanoSEM 450, FEI, USA). The measurements of surface area and pore size were carried out by nitrogen adsorption-desorption at 77 K by a DFT method using a surface area analyzer (Autosorb IQ, Quantachrome, USA). Fourier-transform infrared (FT-IR) spectra of the adsorbents were recorded on an FT-IR spectrometer (VERTEX 70, Bruker, Germany). The oxygen acid groups on the material surfaces were quantified by Boehm titration method (Salame and Bandosz, 2001). The contents of elemental were carried out with elemental analysis (Vario EL cube, Elementar, Germany). The X-ray diffraction (XRD) measurements were analyzed using X-ray diffractometer (Bruker D8 Advance, Bruker, Germany).

2.4. Bath adsorption studies

Adsorption studies were performed by adding 30 mg of each modified biochar to closed polyethylene flask with 25 mL of ILs solutions at a constant speed of 140 rpm with controlled temperature at 25 °C for 24 h in a thermostatted shaker bath. The mixtures were centrifuged and the supernatants were determined by UV–Vis spectrophotometer (TU-1900, Beijing Purkinje General, China) at 211 nm for [BMIM][Cl]. In the pH effect experiments, the initial pH was adjusted using 0.1 mol/L NaOH or HCl to the expected values (4.0 to 10.0). The adsorption kinetic experiments were investigated by mixing 30 mg of the biosorbent with 25 mL of 0.2 mmol/L [BMIM][Cl] at different reaction time. The experimental procedures were the same as those used for the previous tests. All experiments were performed in triplicate and the average values were reported.

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q = (C_0 - C_e) \frac{V}{m} \quad (2)$$

where q (mmol/g) is the adsorption capacity of [BMIM][Cl] onto biosorbent, C_0 and C_e (mmol/L) are the initial and equilibrium concentration of [BMIM][Cl], respectively, m (g) is the mass of the adsorbent, and V (L) is the volume of solution.

3. Results and discussion

3.1. Characterization of materials

The SEM images of the surface morphologies of the biosorbents were shown in Fig. 1. In spite of the fact that the modified biochars were produced from three biomass materials with different components (Vassilev et al., 2012), they all have fully developed and regular porous structure in micron-sized. The nitrogen adsorption-desorption isotherms of all samples (Fig. 2a) clearly exhibited the representative type I behaviour defined by IUPAC (Sing et al., 1985), suggesting microporous nature of the PB-K-N, CB-K-N and WB-K-N. The pore size distribution (Fig. 2b) presented dual peaks was ranging from 0.5 to 2.0 nm, which also indicated the formation of dominated micropores. This phenomenon was ascribed to activation process with lower KOH dosage (Liu et al., 2015). The

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