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Effectiveness and potential of straw- and wood-based biochars for adsorption of imidazolium-type ionic liquids

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ABSTRACT

The growing industrial application of imidazolium-type ionic liquids (ITILs) is likely to result in their release to the environment. Water-soluble ITILs are difficult to remove from wastewaters using traditional adsorbents. In this work, we developed different biochars derived from straw and wood (named as SBB and WBB, respectively) to improve the adsorption effectiveness for removal of ITILs from wastewaters. SBB had high O/C element ratio (0.143), while WBB had high ratio of V_{micro}/V_{total} (61.5%) compared with commercial activated carbon (AC). Both of them showed greater adsorption of ITILs than AC with different adsorption mechanisms. FTIR spectra revealed that electrostatic interactions were the dominant driving force in SBB adsorption, while high micropore volume promoted adsorption in WBB. The adsorption of $[C_2mim][BF_4]$ on SBB and WBB was strongly enhanced by trivalent PO_4^{3-} anions, suggesting that PO_4^{3-} anions could be used as promoter to increase the removal efficiency of ITILs from wastewater. Using HCl solution (pH=0.5) as regenerant, SBB and WBB were regenerated with nearly 100% recovery of adsorption capacity over ten consecutive adsorption-desorption cycles. Straw-based biochar and wood-based biochar are efficient sorbents for removal of water-soluble ionic liquids from aqueous solutions.

1. Introduction

Ionic liquids (ILs) are a series of synthetic room-temperature molten salts consisting of large asymmetrical organic cations (e.g., alkylimidazolium) paired with inorganic/organic anions (e.g., BF_4^-, PF_6^-) (Bubalo et al., 2014). Due to their unique physicochemical characteristics such as low-volatility, non-flammability, high ionic conductivity and thermal stability (Martínez-Palou and Luque, 2014), ILs have been widely used as alternatives to classical organic solvents in the field of green synthesis, catalysis and separation processes (Plechkova and Seddon, 2008). The growing application of ILs in chemical industries has increased their opportunity for release into the environment (Amde et al., 2015; Thi et al., 2010). IL contaminants in effluents have shown low biodegradability and high toxicity or inhibitory effects towards green algae and activated sewage sludge organisms or inhibitory effects on their growth and physiological activities (Liu et al., 2015; Markiewicz et al., 2013). Therefore, appropriate treatment technologies should be developed to dispose of ILs-containing wastewaters.

Artificial methods for destruction of ILs in wastewaters include biodegradation, ultrasonic degradation, electrolytic degradation, UV photodegradation and fenton/fenton-like reactions (Amde et al., 2015). Adsorption is the primary nondestructive technique applied in the treatment of ILs-contained waters due to the recovery potential of ILs. Activated carbon (AC) adsorption is a potential separation method for removing ILs from effluents (Lemus et al., 2012; Palomar et al., 2009). However, the adsorption efficiencies for ILs, even by high-surface-area ACs, are poor (Qi et al., 2013), which is presumably due to their inherent surface hydrophobicity. ILs are usually classified as hydrophilic or hydrophobic in terms of the length of the alkyl chain of IL cations as well as the type of IL anions (Huddleston et al., 2001). Most ILs containing short-alkyl-chain cations ($C_n < 4$), are hydrophilic, which means they have low octanol-water partition coefficients (K_{ow}, 10^{-3}–10^{-1}) and low water solubility (Hassan et al., 2014; Lee and Lin, 2014). Some ILs are composed of long-alkyl-chain cations ($C_n > 4$) and strongly coordinating anions (e.g.,1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide or $[C_6mim][NTf_2]$) making them hydrophobic in character. However, their K_{ow} still remain low (< 2) (Ropel et al., 2005), which are smaller by 2–4 orders of magnitude than many persistent organic pollutants (POPs). Thus, the adsorption of ILs on ACs is significantly less than that of many POPs.

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AC modification by physical or chemical treatments can improve AC pore structure and/or increase the carbon surface groups, thereby enhancing its adsorption affinity to ILs, but may be costly. Biochar, a kind of eco-friendly biomass-derived carbon, has been receiving considerable attention for its ability to remove contaminants, sequester carbon and improve soil fertility (Ahmad et al., 2014; Singh et al., 2010). Biochar is a porous solid material generated from the direct pyrolysis of a sustainable natural biomass (e.g. crop residues, wood, manure and other waste feed stocks) in an oxygen-limited environment (Lehmann and Joesph, 2009). It is regarded as a greener and less expensive adsorbent to replace AC for removal of contaminants from wastewaters (Li et al., 2014).

Typical biochar has less carbonized structure, less surface area but more surface polar functional groups than AC (Azargohar and Dalai, 2006). Qi et al. (2013) prepared a cellulose-derived carbonaceous material (CCM), with surface area only 2% of that of AC. However, the uptake of 1-butyl-3-methylimidazolium chloride on CCM was almost equal to that of AC. They further found that the chemical activation with KOH to CCM had positive effect on hydrophilic ILs sorption, which they attributed to the increase of polar oxygenated surface groups on CCM (Qi et al., 2014). It seems that biochar with more hydrophilic structure would be more suitable for adsorption of polar or ionic chemicals compared with commercial ACs.

Recently, the high sorption of ionic organic compounds on biochar, such as ionizable veterinary antibiotics (Zheng et al., 2013) and water-soluble dyes (Qiu et al., 2009), has been widely reported. For example, wood-based biochar showed the unbelievable adsorption coefficient (K_d) of sulfamethazine ($K_{ow}=1.86$) as high as 10^6 L/kg, which was due to the coupling of coulombic attraction, π^+-π electron-donor-acceptor (EDA) interaction and H-bonding between hydrophilic adsorbate and biochar surface (Teixidó et al., 2011). Analogously, biochar might also be considered a high efficiency absorbent for removal of ionizable ILs from wastewaters.

In the present study, straw- and wood-based biochars with different surface properties and pore size distribution were prepared to test their ability to absorb hydrophilic or hydrophobic imidazolium-type ionic liquids (ITILs). The adsorption effects caused by solution pH and the background cations/anions with different charges were also investigated. Additionally, batch adsorption-desorption tests were conducted to compare the removal efficiency of ITILs by biochars from wastewaters. The object of this work is to clarify the influence of structures and characteristics of both adsorbate and adsorbent on the adsorption of ITILs by biochars, to assess the adsorption effectiveness of ITILs on different biochars, and to discuss the potential application of biochar as a new efficient adsorbent for ITILs removal.

2. Materials and methods

2.1. Materials

Five types of ITILs (purity $>98\%$) with different alkyl-chain cations and different anions were purchased from Shanghai Chengjie Chemical Co. Ltd and listed in Table 1S. All of them were used without additional purification. The straw-derived biochar was prepared according to Qiu et al. (2008). In brief, the ashes from the burned rice straws (*Oryza sativa* L.) were collected and treated by 0.5 mol l^{-1} HCl–HF solution (1:1) three times for removal of Si. After washed with distilled water, the straw-derived biochars named SBB were attained until the effluent pH increased to above 7.0. The wood-derived biochars named WBB were obtained by slow-pyrolyzing from peeled wood chips (*Ziziphus jujuba* L.) at 700 °C for 6 h under oxygen-limited conditions. SBB and WBB were crushed and passed through a nylon sieve with 0.154 mm openings. Wood-based commercial powdered activated carbon (PAC) was donated by Calgon Carbon Co. Limited (Suzhou, China).

The specific surface area (S_{BET}) of biochars and PAC was evaluated from the N_2 adsorption (77 K) isotherms by applying the Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP-2020M (Norcross, GA, USA). Pore volume distributions were analyzed through the application of Density Functional Theory (DFT). Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) was used to investigate the morphological and chemical composition of carbon particles. The percentage of carbon and oxygen in biochars and PAC was determined by EDX analysis. The surface oxygen functional groups of carbons were determined using Boehm's titration method (Qiu et al., 2008). Fourier transform infrared spectroscopy (FT-IR) was recorded by a Nicolet 5700 spectrophotometer (Thermo Electron Scientific Instruments Corp., USA). The biochar samples were scanned in 32 scans over the range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum of biochar before and after adsorption was collected to discuss the potential adsorption mechanism for ITILs.

2.2. Batch sorption experiments

Batch adsorption experiments were carried out in 22 mL glass tubes with ~0.08 g biochar or AC samples and 20 mL ITILs solutions (0.5–3 mmol L^{-1}). Various concentrations of ITILs were prepared with 0.01 M (NaCl) ionic strength solution. All tubes were capped and rotated end-over-end at 40 rpm to mix the contents at 25 °C for 36 h. No ITILs volatilization or degradation occurred during the sorption process, as verified by HPLC analysis. The preliminary tests showed that the sorption of ITILs on SBB, WBB and AC reached equilibrium within 24 h (Fig. 1S). After attainment of equilibrium, the solution was filtered using 0.45 μm-pore-size membrane syringe filters and then analyzed for ITILs concentration by HPLC. All the adsorption experiments were performed in duplicate, and the

Table 1
Selected physicochemical properties of the powder activated carbon, straw-based biochar and wood-based biochar.

	C (%)	O (%)	O/C	S_{BET} ($m^2 g^{-1}$)	D (nm)	V_{total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{micro}/V_{total}	Surface acidity (mmol g^{-1})	Surface basicity (mmol g^{-1})
Powder activated carbon	90.34 ± 0.02	8.24 ± 0.02	0.091	1268.2	2.43	1.164	0.258	0.222	ND*	ND*
Straw-based biochar	86.45 ± 0.05	12.37 ± 0.03	0.143	733.1	4.88	0.894	0.099	0.111	0.89 ± 0.06	0.71 ± 0.04
Wood-based biochar	93.45 ± 0.04	6.55 ± 0.01	0.070	464.8	2.42	0.281	0.174	0.619	0.27 ± 0.02	0.45 ± 0.01

* ND = Not determined.