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Adsorption of 1-Butyl-3-Methylimidazolium Chloride Ionic Liquid by Functional Carbon Microspheres from Hydrothermal Carbonization of Cellulose

Xinhua Qi,*,[†] Luyang Li,[†] Tengfei Tan,[†] Wenting Chen,[†] and Richard L. Smith, Jr.[‡]

[†]Key Laboratory of Pollution Processes and Environmental Criteria (Ministry of Education), College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

[‡]Graduate School of Environmental Studies, Research Center of Supercritical Fluid Technology, Tohoku University, Sendai 980-8579, Japan

S *Supporting Information*

ABSTRACT: Functional carbonaceous material (FCM) loaded with carboxylic groups was prepared by hydrothermal carbonization of cellulose in the presence of acrylic acid. The resulting FCM was used as adsorbent for recovery of a water-soluble ionic liquid, 1-butyl-3-methyl-imidazolium chloride ([BMIM][Cl]). The FCM consisted of microspheres (100–150 nm) and had a low surface area (ca. 20 m²/g), but exhibited adsorption capacity comparable to that of commercial activated carbon which can be attributed to the presence of high content of polar oxygenated groups (−OH, −C=O, −COOH) as revealed by spectral analyses. Sorption of [BMIM][Cl] onto FCM adsorbent could be well-described by pseudo-second-order kinetics. Thermodynamic and adsorption isothermal analyses revealed that the adsorption process was spontaneous, exothermic, and could be described by the Freundlich adsorption model. The FCM adsorbent could be regenerated effectively and recycled for at least three times without loss of adsorption capacity. The results of this work provide a facile method for production of functional carbonaceous materials from renewable resources that can be used for treatment of aqueous streams containing small concentrations of ionic liquid, [BMIM][Cl].
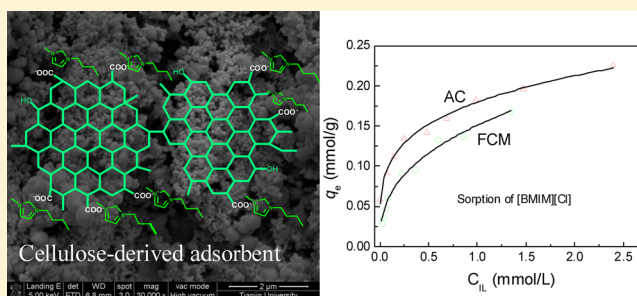
INTRODUCTION

Ionic liquids (ILs) have favorable properties as solvents for chemical reactions and processing and have come into practical use in industry.[1] Since their release to the environment is inevitable, environmental fate and toxicity of ILs have become important topics.[2] ILs exhibit toxicities on organisms, bacteria, algae, duckweed, daphnia, and zebrafish.[3] The sorption behavior of ILs in environmental systems such as natural soils,[4] aquatic sediments,[5] and bacterial and mineral surfaces[6] shows that the migration of ILs readily occurs, especially for water-soluble ILs, leading to a potential hazard for life and ecosystem. Thus, their controlled removal or recovery by oxidation,[7,8] biodegradation,[9] and adsorption,[10,11] from all possible sources, especially water, have been considered, to avoid their long-term adverse consequence to the environment.[12,13]

The octanol−water partition coefficients, K_{ow}, is a key parameter for assessing the environmental risk of a chemical release to the environment. The K_{ow} values of some imidazolium-based ionic liquids vary from 0.003 ([BMIM]-[BF₄]), 0.004 ([BMIM][Cl]) for water-soluble ILs to 11.1 for water-insoluble ILs having the triflate anion (CF₃SO₃⁻).[14] Water-soluble imidazolium-based ILs can be expected to

migrate more readily through the environment than water insoluble ILs, with the strength of their sorption onto soils being stronger for longer alkyl chain ILs due to specific interactions between the imidazolium cation and charged sites on the solid.[15,16] Thus, methods with adsorption for the recovery and regeneration of ILs from aqueous waste streams are needed to minimize environmental risk.[17]

Anthony et al. made a study on the recovery of [BMIM]-[PF₆] from water using adsorption with activated carbon (AC).[18] They found that more than 50 times the amount of AC is required for removing the IL from water over that for toluene and concluded that anionic/cationic ion-exchange resins would perform better than AC.[18] Palomar et al. investigated the adsorption of imidazolium-based ionic liquids from aqueous solutions with a commercial activated carbon adsorbent,[11] and demonstrated that the size and the hydrophobic nature of both cation and anion of ILs as well as the surface chemistry of activated carbon strongly affect the adsorption capacities.[11]

They used the quantum-chemical COSMO-RS model, to develop criteria for adsorption capacity with the chemical structure of the ionic liquids by predicting the partition coefficient at infinite dilution.[19]

Activated carbon is commonly used in wastewater treatment applications, however, its production requires high-temperature (400−1000 °C) carbonization and surface-activation steps that lead to air emissions and waste streams.[20] Sun and Li proposed the production of carbon materials by hydrothermal carbonization (HTC) of soluble sugars such as fructose and glucose using mild conditions.[21] Synthesis and application of HTC carbon materials has received attention as a method for using renewable resources to reduce environmental burden.[22]

In this work, a carbonaceous material that is rich in carboxylic groups was prepared by hydrothermal carbonization of cellulose at relatively low temperatures (250 °C), The adsorption behavior of a representative ionic liquid, 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) onto the resulting functional carbonaceous material was investigated. The ionic liquid [BMIM][Cl] was selected, because it is the main ionic liquid used as a starting material in the production of other ionic liquids and also since it is a water-soluble, stable with changes in pH,[23] and has many uses in processing renewable resources.[24] The aim of this work is to study the adsorption, separation, and recovery of [BMIM][Cl] from an aqueous solution with an adsorbent that can be synthesized from renewable materials at relatively mild conditions. The functional adsorbent was synthesized with a hydrothermal carbonization method that uses cellulose as the raw material.

■ MATERIALS AND METHODS

Materials. 1-Butyl-3-methyl imidazolium chloride ([BMIM][Cl] (99%) was purchased from Henan Lihua pharmaceutical Co., Ltd. (Xinxiang). Microcrystalline cellulose (pharmaceutical grade, particle size 50 μm, DP_V 219) was obtained from the Boya Company (Tianjin). Acrylic acid and ethanol were used as received from Guangfu Fine Chemicals Research Institute (Tianjin). Commercial powder activated carbon was supplied by Hengtai Co., Ltd. (Gongyi).

Preparation and Characterization of Functional Carbon Material (FCM) Absorbent. The FCM absorbent was prepared by incomplete hydrothermal carbonization of cellulose with addition of acrylic acid monomer. Typically, 19.2 g of cellulose and 1.92 g of acrylic acid (10 wt % with respect to cellulose concentration) were dispersed in 60 mL of water, and then loaded into a 100-mL stainless steel autoclave and heated at 250 °C for 10 h at the autogenous pressure. 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 when prepared with acrylic acid and CM when prepared without acrylic acid.

Prepared material were characterized by SEM (S4800, HITACHI), FT-IR (FTS 6000, Bio-Rad), and BET surface area technique (ASAP2020, Micromeritics Instrument Corp., USA). BET surface area of samples was determined on the basis of nitrogen adsorption−desorption isotherms at −196 °C by a multipoint BET method. FT-IR spectrum was recorded over the range from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Elemental analysis was carried out using Elementar Vario EL cube (Germany).

Sorption Experiments. Batch sorption experiments were carried out at 120 rpm equivalent shaking rate in a thermostatted shaker bath (model THZ-82, Jiangsu) with 0.05 g of adsorbent in 100-mL flasks containing 20 mL [BMIM][Cl] aqueous solution for 24 h. Initial ionic liquid concentrations ($C_{IL,0}$) of 0.05 to 2 mmol/L were used. Kinetics experiments demonstrated that 24 h was sufficient for reaching adsorption equilibrium (Figure S1, Supporting Information (SI)). In most experiments, solution pH was not adjusted and had a value of 6.9 as measured with a pH-meter (PHS-3C, Shanghai). For cases where pH was adjusted, a 0.1 mol/L NaOH or HCl solution was used to change the initial pH value.

After each sorption experiment, mixtures were filtered and [BMIM][Cl] concentration in the filtrate was determined with a spectrophotometer (Cary-50 model UV, Varian Inc.) at 211 nm and a standard curve. Sorption amount was calculated according to the difference in [BMIM][Cl] concentrations before and after sorption. At each condition, sorption experiments were performed in triplicate and averaged.

Desorption Experiments. After the sorption experiments, spent FCM was separated by centrifugation, and dried in an oven at 80 °C. Spent FCM was added to 20 mL of 0.1 mol/L HCl aqueous solution, and shaken at 120 rpm for 24 h at 25 °C. Then the solution was centrifuged and separated from the adsorbent and [BMIM][Cl] desorbed was determined with spectrophotometer as previously described. The desorption ratio was defined as follows:

$$[BMIM][Cl] \text{ desorption ratio}$$
$$= \frac{\text{final mass of } [BMIM][Cl] \text{ in solution}}{\text{initial mass of } [BMIM][Cl] \text{ on FCM}} \times 100\% \quad (1)$$

^{1}H NMR spectra of fresh and recovered [BMIM][Cl] were recorded on a Varian Mercury Vx-300 spectrometer.

■ RESULTS AND DISCUSSION

Characterization of the Carbon Material. Figure 1 shows SEM images of the carbonaceous material obtained by
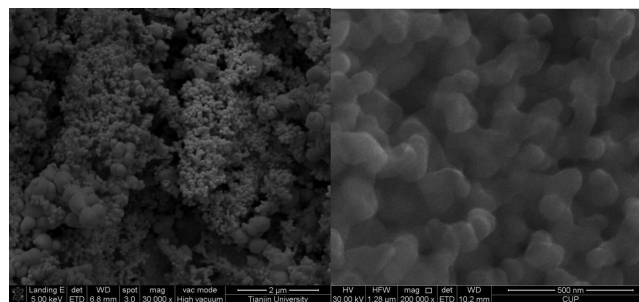

Figure 1. SEM images of the functional carbonaceous material prepared by hydrothermal carbonization of cellulose in the presence of acrylic acid. (Conditions: 250 °C, 10 h reaction time, 10 wt % acrylic acid, 23.7 wt % cellulose).

hydrothermal carbonization of cellulose in the presence of acrylic acid. The obtained material consisted mainly of aggregates of carbonaceous microspheres having an average size of about 100−150 nm with some large particles (ca. 500 nm) being apparent (additional SEM images, SI Figure S2). Particle sizes were much smaller than that obtained in our previous work where the carbon material was produced in the absence of acrylic acid and consisted of micrometer-order size spheres that had a BET surface area of less than 0.5 m^2/g.[25] The small BET surface areas for the carbonaceous materials are

evidence of their nonporous nature (SI Table S1). Based on the adsorption isotherm using the standard BET equation and t-plot analysis, FCM material had a small micropore volume (0.051 cm^3/g) and low surface area (ca. 20 m^2/g), which is common for carbonaceous materials prepared from carbohydrates with hydrothermal methods.[22] Difference between particle sizes of carbonaceous materials formed under hydrothermal conditions between this work and previous works can be attributed to the presence of acrylic acid which seemed to stabilize initially formed particles and inhibit their growth.

According to the formation mechanism of carbohydrate-derived hydrothermal carbonization (HTC) material,[22,26] the formation of the carbon particles in this work can be described (SI Scheme S1) as: (1) hydrolysis of cellulose into glucose; (2) dehydration of glucose into 5-hydroxymethylfurfural (5-HMF) and intermediate molecules (levulinic acid, formic acid, furfural, dihydroxyacetone, erythrose, and 1,2,4-benzenetriol); (3) formation of a condensed furanic system terminated by hydroxyl, carbonyl, and carboxylic functional groups through a series of dehydration, polymerization, condensation, and aromatization reactions among 5-HMF with other intermediate molecules as well as added comonomer; and (4) nucleation and subsequent particle growth leading to spherical carbonaceous particles. The addition of acrylic acid probably plays multiple roles in the process: first, it catalyzes hydrolysis of cellulose and the dehydration of the formed glucose; second, it provides functionality (carboxylic groups) during formation of the furanic structure; and third, it may stabilize initially formed small droplets and inhibit growth of micrometer-sized particles due to steric effects.

FT-IR spectra of the prepared carbonaceous materials are shown in SI Figure S3. The bands in the range of 1000−1300 cm^{-1} can be assigned to C−OH stretching vibration and −OH bending, indicating the existence of a large number of hydroxyl groups of the hydrophilic surface on the as-prepared carbonaceous material.[21] The band at ca. 3321 cm^{-1} is attributed to O−H stretching vibration of adsorbed water molecules and surface hydroxyl groups including phenolic groups.[21,27] The band at 2929 cm^{-1} corresponds to the stretching vibrations of aliphatic C−H and is evidence of aliphatic structures.[28] The absorption band at 1707 cm^{-1} is attributed to C=O stretching of the COOH group,[28,29] demonstrating the existence of a high degree of carboxylic groups in the prepared material that may favor adsorption of cationic species. Other bands belong to C=C stretching vibrations of aromatic and furanic rings (1612 cm^{-1}), and aromatic C−H out-of-plane bending vibration (802 cm^{-1}).[30]

An FT-IR spectrum of carbonaceous material (CM) prepared by the hydrothermal carbonization of cellulose in the absence of acrylic acid is shown in SI Figure S3. The CM and FCM materials possess almost the same bands in their FT-IR spectra, but the intensity of the band at 1707 cm^{-1} greatly increases for the FCM sample upon addition of acrylic acid during hydrothermal carbonization of cellulose, indicating higher degree of carboxylic groups in the FCM sample. The existence of carboxylic acid groups in the CM sample should be due to acids (e.g., levulinic acid) that form from decomposition of glucose, and some of these acids as well as acrylic acid could be incorporated within the furanic structure as terminal groups in the carbon matrix (SI Scheme S1).[30]

Sorption Kinetics. Figure 2 shows sorption kinetics of [BMIM][Cl] for different amounts of adsorbent. About 120 min was required to reach sorption equilibrium in all cases.
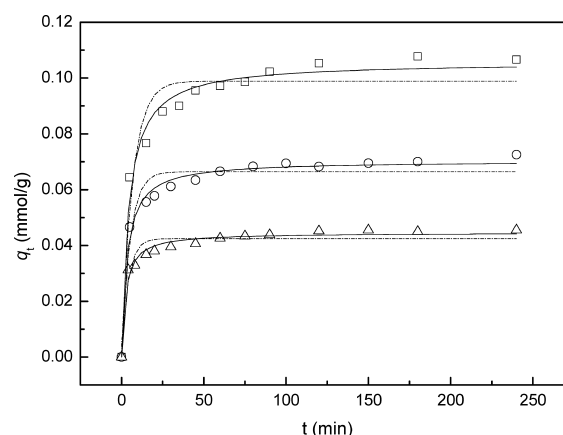

Figure 2. Sorption kinetics of the prepared functional carbonaceous material adsorbent (FCM) for [BMIM][Cl] (Conditions: 25 °C, pH 6.94, initial [BMIM][Cl] concentration ($C_{[BMIM][Cl],0}$), 0.3 mmol/L). FCM adsorbent dosage: □ 1 g/L, ○ 2.5 g/L, △ 5 g/L. Fitted by pseudo-first-order model (- - -) and pseudo-second-order model (—).

Pseudo-first- and pseudo-second-order models were fit to the data. Considering Figure 2 and Table 1, the pseudo-second-order model gave a better representation of the data than the pseudo-first-order model consistent with results obtained by Stepnowski et al., who investigated sorption of imidazolium-type ILs onto kaolinite.[31] The second-order model fits all the experimental data well implying that chemical interactions were involved in the sorption process,[32,33] and that there were strong interactions between the 1-butyl-3-methyl imidazolium cation and carboxylic groups in the adsorbent. Adsorption rate constants (k_1 and k_2) were found to be proportional to the adsorbent dosage.

As shown in Table S2, removal rate of [BMIM][Cl] increased with increasing FCM dosage, which can be ascribed to the increase of applicable binding sites on the FCM adsorbent. At a given initial [BMIM][Cl] concentration, FCM adsorption capacity decreased with an increase in adsorbent dosage, which can be explained by desorption being competitively favored over adsorption at equilibrium conditions (Table S2) according to analyses with adsorption models discussed later.

Sorption Isotherms. The amount of [BMIM][Cl] adsorbed onto prepared adsorbent at different temperatures was studied as a function of the equilibrium concentration in solution (Figure S4). The Langmuir and Freundlich equations,[34] which are given as

$$q_e = bq_m C_e/(1 + bC_e) \qquad (2)$$

$$q_e = KC_e^{1/n} \qquad (3)$$

were used to analyze the data. In eqs 2 and 3, q_e is the equilibrium adsorption amount (mmol/g), C_e is the equilibrium concentration (mmol/L) of [BMIM][Cl] in solution, q_m is the maximum adsorption capacity (mmol/g), b is the adsorption equilibrium constant (L/mmol), K is a constant representing the sorption capacity (L/mmol), and n is a constant depicting the sorption intensity.

As shown in Table 2, the Freundlich model could provide better representation of the adsorption isotherms of [BMIM]-[Cl] than the Langmuir model (Figure S4). The adsorption of [BMIM][Cl] on the prepared adsorbent decreased with an increase in temperature (Table 2). When the temperature was

Table 1. Kinetic Parameters for the Pseudo-First-Order and Pseudo-Second-Order Models for [BMIM][Cl] Sorption onto the Prepared Functional Carbonaceous Material Adsorbent with Different Dosages

	pseudo-first-order model[a] $q_t = q_e(1 - e^{-k_1 t/2.303})$			pseudo-second-order model[a] $t/q_t = 1/k_2 q_e^2 + t/q_e$		
adsorbent amount (g/L)	$q_{e,cal}$ (mmol/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mmol/g)	k_2 (g·mmol^{-1}·min^{-1})	R^2
1.0	0.0989	0.339	0.9369	0.106	2.241	0.9843
2.5	0.0665	0.440	0.9454	0.070	4.444	0.9884
5.0	0.0425	0.564	0.9346	0.045	9.441	0.9818

[a]q_e and q_t are the amount of [BMIM][Cl] adsorbed on the adsorbent (mmol/g) at equilibrium and time t, respectively; k_1 is the adsorption rate constant of pseudo-first-order model (min^{-1}); and k_2 is the adsorption rate constant of pseudo-second-order model (g·mmol^{-1}·min^{-1}).

Table 2. Fitting Parameters of the Langmuir and Freundlich Equations for [BMIM][Cl] Sorption onto the Prepared Functional Carbonaceous Material (FCM) Adsorbent (Conditions: Dosage of FCM Adsorbent 2.5 g/L, 24 h, pH 6.94)

	Langmuir model ($q_e = bq_mC_e/(1 + bC_e)$)			Freundlich model ($q_e = KC_e^{1/n}$)		
T (°C)	q_m (mmol/g)	b (L/mmol)	R^2	K	$1/n$	R^2
25	0.171	19.258	0.9430	0.151	0.248	0.9894
35	0.129	12.177	0.8762	0.125	0.292	0.9983
45	0.116	5.978	0.8192	0.118	0.380	0.9810

Table 3. Standard Thermodynamic Values (ΔG^0, ΔH^0, ΔS^0) for the Adsorption of [BMIM][Cl] on the Prepared Functional Carbonaceous Material (FCM) Adsorbent at Different Temperatures (Conditions: Dosage of FCM 2.5 g/L, 24 h, pH 6.94)

T (°C)	b (L/mol)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))	R^2
25	19258	−24.4	−45.39	−70.0	0.9497
35	12177	−24.1			
45	5978	−23.0			

varied from 25 to 45 °C (Table 2, Figure S4), the maximum adsorption capacity of [BMIM][Cl] (q_m) decreased from 0.171 to 0.116 mmol/g. Thus, although higher temperatures can increase the adsorption rate constant (Table S3), the conditions do not favor adsorption and this leads to a decrease in the adsorption capacity of the adsorbent. The Langmuir constant b is an indication of the equilibrium adsorption so that if it decreases with temperature, the amount of adsorbate decreases. The Freundlich model is considered to be suitable for describing the adsorption behavior of solutes onto heterogeneous surfaces. Since carbonaceous adsorbents have a heterogeneous surface composed of functional groups such as −CH, −OH, and −COOH, this is probably a primary reason that the Freundlich equation provided better representation of the data than the Langmuir equation. In the model, $n^{-1} = 1$ represents a linear isotherm so that the nonlinear portion of the isotherms can be ascribed to electrostatic attraction, adsorption site heterogeneity, and sorbent−sorbate interactions.[35]

Thermodynamic Analysis. Thermodynamic analysis of an adsorption process provides information on its spontaneity and on the stability of the adsorbed phase. The changes in the standard Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0), were calculated from experimental data obtained at different temperatures. The ΔG^0 of the sorption reaction was calculated from eq 4 as

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{4}$$

where

$$\Delta G^0 = -RT\ln b \tag{5}$$

and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), T is absolute temperature (K), and b is the equilibrium constant obtained from the Langmuir isotherm for different temperatures. The ΔH^0 and ΔS^0 were obtained from the slope and intercept of a plot of ΔG^0 versus T (Table 3).

Calculated values of ΔG^0 were negative, indicating the spontaneous nature of [BMIM][Cl] adsorption on FCM adsorbent. The ΔH^0 and ΔS^0 of the adsorption reaction were

−45.39 kJ/mol and −70 J·mol^{-1}·K^{-1}, respectively. Adsorption of the ionic liquid was exothermic so that lower temperatures can be expected to favor stronger adsorption. Negative values of ΔS^0 imply a lower degree of freedom of the [BMIM][Cl] at the solid/solution interface during adsorption.

Generally, absolute values of ΔG^0 for physical adsorption (−20 to 0 kJ/mol) are smaller than those of chemisorption (−80 to −400 kJ/mol).[36,37] Polomar et al. studied the adsorption of 1-methyl-3-octalimidazolium hexafluoroborate ([OMIM][PF$_6$]) on activated carbon and reported values of ΔG^0 to be between −12 and −10 kJ/mol implying physical adsorption phenomenon.[11] Values of ΔG^0 (around −24 kJ/mol) obtained in this work were between values for physical adsorption and chemisorption, indicating that adsorption of [BMIM][Cl] on FCM adsorbent involves both physical adsorption and chemisorption.

Effect of pH and Ionic Strength. Solution pH is an important parameter that affects adsorption due to the strong reactivity of H$^+$ (or OH$^-$) in solution, especially in ionic adsorption processes. Solution pH not only affects sorbate speciation in solution, but also changes the properties of the adsorbent surface.[38] The adsorbent surface changes through the protonation or deprotonation of functional groups, so that electrostatic interactions between sorbates and adsorbents usually play a predominant role.[33] The effect of solution pH on the removal rate of [BMIM][Cl], as depicted in Figure 3, shows that the adsorption of [BMIM][Cl] onto FCM adsorbent was strongly pH dependent. When initial solution pH was adjusted to 1.2, only 4% of [BMIM][Cl] could be absorbed from solution. The adsorbed amount or the removal of [BMIM][Cl] increased with increasing solution pH and 72% could be removed when the initial solution pH was adjusted to 11.2. This tendency was the same as that reported by Farooq et al., who studied the adsorption of ionic liquids onto several types of activated carbon, and found that pH values from 2 to 9 led to a strong increase in adsorption uptake for ionic liquids.[10]

In the pH range studied, the sorbate [BMIM][Cl] exists as 1-butyl-3-methyl-imidazolium ([BMIM]) cation and [Cl] anion in aqueous solution, while the carboxylic groups on the carbonaceous adsorbent will be strongly protonated at low pH,
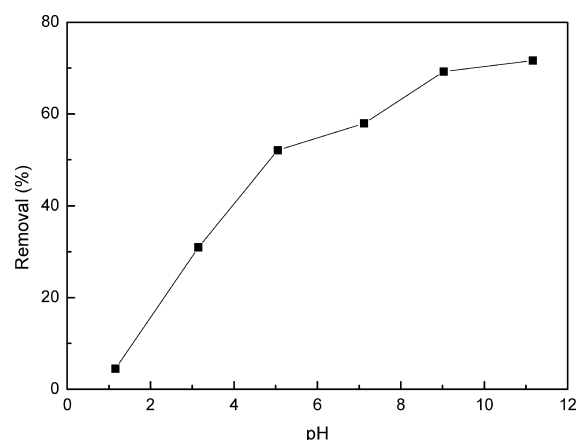
Figure 3. Effect of pH on the adsorption of [BMIM][Cl] onto prepared functional carbonaceous material FCM adsorbent. (Conditions: $C_{[BMIM][Cl],0}$, 0.3 mmol/L, dosage of FCM adsorbent 2.5 g/L, 24 h, 25 °C).
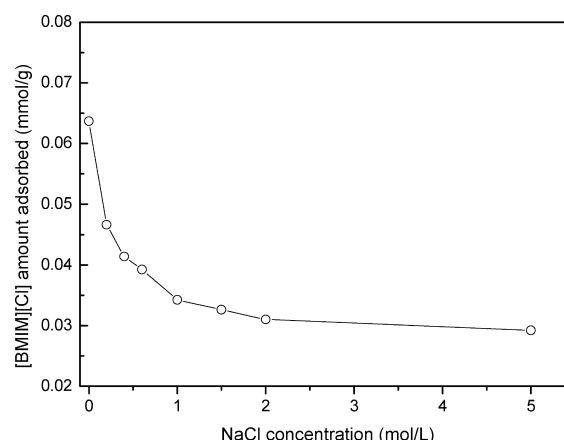

Figure 4. Effect of ionic strength on the adsorption of the prepared functional carbonaceous material adsorbent FCM for [BMIM][Cl]. (Conditions: $C_{[BMIM][Cl],0}$, 0.3 mmol/L, dosage of FCM adsorbent 2.5 g/L, 24 h, 25 °C, pH 6.94).

so that the adsorbent surface should be positively charged. Therefore, adsorption of [BMIM] cation onto FCM adsorbent was most likely inhibited at acidic pH values due to electrostatic repulsion interaction. As pH increased to high values (Figure 3), carboxylic groups of the FCM adsorbent probably became deprotonated, and negative functional carboxylic groups became released. This would lead to the promotion of adsorption of [BMIM] cation onto the adsorbent due to increased ionic, chemical, and electrostatic attractions. The Cl⁻ concentration in the solution was found to vary little from 10.1 to 9.9 mg/L before and after adsorption at pH 11, indicating that the sorption characteristics of FCM adsorbent has some similarities with ion exchange resins.[39] Adsorption of [BMIM]-[Cl] onto FCM adsorbent seems to be mainly due to the hydrogen bonding and electrostatic interactions, since the contribution of other interactions such as hydrophobic interactions (polar) were probably extremely limited, which is supported theoretically by predictions by COSMO-RS for IL−AC and IL−water interactions.[11]

The effect of background ions is important in practical adsorption processes. NaCl was used as a representative background electrolyte to investigate the effect of ionic strength on adsorption of [BMIM][Cl] onto FCM adsorbent (Figure 4). As shown in Figure 4, the adsorbed amount of [BMIM][Cl] decreased with increasing NaCl concentration from 0 to 2 mol/L and almost remained constant at salt concentrations above 2 mol/L. The decrease in the amount of [BMIM][Cl] adsorbed is probably the result of competitive adsorption of Na⁺ with [BMIM] cation, as the salting-out effect is unlikely to have any contribution on [BMIM][Cl] adsorption since [BMIM][Cl] is completely miscible with water.

Adsorption of [BMIM][Cl] onto a Commercial Activated Carbon. A commercial activated carbon (AC) with high surface area (980 m²/g) was used to compare adsorption of [BMIM][Cl] with that of the prepared FCM adsorbent. Results are shown in Figure 5 and Table 4. The adsorption capacity of the commercial adsorbent for [BMIM][Cl] was slightly higher (0.206 mmol/g) than FCM adsorbent (0.171 mmol/g) despite large differences in surface areas. Lemus et al. proposed that the pore volume within a size range up to 8 nm width (micropore and narrow mesopore) of the adsorbent plays a crucial role in adsorption capacity for removing ILs from aqueous solution.[19] Pore volumes below 8 nm width of the AC and FCM adsorbent
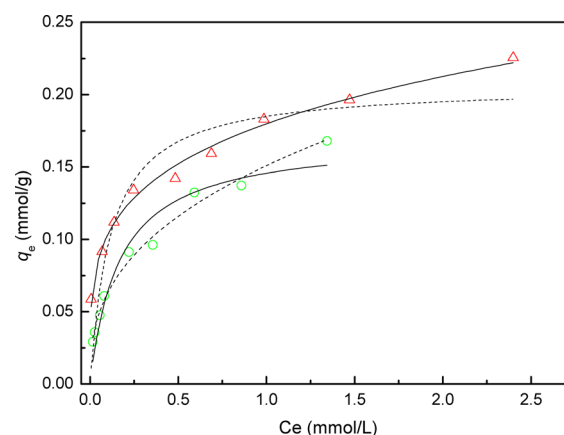

Figure 5. Adsorption isotherms of the prepared functional carbonaceous material adsorbent (FCM) and commercial activated carbon (AC) for [BMIM][Cl] (Conditions: 25 °C, dosage of AC or FCM adsorbent 2.5 g/L, 24 h, pH 6.94). ○ FCM, △ AC. Simulation by Langmuir model (- - -) and Freundlich model (—).

Table 4. Fitting Parameters for Langmuir and Freundlich Equations for [BMIM][Cl] Sorption onto the Prepared Functional Carbonaceous Material (FCM) Adsorbent and Commercial Activated Carbon (AC) (Conditions: 25 °C, dosage of prepared FCM or AC 2.5 g/L, 24 h, pH 6.94)

	Langmuir model $(q_e = bq_mC_e/(1 + bC_e))$			Freundlich model $(q_e = KC_e^{1/n})$		
adsorbent	q_m (mmol/g)	b (L/mmol)	R^2	K	$1/n$	R^2
FCM	0.171	19.3	0.9430	0.151	0.248	0.9894
AC	0.206	8.63	0.8088	0.180	0.241	0.9909
AC[a]	0.17	1.57	0.993	0.10	0.28	0.892
AC[b]	0.25	3.01	0.994	0.18	0.16	0.903

[a]Values from the work of Palomar et al. where an activated carbon (AC-MkU) was used as adsorbent,[11] T = 308 K. [b]Values from the work of Palomar et al. where the activated carbon (AC-MkU) was oxidized by $(NH_4)_2S_2O_8$ and was used as adsorbent (AC-MkS),[11] T = 308 K.

were determined to be 0.41 and 0.067 cm³/g, respectively, indicating small difference compared with their difference in surface area (Table S1). Moreover, compared with AC, high

content of polar oxygenated surface groups such as −OH, −C=O, and −COOH of FCM probably promoted adsorption of the hydrophilic ionic liquid [BMIM][Cl], since these polar groups favor hydrogen bonding adsorbate−adsorbent interactions.[11,19] Therefore, adsorption capacity for [BMIM][Cl] by the prepared FCM adsorbent was comparable with that of AC despite the large difference in their surface areas.

Palomar et al.[11] examined the adsorption of [BMIM][Cl] onto a commercial AC (AC-MkU, with BET surface area of 927 m²/g) that had an adsorption capacity of 0.17 mmol/g. Adsorption capacity of the prepared carbonaceous solid in this work was comparable to the commercial product evaluated by Palomar et al.[11] Furthermore, Palomar et al. investigated adsorption of [BMIM][Cl] on oxidized AC-MkU adsorbent (oxidized by HNO_3 and $(NH_4)_2S_2O_8$, denoted as AC-MkN and AC-MkS, respectively), and found that the adsorption capacities of [BMIM][Cl] onto AC-MkS and AC-MkN adsorbents were about 40−100% higher than the commercial untreated AC-MkU adsorbent. They ascribed the increase in the adsorption performance to the presence of hydrogen donor groups such as hydroxyls on activated carbon surface that favors adsorption of hydrophilic ILs,[11] which supports the present results for the good adsorption capacity of FCM for [BMIM][Cl] despite its small surface area.

Desorption Studies and [BMIM][Cl] Chemical Stability.
Desorption was carried out with batch experiments in HCl aqueous solutions at different concentrations (0.001, 0.01, and 0.1 mol/L), respectively (Table S4). About 50.3% and 63.8% of the adsorbed [BMIM][Cl] (adsorbed amount 0.064 mmol/g) could be stripped from the carbonaceous material with 0.001 and 0.01 mol/L HCl aqueous solutions, respectively. When 0.1 mol/L HCl aqueous solution was used, the stripping rate increased to 76.8%, indicating that desorption of [BMIM][Cl] from the as-prepared FCM adsorbent was promoted in acidic solutions of low pH values. Therefore, the adsorbed ionic liquids can probably be desorbed from the adsorbent for recovery and the adsorbent can be generated and recycled by relatively mild regeneration procedures.

To examine the chemical stability of the regenerated [BMIM][Cl], the ¹H NMR spectra of fresh and recovered [BMIM][Cl] were analyzed (Figure S5). The ¹H NMR spectra peaks, for [BMIM][Cl] before and after recovery, were the same, showing that no structural changes in [BMIM][Cl] occurred during recovery.

Recycle Studies. The recycle of FCM adsorbent for the adsorption−desorption of [BMIM][Cl] was studied. Sorption experiments were conducted for [BMIM][Cl] aqueous solution with an unadjusted pH value of 6.94, while desorption experiments were carried out in 0.1 mol/L HCl aqueous solutions (Figure 6). Figure 6 shows that the adsorption capacity remained within values between 0.060 and 0.064 mmol/L, and desorption rates were from 73% to 75% for each recycle run. These results demonstrate that FCM adsorbent can be regenerated and reused for adsorption of [BMIM][Cl] without loss in adsorption capacity for at least three uses, which shows the stability of the adsorbent and implies that it can find application in a variety of environmental and chemical fields.

In summary, this work provides a mild preparation method for a carbonaceous material rich in carboxyl functional groups through hydrothermal carbonization of cellulose in the presence of acrylic acid. The prepared carbonaceous material was evaluated as an absorbent for the recovery of a water-soluble ionic liquid, 1-butyl-3-methyl-imidazolium chloride,
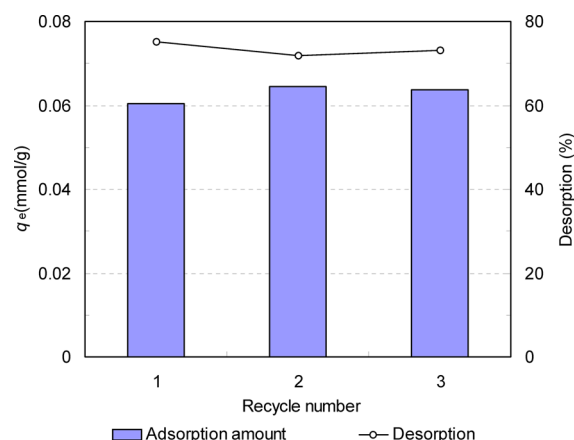

Figure 6. Adsorption−desorption cycles of the prepared functional carbonaceous material (FCM) for [BMIM][Cl]. (Adsorption conditions: $C_{[BMIM][Cl],0}$, 0.3 mmol/L; volume, 20 mL; 25 °C; dosage of FCM adsorbent, 2.5 g/L; 24 h, unadjusted pH of 6.94. Desorption conditions: 25 °C, stripping solution, 20 mL, 0.1 mol/L HCl aqueous solution; dosage of adsorbent, 2.5 g/L, 24 h).

from aqueous solutions. The adsorbent exhibited adsorption capacity comparable to a commercial activated carbon even though the prepared carbonaceous adsorbent had a low surface area. The cellulose-derived carbonaceous material has potentially broad application in a variety of environmental and chemical fields. Further studies are needed to investigate structure−activity relationships of ionic liquids and adsorption onto the similar functionalized HTC adsorbents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Additional information (Figures S1−S5, Scheme S1, and Table S1−S4) as noted in the text. This information is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: qixinhua@nankai.edu.cn; phone and fax: 86-22-2350-8807.
Notes
The authors declare no competing financial interest.

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