



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Removal of ionic liquid by engineered bentonite from aqueous solution

Yinghao Min, Yanmei Zhou*, Min Zhang, Han Qiao, Qi Huang, Tongsen Ma

Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China

ARTICLE INFO

Article history:

Received 21 October 2014

Revised 14 January 2015

Accepted 25 February 2015

Available online xxx

Keywords:

Bentonite

Ionic liquids

Adsorption

BMImCl

Aqueous solution

ABSTRACT

The removal of ionic liquid (1-butyl-3-methyl imidazolium chloride: BMImCl) was studied from aqueous solution by raw bentonite, acid-activated bentonite and organic-modified bentonite. These types of bentonite sample were characterized by FT-IR, TGA and XRD. The effects of contact time, BMImCl initial concentration, pH, ionic strength, and humic acid on the removal of BMImCl were investigated via batch adsorption experiments. The adsorption kinetics models were applied to predict the adsorption constants, and the kinetic data indicated that the pseudo-second-order model gave a better fit. Furthermore, the Langmuir, Freundlich and Temkin isotherms models were also introduced to describe adsorption process in order to obtain possible mechanism of the removal. The applied isotherms models demonstrated that the adsorption data of acid-activated bentonite samples were well described by Temkin adsorption isotherm, and the isotherm model of organic-modified bentonite was Langmuir adsorption isotherm. The adsorption experiments indicated that these bentonite samples might be applied in repair of soil and water contaminated by ionic liquids.

© 2015 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are ionic compound consisting of dissociated ions [1]. In recent decade, ILs have attracted more and more attention and research of academy and industry [2], because they possess special physical properties such as near zero vapor pressure, non-flammable, high chemical and thermal stability, high solvent capacity and enability [3,4]. Thus, ILs have been widely employed as green solvents in contrast to the general organic solvents in chemical process, especially the applications of hydrophilic ILs in the chemical industry [5,6]. However, at the same time, the applications of soluble ILs in the industry may cause a potential environment hazard with releasing them into the water [7,8]. For this reason, the removal of ILs from water has become an important topic [7], it will be necessary to find treatment steps to avoid any negative effects on ecosystems [9].

At present, some articles have been published about the removal of ILs with different techniques including oxidation [10,11], biological removal method [12–14], photocatalysis [15], ion exchange [16] and adsorption [17]. Adsorption is a common separation method for the removal of wastewater pollutants [18]. Recent studies for the adsorption of ILs onto activated carbon [2], soils [19], fermentation waste [20], bacterial and mineral surfaces [21] have been reported. The natural bentonite as a common, effective and low-cost adsorption material is often applied to remove various pollutants in water [22–25]. Bentonite is mainly composed of montmorillonite with a

typical 2:1 layered structure of which consists of an alumina octahedral layer between two tetrahedral layers of silica and negative surface charge [26,27]. It is treated as a good adsorption material because of its large surface area, excellent swelling ability and high adsorption capacity [28]. The environmental applications of bentonite have presented an interest for researchers. The chemically modified surfaces of bentonite have been widely investigated in recent years [29], and the purified bentonite (montmorillonite) has also been used to adsorb ILs from the aqueous phase [30]. However, the removal of hydrophilic ILs using engineered bentonite from this work has not been reported through our current inspection.

This is a series of experiments for the removal of ionic liquid (BMImCl) from water by the natural bentonite, acid-activated bentonite and modified bentonite. BMImCl as adsorbate is selected since it is used as a starting material to produce other ILs and is also soluble in water [31]. The present work aimed at investigating the adsorption behavior of BMImCl on bentonite products under different conditions. The kinetics and isotherm models were studied to understand and predict the adsorption behavior of BMImCl on bentonite samples with experimental adsorption data.

2. Materials and methods

2.1. Materials

The natural sodium bentonite (SB) was obtained from Xinyang (Henan, China) and used without any further purifications. Chemical composition of SB contains 73.45% SiO₂, 12.32% Al₂O₃, 0.99% Fe₃O₄, 2.68% CaO, 3.52% MgO, 0.45% Na₂O, 0.73% K₂O, 5.73% others.

* Corresponding author. Tel.: +86 371 22862833x3422; fax: +86 371 23881589
E-mail address: zhouyanmei@henu.edu.cn, zhouymhd@163.com (Y. Zhou).

The particle size is 100–200 mesh. The cations exchange capacity (CEC) of SB determined by using the methylene blue test was about 77.5 mequiv./100 g.

1-Butyl-3-methylimidazolium chloride (BMImCl: $C_8H_{15}N_2Cl$, 99%) was purchased from Henan Lihua Pharmaceutical Co., Ltd (Xinxiang, China). *N*-Heptane (99%) was obtained from Kermel (Tianjin, China). (3-Chloropropyl)-trimethoxysilane (98%, CPTMS) was purchased from Aladdin (Shanghai, China). In addition, all other chemical reagents for adsorption tests were analytical grade and used without any purifications. The distilled water was used throughout the experiments.

2.2. Activation and modifications of bentonite

2.2.1. Activation of bentonite by phosphorus acid (P-SB)

About 10 g SB was immersed in 100 mL phosphorus acid solution (1 M) under vigorous stirring at room temperature for 15 h. The mixture was filtered, then washed with distilled water until the pH of water was neutral. The resulting solids were dried in an oven at 80 °C.

2.2.2. Activation of raw bentonite by nitric acid (N-SB)

Ten grams SB and 100 mL nitric acid (1 M) were mixed completely in a flask. The reaction was carried out at the 110–120 °C by oil bath for 7 h under magnetic stirring. Then the mixture was filtered, washed until the distilled water was neutral and the resulting solids were dried at 80 °C.

2.2.3. Modifications of activated bentonite by CPTMS (CP-SB)

The amount for 7 g of N-SB was mixed completely with 25 mL *n*-heptane in a flask and then 2.8 mL CPTMS was added. The flask was immersed in oil bath for 24 h under magnetic stirring and refluxing at 76 °C. After completion of the reaction, the mixture was filtered, then washed with methanol and water, and finally dried at 80 °C.

2.3. Characterization of adsorbents

The FT-IR spectra of samples were recorded from 4000 cm^{-1} to 400 cm^{-1} on a Thermo Nicolet Avatar 360 FTIR Spectrometer (US) using the KBr pellets. Wide angle powder X-ray diffraction (XRD) patterns of dried samples were measured on XRD diffractometer (X-PertPro, Philips, Holland) using $Cu K\alpha$ radiation (the wavelength $\lambda = 0.15406$ nm) at 40 kV and 40 mA, samples were scanned at a speed of 0.08 s^{-1} from 5° to 50°. Thermal stability of dried samples was analyzed on a thermogravimetric analysis (TGA, Mettler-Toledo DTA/TGA) with the temperature range from 25 °C to 800 °C at a heating rate of 10 °C/min by using nitrogen at a flow rate of 20 mL/min. The specific surface areas of the prepared samples were determined by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption technique with a Micromeritics ASAP2010 gas adsorption apparatus. Surface potential charge of samples was determined by isoelectric point titration as a function of pH by using Zetasizer Nano (ZS90, Malvern).

2.4. Adsorption experiments

Adsorption of BMImCl on bentonite was carried out via batch adsorption experiments [25]. Twenty-five milliliters of 0.2 mmol/L

BMImCl solutions was poured into a conical flask containing 0.1 g adsorbent, and the conical flask was placed in a temperature controlled shaker by keeping 160 rpm at 25 °C for a few hours. All the adsorption experiments were performed in duplicate and the average values were reported here. Additional analyses would be conducted whenever two parallel measurements showed a difference of larger than 5%. The pH of the BMImCl solutions was adjusted by adding small amounts of NaOH and HCl solutions and measured by a pH meter (PHS-3D). Then, separating the adsorbent from the solution and analyzing absorbance of filtrate by double beam UV–vis spectrophotometry (TU-1900) at 211 nm [31]. The adsorption rate (%) and adsorption capacity (q_e) of BMImCl on bentonite samples were calculated based on the difference between the initial and final concentration in the supernatant and expressed as Eqs. (1) and (2), respectively.

$$\text{Removal rate} = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_1}{m} \times M \times V \quad (2)$$

where C_0 is initial concentration of BMImCl solutions (mmol/L); C_1 is final concentration after adsorption equilibrium (mmol/L); q_e is the adsorption capacity of the adsorbate (mg/g); M is the relative molecular mass of the BMImCl; m is the weight of adsorbent (g); V is the volume of solution (L).

3. Results and discussion

3.1. Characterization of the bentonite materials

Table 1 listed the results of surface area and zeta potential measurements. Nitrogen adsorption experiments showed that P-SB, N-SB and CP-SB had higher surface area compared to the raw bentonite. This result verified that the crystal layer of bentonite was amplified with acidification, and nitrogen gas could reach these internal surfaces. The increased surface area provided highly efficient adsorption sites for adsorbate cations. The particle sizes of SB, P-SB, N-SB and CP-SB also became smaller gradually. This was probably related to the removal of impurities and replacement of exchangeable cations with hydrogen ions which resulted in exposure of the crystal layer [25].

Zeta potential measurements showed that SB, P-SB, N-SB and CP-SB did not reach point of zero charge (PZC) and exhibited negative zero potential values at pH 1, 5 and 10. The zero point could not obtain for all samples due to the negative charge of the bentonite surface [25–27]. This result indicated that the value of adsorption pH was greater than the corresponding pH value of PZC and this helped to adsorb positively charged species. This was also a proof of negative charge nature on bentonite surface.

FT-IR spectra of the raw SB, P-SB, N-SB and CP-SB were given in Fig. 1(A). The absorption peak at 3628 cm^{-1} was observed, resulting from hydroxyl group vibration in Al–OH–Al in the octahedral layer. The observed two bands at 1043 cm^{-1} , 795 cm^{-1} were assigned to Si–O–Si stretching vibrations and Si–O–Al bending vibrations respectively in all bentonite samples spectra [32]. The band in the 3000–2600 cm^{-1} range was signified the C–H vibrations of CH_2

Table 1
BET surface area, particle size and zeta potentials for SB, P-SB, N-SB and CP-SB.

Adsorbent	BET surface area (m^2/g)	Particle size (μm)	Zeta potentials (mV)		
			pH 1	pH 5	pH 10
SB	25.9	21.8	–12.2	–33.9	–42.1
P-SB	43.4	11.6	–19.6	–30.1	–38.2
N-SB	72.6	8.64	–13.6	–25.1	–40.1
CP-SB	63.7	9.78	–1.19	–36.7	–44.5

Download English Version:

<https://daneshyari.com/en/article/691028>

Download Persian Version:

<https://daneshyari.com/article/691028>

[Daneshyari.com](https://daneshyari.com)