



Surfactant modified zeolite as amphiphilic and dual-electronic adsorbent for removal of cationic and oxyanionic metal ions and organic compounds



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ARTICLE INFO

Keywords:

Hexadecyltrimethylammonium
Zeolite
Dual-electronic adsorbent
Amphiphilic adsorbent
Organic compounds
Potentially toxic metals
Adsorption

ABSTRACT

A hydrophilic Y zeolite was primarily treated with sodium hydroxide to enhance its cation exchange capacity (Na-zeolite). The organo-zeolite (Na-H-zeolite) was prepared by a modification process of the external surface of Na-zeolite with a cationic surfactant (hexadecyltrimethylammonium; HDTMA). Three adsorbents (i.e., pristine zeolite, Na-zeolite, and Na-H-zeolite) were characterized with nitrogen adsorption/desorption isotherms, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, cation exchange capacities, and zeta potential. Results demonstrated that HDTMA can be adsorbed on the surface of Na-zeolite to form patchy bilayers. The adsorption capacity of several hazardous pollutants (i.e., Pb^{2+} , Cu^{2+} , Ni^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, propylbenzene, ethylbenzene, toluene, benzene, and phenol) onto Na-H-zeolite was investigated in a single system and multiple-components. Adsorption isotherm was measured to further understand the effects of the modification process on the adsorption behaviors of Na-H-zeolite. Adsorption performances indicated that Na-H-zeolite can simultaneously adsorb the metal cations (on the surface not covered by HDTMA), oxyanions (on the surface covered by HDTMA). Na-H-zeolite also exhibited both hydrophilic and hydrophobic surfaces to uptake organic compounds with various water solubilities (from 55 to 75,000 mg/L). It was experimentally concluded that Na-H-zeolite is a potential dual-electronic and amphiphilic adsorbent for efficiently removing a wide range of potentially toxic pollutants from aquatic environments.

1. Introduction

Currently, approximate 50 different kinds of natural zeolite are known and more than 150 kinds zeolites have been synthesized for different applications (Dionisiou and Matsi, 2016). Zeolite with a permanent negative charge results from the extended isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedra of its crystal lattice. Therefore, zeolite has been utilized to effectively adsorb cations (i.e., Mn^{2+} , Cr^{2+} , Pb^{2+} , La^{3+} , and cationic dyes) but a negligible affinity for anions (Zamzow et al., 1990; Haggerty and Bowman, 1994; Dionisiou and Matsi, 2016). In addition, the electrostatically charged material results in the hydrophilic surface of zeolite also limits the adsorption of non-polar organic compounds with low solubility (S_w) from aqueous solution (Chao et al., 2012).

To enhance the simultaneous adsorption capacity of zeolite toward specific hydrophilic and hydrophobic solutes (adsorbates), several researchers have developed an amphiphilic adsorbent by adsorption of certain substances (i.e. cationic surfactants) onto its external surface. The surfactant-modified zeolite (SMZ) became organozeolite (Haggerty

and Bowman, 1994). Such organic cationic surfactants—often quaternary ammonium salts with chloride or bromide—comprised tetraethylammonium and tetramethylammonium (Park et al., 2017), cetylpyridinium (Krajišnik et al., 2011; Serri et al., 2016), dodecyltrimethylammonium, benzyldimethyltetradecylammonium, cetyltrimethylammonium, octadecyltrimethylammonium, and tetramethylammonium (Zhu et al., 2000), octadecyltrichlorosilane (Chao et al., 2012), benzyldimethylhexadecylammonium (Majdan et al., 2009), and hexadecyltrimethylammonium (Haggerty and Bowman, 1994; Majdan et al., 2009; Rožić et al., 2009; Chao and Chen, 2012; Sun et al., 2017). The cationic surfactants are amphiphilic molecules that often contain a positively charged hydrophilic head (usually quaternary ammonium and a counter-anion such as Cl^- , Br^- , or SO_3^{2-}) and a relatively long (8–24 carbon atoms) hydrophobic tail.

Among tested cationic surfactants, hexadecyltrimethylammonium (HDTMA) salt is commonly used for modification on the surface of zeolite. This is because HDTMA is a tetrasubstituted ammonium cation with a permanently charged pentavalent nitrogen and along straight alkylchain (C16), which imparts a high degree of hydrophobicity

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(Haggerty and Bowman, 1994); and thus it cannot penetrate into the intra-particle surfaces of zeolite or enter into micropore of zeolite. In addition, the longer the tail group of HDTMA can make it become more stable the surfactant retained on the surface of zeolite (Li et al., 1998). Furthermore, Li and Bowman (1997) investigated the effects of selected counterions (Cl^- , Br^- , and HSO_4^-) on the sorption of the cationic surfactant HDTMA on clinoptilolite zeolite, concluding that counterions have significant effects on the HDTMA sorption on the zeolite. The HDTMA sorption capacity on the zeolite followed the order $\text{Br}^- > \text{Cl}^- > \text{HSO}_4^-$. In addition, previous studies demonstrated that when HDTMA adsorbed onto the external surface of zeolite, the zeolite's properties could transform from hydrophilic to hydrophobic surface and from negative charge to positive charge surface (Rožić et al., 2009; Dionisiou and Matsi, 2016). Therefore, hexadecyltrimethylammonium bromide was used as an organic cationic surfactant in this study.

When the concentration of HDTMA exceeds a critical value (critical micelle concentration; CMC), the HDTMA molecules can be adsorbed on the external surface of zeolite to form structural complete bilayers or patchy bilayers. The hydrophilic head groups (positively charged) of the surfactant units adsorb onto the zeolite surface to form a monolayer through electrostatic attraction. The hydrophobic tails of the surfactant molecules on the zeolite surface then associate with the tails of other surfactant units to form a bilayer through tail–tail hydrophobic interaction, with positive charges oriented toward the solution (Li and Bowman, 1997; Li et al., 1998; Chao and Chen, 2012; Dionisiou and Matsi, 2016). Notably, SMZ can exhibit both hydrophilic and hydrophobic characteristics on its surface if HDTMA molecules adsorbed on the partial surface of zeolite form patchy bilayers. In this case, the negative charge and positive charge of SMZ might be equal and its isoelectric point (EIP) might reach a neutral value. Similarly, if the HDTMA can block whole pores on the surface of zeolite or occupy whole exchange sites, the surface of SMZ can become completely positively charged. In this case, the specific surface area and total pore volume of SMZ are significantly lower than those of the raw zeolite. Otherwise, SMZ is regarded as a dual-electronic adsorbent with a positively charged external surface and a negatively charged internal surface.

In this study, to enhance cation exchange capacity (CEC) and external cation exchange capacity (ECEC), the hydrophilic zeolite was treated with NaOH. Na-zeolite was used as a precursor to prepared HDTMA-modified zeolite. Three adsorbents (pristine zeolite, Na-zeolite, and Na-H-zeolite) were characterized by the analyses of N_2 adsorption/desorption isotherms, zeta potential (ζ), scanning electron microscopy and energy dispersive X-ray spectroscopy. The adsorption characteristics of the adsorbents were evaluated through the adsorption isotherms of each toxic metal ion (i.e., Pb^{2+} , Cu^{2+} , and Ni^{2+} , and $\text{Cr}_2\text{O}_7^{2-}$) and organic compound (i.e., propylbenzene, ethylbenzene, toluene, benzene, and phenol). The adsorption isotherms of multiple-components (i.e., cationic metal, oxyanionic metal, and organic compound) also were herein investigated.

2. Materials and methods

2.1. Preparation of zeolite-based adsorbent

Hexadecyltrimethylammonium bromide (HDTMA; $(\text{CH}_2)_{15}\text{CH}_3\text{Br}$) and Y zeolite (CBV 400) were purchased from Alfa Aesar and Zeolyst, respectively. The relative hydrophobicity of Y zeolite surface is closely related to the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$. In this study, the selected Y zeolite (Zeolite) has a relatively low ratio (around 5.0) of $\text{SiO}_2/\text{Al}_2\text{O}_3$, indicating that Y zeolite possesses relatively higher surface hydrophilicity. This assumption is well consistent with the results observed in Fig. 1a. Furthermore, zeolites with relatively high levels of SiO_2 will become more charged because this provides more opportunities for isomorphous substitution and thus more charge.

The Na-treated zeolite sample was synthesized in the laboratory by



Fig. 1. Distributions of raw adsorbents: (a) pristine zeolite, (b) Na-zeolite, and (c) Na-H-zeolite; and adsorbent after saturated adsorption of Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$: (d) Na-H-zeolite-(Cu, Cr) in *n*-hexane/water mixture.

mixing approximately 1.0 g of zeolite with 100 mL NaOH (0.3 M). The mixture was stirred for 24 h at 25 °C. The obtained zeolite was washed with distilled water to remove the residual solution and dried in an oven at 105 °C for 24 h to produce Na-zeolite.

Meanwhile, the Na-zeolite sample modified with a cationic surfactant HDTMA (Na-H-zeolite) was synthesized following a previously published work (Chao and Chen, 2012). Na-zeolite (1.0 g) and HDTMA (1.2 g) were placed in a beaker and then deionized water was added up to 100 mL. The added amount of HDTMA exceeded the potential maximum adsorption capacity for Na-zeolite. The critical micelle concentration (CMC) of HDTMA-Br was approximately 0.94 mmol/L, as estimated by conductivity measurements of aqueous HDTMA-Br solutions at different concentrations (Rožić et al., 2009). Therefore, the resulting concentration was greater than the CMC. The solution was stirred for 24 h at 25 °C and then passed through a 0.2- μm nylon syringe filter. The solid was washed with deionized water until bromide ions were not detected (AgNO_3 test). Finally, the solid was dried at 105 °C for 24 h to obtain Na-H-zeolite.

Fig. 1b and c show the phase distribution of Na-zeolite and Na-H-zeolite in the *n*-hexane/water phase system, respectively. Clearly, Na-zeolite favors the water phase, while Na-H-zeolite favors *n*-hexane phase. It means that Na-zeolite possesses the dominant hydrophilic surface, whereas Na-H-zeolite exhibits the dominant hydrophobic surface (Nur et al., 2005).

2.2. Characteristics of adsorbent

Textural properties of three adsorbents (i.e., pristine zeolite, Na-zeolite, and Na-H-zeolite) were measured using a Micromeritics TriStar 3000 sorptometer at 77 K. The Brunauer–Emmett–Teller (BET) method was employed to estimate the specific surface areas (S_{BET}). Furthermore, the micropore surface area (S_{micro}) and micropore volume (V_{micro}) were determined using De Boer's *t*-plot (statistical thickness) method. The external (non-micropore) surface area (S_{external}) was calculated as the difference between S_{BET} and S_{micro} . The total pore volume (V_{total}) was determined in terms of the amount of adsorption at a relative pressure (P/P_0) of 0.98 by using the Horvath–Kawazoe method. Pore size distributions were measured using Brunauer's MP method, and the non-micropore volume ($V_{\text{non-micro}}$) was computed by subtracting the micropore volume from the total pore volume.

Morphological property and superficial element composition of adsorbent were obtained using a scanning electron microscopy (SEM, Hitachi S-3000 N) coupled with energy dispersive X-ray spectroscopy (EDS, HORIBA 7021H). The electrical state of the adsorbent surfaces in solutions was characterized by the isoelectric point (EIP) using a zeta potential meter (ZEN3600, MALVERN Nano-ZS). In addition, the cation exchange capacity (CEC) and external cation exchange capacity (ECEC) were determined based on literature (Pansu and Gautheyrou, 2006).

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