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Preparation of highly ordered cubic NaA zeolite from halloysite mineral for adsorption of ammonium ions

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ABSTRACT

Well-ordered cubic NaA zeolite was first synthesized using natural halloysite mineral with nanotubular structure as source material by hydro-thermal method. SEM and HRTEM images indicate that the synthesized NaA zeolite is cubic-shaped crystal with planar surface, well-defined edges and symmetrical and uniform pore channels. The adsorption behavior of ammonium ions (NH_4^+) from aqueous solution onto NaA zeolite was investigated as a function of parameters such as equilibrium time, pH, initial NH_4^+ concentration, temperature and competitive cations. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. A maximum adsorption capacity of 44.3 mg g^{-1} of NH_4^+ was achieved. The regeneration and reusable ability of this adsorbent was evaluated, and the results indicated that the recovered adsorbent could be used again for NH_4^+ removal with nearly constant adsorption capacity. Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also determined, which indicated that the adsorption was a spontaneous and exothermic process at ambient conditions. Compared with other adsorbents, the as-synthesized NaA zeolite displays a faster adsorption rate and higher adsorption capacity, which implies potential application for removing NH_4^+ pollutants from wastewaters.

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1. Introduction

Recently, people pay more attention on removal of ammonium ions (NH_4^+) from wastewaters because accumulation of NH_4^+ in water will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms [1]. Various methods including physical, chemical and biological methods have been used for NH_4^+ removal [2–4]. Among these methods available for NH_4^+ removal, adsorption is considered to be an attractive and effective technique [5–8]. Activated carbon was widely recognized as effective material for removing NH_4^+ from wastewaters [9,10]. However, its relatively high price restricts the practical industrial application. Zeolite is a promising alternative because of its low cost, selectivity and compatibility with the natural environment. Zeolite is framework aluminosilicate with pore dimensions of molecular sizes generated by corner-sharing Al^{3+} and Si^{4+} oxygen tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium and/or calcium, etc.). These exchangeable cations give rise to the ion-exchange or adsorption capability with NH_4^+.

Natural zeolite from different deposits has been widely reported as adsorbent for NH_4^+ removal in wastewaters [11–14]. Due to synthetic zeolite having uniform micropore structure and high surface area, it usually has a higher adsorption capability compared with natural zeolite. Therefore, in order to obtain low-cost and effective synthetic zeolite, many researchers have investigated the synthesis of zeolite from coal fly ash, asbestos, fly ash, metakaolinite, chrysotile and rice husk etc. [15–20]. However, in many of these studies, the total conversion time was generally long (24–72 h or more); the synthesis temperature was high (363–498 K); and the synthetic zeolite products still contained a significant amount of residual raw materials and/or other phases. The presence of non-zeolitic phases in the converted products limits the cation exchange capacity of the products and greatly reduces the applicability of synthetic zeolite. Therefore, developing effective, high adsorption capacity and low-cost synthetic zeolite for NH_4^+ removal continues to be a great challenge.

Halloysite is a two-layered aluminosilicate clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in a 1:1 stoichiometric ratio, and it is available in abundance in some countries such as China, America, Brazil and France [21,22]. Halloysite has a similar structure and composition as kaolinite, but the unit layers are separated by a monolayer of water molecules.

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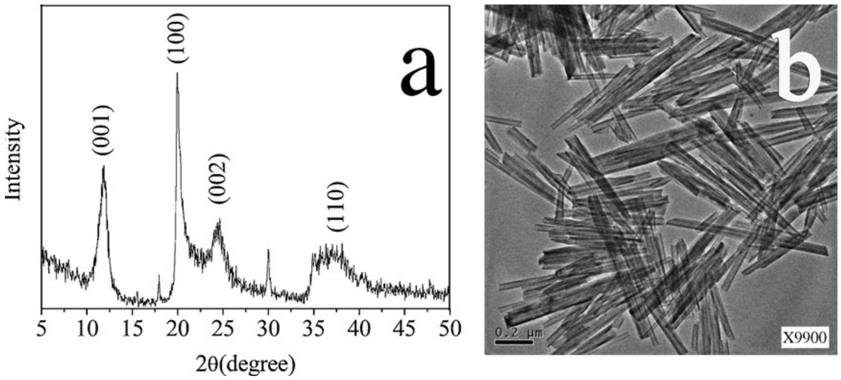

Fig. 1. The characterization of halloysite (a) XRD pattern and (b) TEM micrograph.

Due to its high surface area and hollow structure, halloysite could be used as promising material with high reactivity to synthesize highly pure zeolite. Up to now, we have found no studies on the synthesis of zeolite from halloysite.

Herein, in this paper, we introduce halloysite mineral as a source material to prepare pure, single phase, highly crystalline NaA zeolite by hydro-thermal method under lower temperature (363 K) and shorter conversion time (5 h). Meanwhile, the prepared NaA zeolite was used as adsorbent to remove NH_4^+ from aqueous solution. Parameters affecting the adsorption such as equilibrium time, pH, initial NH_4^+ concentration, temperature and competitive cations were investigated, and the isotherms and thermodynamics were also studied. In addition, the regeneration and reusable ability of NaA zeolite were evaluated. The results indicated that the prepared NaA zeolite exhibited fast adsorption rate, high adsorption capacity and the recovered adsorbent can be used again for NH_4^+ removal.

2. Experimental and methods

2.1. Raw materials

Natural halloysite mineral, used as silicon and aluminum sources in this work, was obtained from clay minerals in Henan Province, China. The composition of halloysite was analyzed by chemical method. The analysis result indicates it contains 46.15% SiO_2, 38.70% Al_2O_3, 0.033% MgO, 0.192% CaO, 0.05% Fe_2O_3, 0.03% K_2O, 0.04% Na_2O, 0.004% TiO_2 and 14.60% loss on ignition.

Fig. 1 displays the typical XRD pattern and TEM image of the natural halloysite mineral. Fig. 1a shows that the diffraction peaks of original mineral can be indexed to the hexagonal structured $Al_2Si_2O_5(OH)_4$, which are in agreement with the reported values of Halloysite-7 Å with the lattice constants $a = 5.13$, $c = 7.16$ (JCPDS Card No. 29-1487). The diffraction peak (0 0 1) at 12.1° in 2θ, corresponding to a basal spacing of 0.72 nm, which further identifies the mineral as halloysite-7 Å. The significant broadening of the diffraction peaks are ascribed to the very small crystallite size. Fig. 1b shows that the halloysite particles have a cylindrical shape and contain a transparent central area that runs longitudinally along the cylinder, indicating that the nanotubular particles are hollow and open-ended. The morphological parameters of the halloysite sample, measured from the TEM image, are an average length of 0.5–1 μm, a diameter in the range of 20–50 nm, and an average pore diameter of 10–40 nm. The small crystallite size and hollow structure endow halloysite mineral with a high specific surface area of about 79.62 $m^2 g^{-1}$, which is favourable for hydro-thermal reaction.

Other inorganic chemicals used in the study, such as ammonium chloride (NH_4Cl), sodium chloride (NaCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were all analytical grade reagents. A stock solution (1000 mg L^{-1}) was prepared by dissolving NH_4Cl in distilled water; desired concentrations were obtained when needed by diluting the stock solution with distilled water. HCl and NaOH solutions were used for pH adjustment.

2.2. Preparation of NaA zeolite

NaA zeolite was prepared using alkaline fusion followed by hydro-thermal treatment method. 2 g of halloysite powder was placed in a Ni crucible and fused with 2.6 g NaOH powder at 673 K for 2 h to promote their reactivity. The fused mass obtained was cooled and mixed with deionized water (38 mL) by magnetic stirring for 30 min until the reaction gel was homogenized. The aluminosilicate gel was aged for 2 h at 313 K in the sealed Teflon reactor to rearrange the reactant for forming nuclei. After that, the mixture was crystallized at 363 K for 5 h under static condition. Solid powder was filtered-off, washed, dried at 383 K for 12 h and the product was obtained.

2.3. Characterization

The as-prepared NaA zeolite was characterized by XRD, FTIR, SEM and TEM. XRD pattern was obtained using a Philips X Pert-Pro diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation operating at 35 kV and 25 mA and a step width of 0.04°. Fourier transformed infrared spectroscopy (FTIR) was recorded on a Nicolet Nexus 470 FTIR spectrometer in the range 400–4000 cm^{-1}. Field emission scanning electron microscopy (FE-SEM) was performed using a JSM-6700F SEM (JEOL), operating in backscatter mode at 20 kV accelerating voltage. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were obtained with a FEITECNA1G2 electron microscope operating at an acceleration voltage of 120 kV.

2.4. NH_4^+ adsorption experiments

The batch experiments were carried out in stopper conical flasks containing 50 mL varying initial concentration of NH_4^+ solutions and adsorbent dose. Then the samples were agitated on a thermostated shaker with a shaking of 180 rpm at 288–338 K. On reaching equilibrium the adsorbent was eliminated by centrifugation at 3000 rpm and then filtered with 0.45 μm membranes. The initial and final ammonium concentrations remaining in solutions were analyzed using a UV spectrophotometer (Shimadzu, UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (420 nm). The removal efficiency (R, %), the amount of ammonium adsorbed at time t (q_t, mg g^{-1}) and at equilibrium (q_e, mg g^{-1}) was calculated by using the following

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