Carbohydrate Polymers 107 (2014) 103–109

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

In-situ preparation of NaA zeolite/chitosan porous hybrid beads for removal of ammonium from aqueous solution

Kai Yang, Xiang Zhang, Cong Chao, Bing Zhang*, Jindun Liu

School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, PR China

ARTICLE INFO

Article history:
Received 6 September 2013
Received in revised form 4 December 2013
Accepted 2 February 2014
Available online 8 February 2014

Keywords:
Halloysite
Hydrothermal synthesis
NaA zeolite
Chitosan beads
Ammonium removal

ABSTRACT

Inorganic/organic hybrid materials play important roles in removal of contaminants from wastewater. Herein, we used the natural materials of halloysite and chitosan to prepare a new adsorbent of NaA zeolite/chitosan porous hybrid beads by in-situ hydrothermal synthesis method. SEM indicated that the porous hybrid beads were composed of 6–8 μm sized cubic NaA zeolite particles congregated together with chitosan. The adsorption behavior of NH_4^+ from aqueous solution onto hybrid beads was investigated at different conditions. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. A maximum adsorption capacity of 47.62 mg/g at 298 K was achieved according to Langmuir model. The regenerated or reused experiments indicated that the adsorption capacity of the hybrid beads could maintain in 90% above after 10 successive adsorption–desorption cycles. The high adsorption and reusable ability implied potential application of the hybrid beads for removing NH_4^+ pollutants from wastewater.

1. Introduction

Nitrogen compounds, as an essential nutrient existing in all forms of life, are basic components of amino acid, proteins, and genetic material. They play an important role in material cycle in nature and energy cycle in living body. However, nitrogen compounds of high concentration in aqueous can cause serious environment problems, such as accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water, which can lead a number of health problems involving living species (Guo, 2007). Total removal or at least a significant reduction of ammonium is thus obligatory prior to dispose into the environment. A variety of methods (Erbil, Soyer, & Beler Baykal, 2011; Feng, Yu, Duan, Tan, & Zhao, 2010; Schreiber & Mitch, 2007; Walker, Iyer, Heaven, & Banks, 2011) have been used for ammonium removal from wastewater. Most of these methods require not only high capital and operational cost, but also a large amount of chemicals in the actual application. Among these methods available for ammonium removal, adsorption is considered to be an attractive and effective technique.

In recent years, a wide variety of natural, synthetic and modified zeolites (Liang & Ni, 2009; Lin et al., 2013; Zhang et al., 2011; Zhao et al., 2010a) have been reported as effective adsorbents for ammonium removal because of their low cost, selectivity and compatibility with natural environment. However, zeolites often consist of fine crystalline particles with a size in the range of several nanometers to few micrometer (<5 μm), and usually suspend in water, which results in the difficulty of recycling from wastewater and reuse. Moreover, industrial requirements for adsorbents usually involve their adaptability to continuous process such as a fixed adsorption bed, and the fine zeolites particles are usually shaped into macroscopic beads before their use to avoid high pressure drop caused by the fine adsorbents.

Chitosan (CTs) is a cationic biopolymer obtained from deacetylation of chitin which is the second most abundant biopolymer in nature. Chitosan beads have received considerable attention as an excellent natural adsorbent to remove many pollutants including fluoride, dyes, heavy metal ions and other ions (Crini, 2006; Kumar et al., 2010; Menkouchi Sahli et al., 2007). However, pure chitosan beads are soft and have a tendency to agglomerate or form a gel in aqueous media, leading to a decrease of effective adsorption ability. In addition, pure chitosan beads are very sensitive to pH as they can dissolve in acidic media (Dash, Chiellini, Ottenbrite, & Chiellini, 2011). Some results have demonstrated that the chitosan-inorganic hybrid beads have high adsorption capacity and resistance to acidic environment in contrast with the pure chitosan beads (Dalida et al., 2011). So different kinds of substances, such as sand (Wan, Kan, Rogel, & Dalida, 2010), bentonite (Futalan, Kan, Dalida, Pascua, & Wan, 2011), attapulgite (Deng et al., 2012), magnesia (Sundaram, Viswanathan, & Meenakshi, 2009), montmorillonite (Yao, Tan, Fang, & Yu, 2010), activated clay (Tirtom, Dinçer, Becerik, Aydemir, & çelik, 2012) and granular activated carbon (Auta &

* Corresponding author. Tel.: +86 371 67781724.
E-mail address: zhangb@zzu.edu.cn (B. Zhang).

0144-8617/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2014.02.001

Hameed, 2013), have been used to form stable hybrid beads with chitosan.

Halloysite (HNT) is a kind of natural aluminosilicate clay mineral, consisting of SiO_2 and Al_2O_3 with stoichiometric ratio of 1:2. The chemical composition is very close to NaA zeolite. With using halloysite as original material, NaA zeolite can be synthesized simply through adding a certain amount of sodium hydroxide. In addition, halloysite is very cheap and easily available in many regions of the world. Due to its high surface area and hollow nanostructure, halloysite has been used as a high reactivity source material to synthesize highly pure zeolites (Zhao et al., 2010b). Based on the above ideas, we used the natural halloysite as a starting material to prepare activated halloysite/chitosan hybrid beads, and further transformed the beads into NaA zeolite/chitosan hybrid porous beads through in-situ hydrothermal reaction in alkaline solution. Meanwhile, the prepared NaA zeolite/chitosan hybrid beads were used as adsorbent to remove NH_4^+ from aqueous solution. Parameters affecting the adsorption such as adsorbent dosage, equilibrium time, pH, initial NH_4^+ concentration, temperature were investigated, and the isotherms were also studied. In addition, the regeneration and reusable ability of NaA zeolite/chitosan hybrid beads were evaluated. The results indicated that the prepared NaA zeolite/chitosan porous hybrid beads could be used for NH_4^+ removal from wastewater.

2. Materials and methods

2.1. Materials

Natural halloysite mineral used in this study was obtained from clay mineral in Henan Province, China. The halloysite was analyzed for its chemical composition and found to contain Al_2O_3 38.70%, SiO_2 46.16%, CaO 0.191%, MgO 0.033%, Fe_2O_3 0.05%, Na_2O 0.04%, K_2O 0.03%, TiO_2 0.004%, and H_2O 14.6%, and the atomic ratio of Al to Si (1:1) was in agreement with that of NaA zeolite (Zhao et al., 2010b).

Chitosan (92% deacetylated) was purchased from Shanghai Shenggong Chemical Industry Company. Acetic acid and other inorganic chemicals used in this study were all analytical grade reagents and without further treatment.

2.2. Preparation of NaA zeolite/chitosan hybrid beads

A flow chart of fabricating NaA zeolite/chitosan hybrid beads is presented in Fig. 1. Natural halloysite was first activated at 873 K for 2.5 h in muffle to destroy its structure. The activated halloysite (1.2 g) was added to distilled water (20 mL), followed by addition of chitosan (0.4 g). An acetic acid aqueous solution (0.1 mL) was added under stirring. The mixture was stirred for 12 h at room temperature. Then the mixture was slowly dropped into 2% (m/V) sodium hydroxide solution by syringe under continuous stirring. After that, the initial beads were formed in the mixture solution. The beads were washed several times by distilled water and impregnated in sodium hydroxide solution contained in a tightly capped 100 mL Teflon-lined stainless steel reactor at room temperature for 24 h. The sodium hydroxide solution was prepared by dissolving 1.56 g NaOH in 22 mL of distilled water. The reactor was kept in an oven under static condition at 363 K for 24 h. The samples were filtered and washed with distilled water several times to remove excess alkali. The NaA zeolite/chitosan hybrid beads were finally obtained after drying in an oven at 303 K for first 12 h and at 363 K for another 12 h.

2.3. Instrumentation and characterization

In order to confirm the crystal structure and mineralogy of the zeolites, X-ray Diffraction (XRD) was performed by Philips X Pert-Pro diffractometer with CuKα (λ = 0.154 nm) radiation operating at 35 kV and 25 mA. The structure and morphology of the beads were determined by scanning electron microscopy (SEM) using a JEOL (Model JEM 6701F; Japan).

2.4. Ammonium absorption experiment

The adsorption experiments were performed according to the batch experiments in stopper conical flask containing 50 mL of

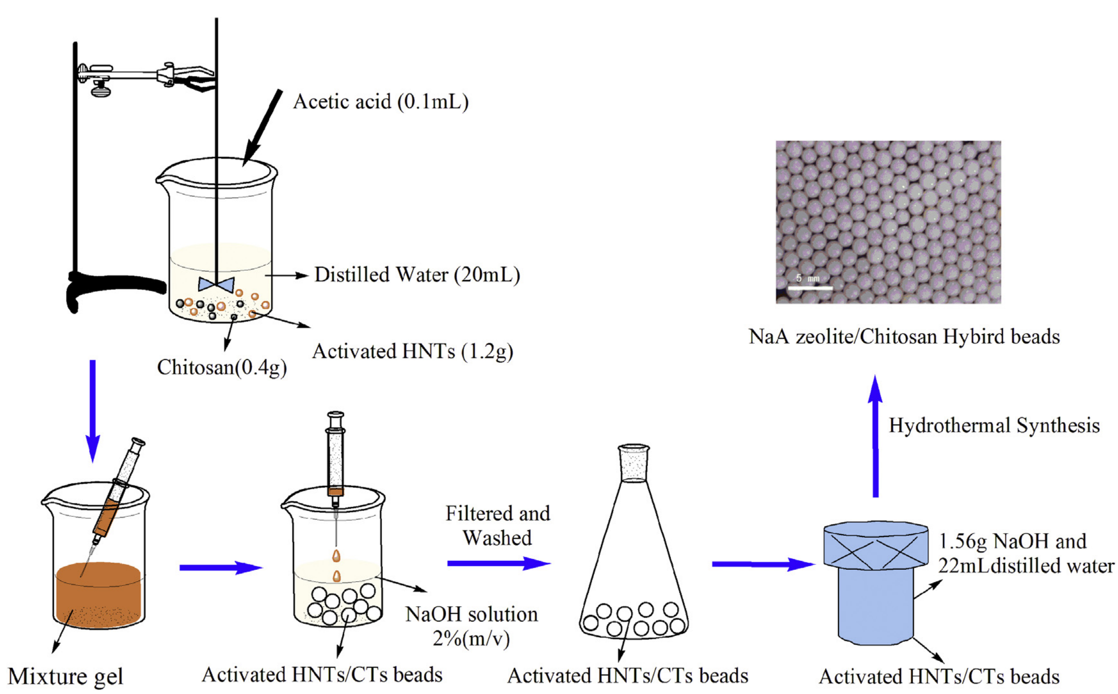

Fig. 1. A flow chart of fabricating NaA zeolite/chitosan hybrid beads.