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

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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 &

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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

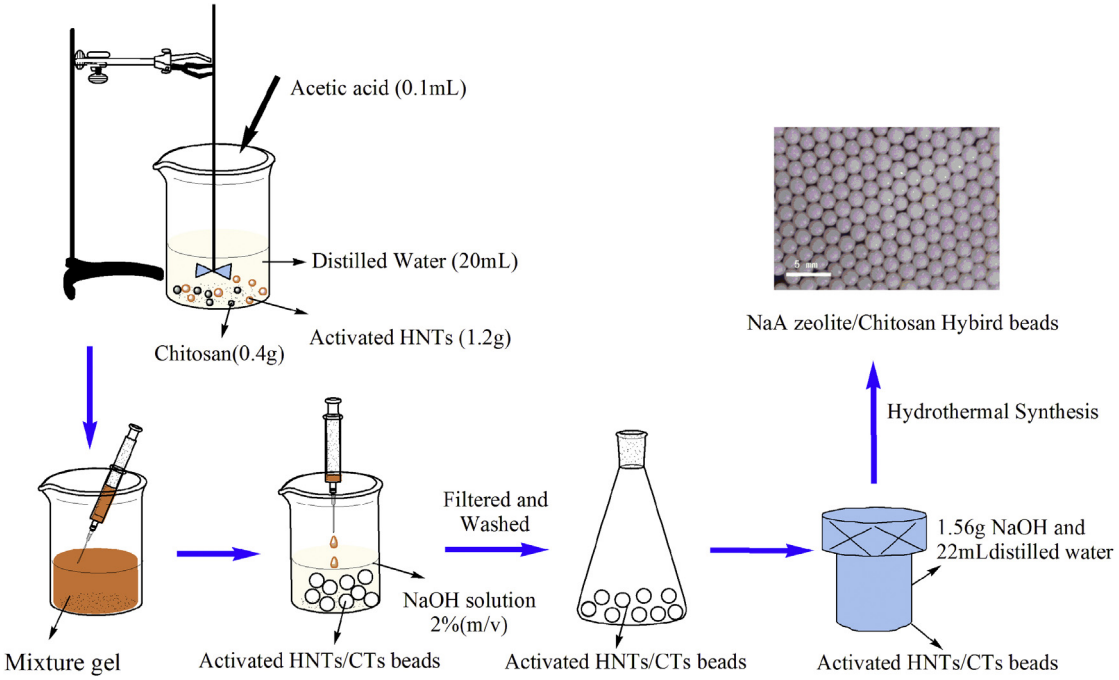

Fig. 1. A flow chart of fabricating NaA zeolite/chitosan hybrid beads.

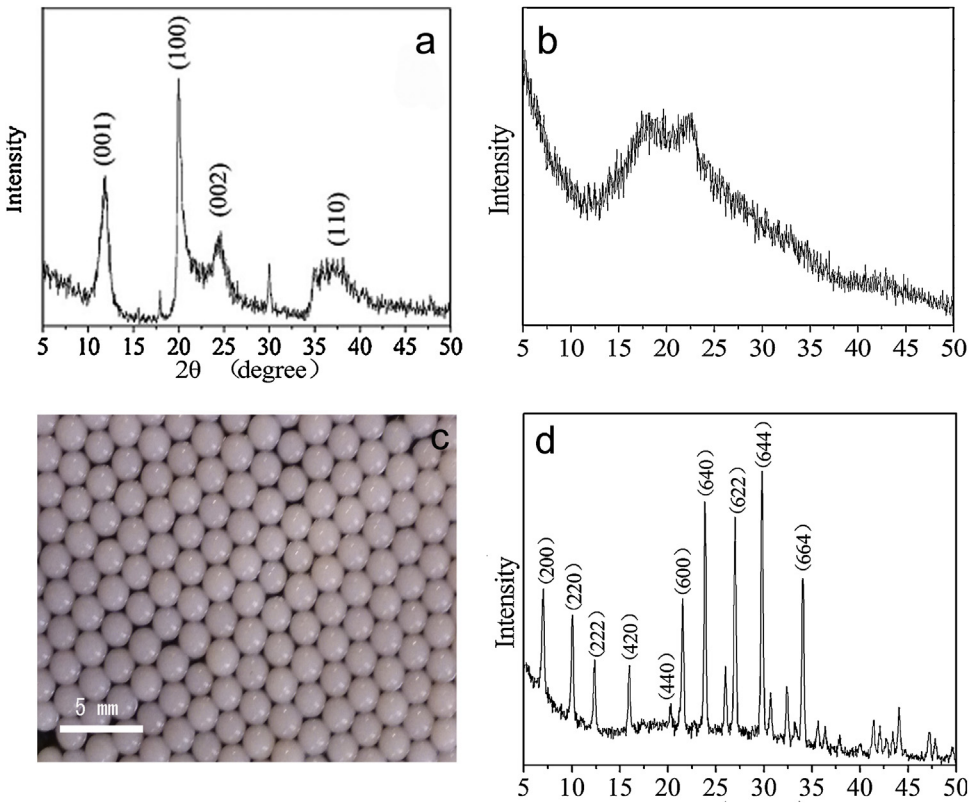

Fig. 2. The characterization of HNTs (a) and activated HNTs (b) XRD patterns; Digital photograph of wet NaA zeolite/chitosan hybrid beads (c); XRD patterns of synthesized NaA zeolite/chitosan hybrid beads (d).

varying initial concentrations of ammonium and the given dosage of adsorbent. The samples were agitated on a thermostated shaker with a shaking of 180 rpm at 288–308 K. The initial and final ammonium concentrations remaining in solutions were analyzed with the standard Nesslerization method (Zhao et al., 2010a) via using a UV spectrophotometer to monitor the absorbance changes at a wavelength of ammonium adsorbed (420 nm). The removal efficiency (R, %) and the amounts of ammonium adsorbed at time t (q_t, mg/g) and at equilibrium (q_e, mg/g) were calculated by using the following equations:

$$q_t = (C_0 - C_t) \cdot \left(\frac{V}{M}\right) \quad (1)$$

$$q_e = (C_0 - C_e) \cdot \left(\frac{V}{M}\right) \quad (2)$$

$$R = 100 \cdot \left[\frac{(C_0 - C_e)}{C_0}\right] \quad (3)$$

where C_0, C_t and C_e (mg/L) are the initial, time t and equilibrium concentrations of ammonium solution, respectively; V (L) is the volume of ammonium solution and M (g) is the weight of absorbent.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 2a shows the typical XRD pattern of original HNTs. The diffraction peaks in the pattern can be indexed to the hexagonal structured $Al_2Si_2O_5(OH)_4$, which is in agreement with the reported values of halloysite-7 Å with the lattice constants $a = 5.13$, $c = 7.16$ (JCPDSCard No. 29-1487). However, in Fig. 2b, the peaks of halloysite disappeared, and the peaks of amorphous phase appeared after the activation at 873 K for 2.5 h, indicating that the halloysite had converted into amorphous silicon oxide and aluminium oxide.

The morphology of the hybrid beads depended much on the ratio of chitosan and activated halloysite. The experiments exhibited that the uniform and stretchy beads could be prepared with chitosan and activated halloysite at the ratio of 1:3. The digital photograph of wet NaA zeolite/chitosan hybrid beads (chitosan and activated halloysite ratio of 1:3) in Fig. 2c shows that the hybrid beads had a smooth surface and uniform size with the average diameter of about 2 mm. The dried samples power was prepared for XRD by grinding the beads using a mortar and pestle. Fig. 2d shows the XRD pattern of the samples. All the XRD peaks agreed well with the characteristic peaks of NaA zeolite ($Na_{96}Al_{96}Si_{96}O_{384}{\cdot}216H_2O$) with the lattice constants $a = 24.610$, $b = 24.610$, and $c = 24.610$ by comparing the d-values of the products obtained with JCPDS data of card No.39-0222, and no additional peaks were observed, indicating that the activated halloysite had converted into pure NaA zeolite in the hybrid beads.

Fig. 3a shows SEM picture of the external structure of NaA zeolite/chitosan hybrid beads obtained after drying, indicating a smooth sphere with a diameter of about 1 mm. Closer observation of the surface of obtained beads (Fig. 3b) revealed that there were abundant pores on the surface, which was in favor of transfer and adsorption of ammonium ions. The inner structure of the beads is showed in Fig. 3c, which confirmed that the hybrid beads consisted of homogeneous distributed cubic particles and small amount of chitosan. A high magnification of the inner structure (Fig. 3d) showed that well-defined cubic particles with sizes ranging from 6 μm to 8 μm were congregated by chitosan to form a porous and loose structure. In addition, the size of particles was bigger than those of NaA zeolite (1–2 μm) synthesized with the same recipe under the hydrothermal condition without addition of chitosan (Zhao et al., 2010b). Probably because the chain like chitosan affects the rate of forming nuclei or the long reaction time for crystallization affects the growth of crystal (Cundy & Cox, 2003).

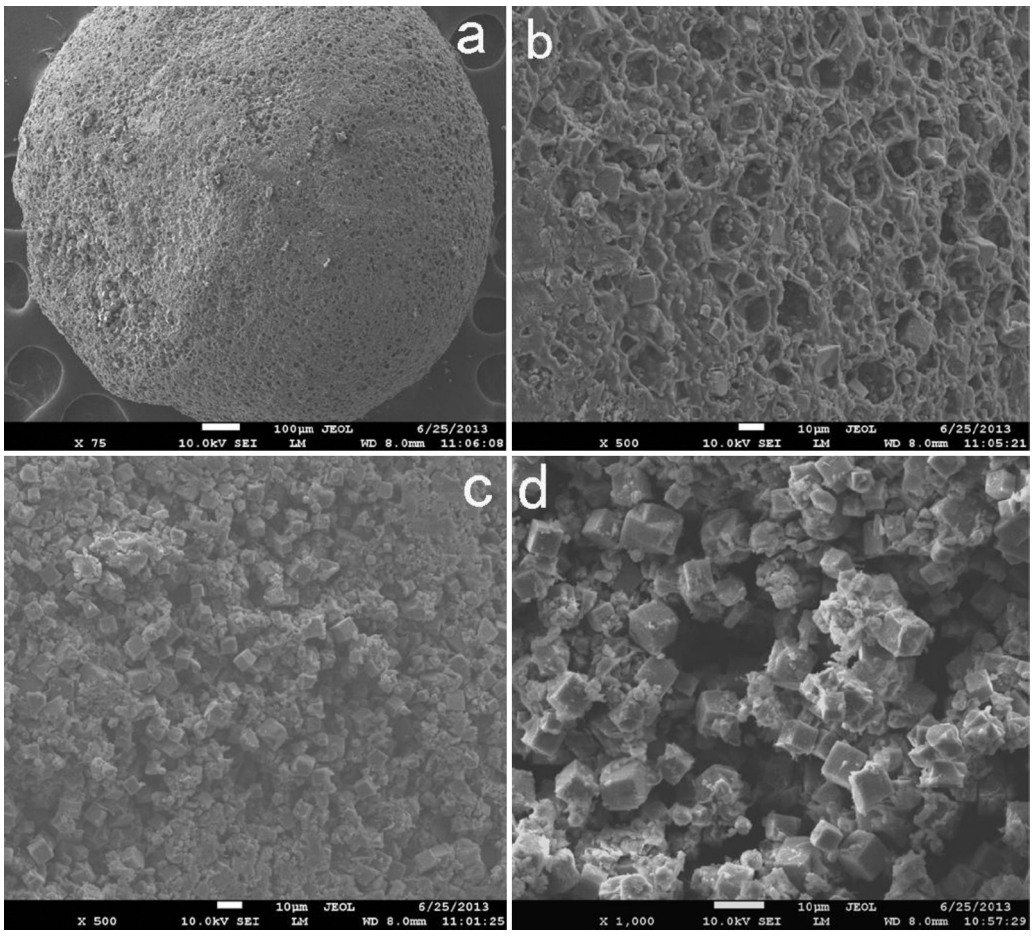

Fig. 3. SEM image of NaA zeolite/chitosan hybrid beads (a); the surface of the beads (b); the inner structure of the beads (c); a high magnification of the inner structure (d).

3.2. Effect of adsorbent dosage

In order to investigate the effect of the adsorbent dosage, various amounts of the NaA zeolite/chitosan hybrid beads were added to 50 mL 100 mg/L ammonium solution at 298 K. As demonstrated in Fig. 4, with an increase in hybrid beads dosage from 0.05 g to 0.7 g, the removal efficiency of ammonium ions increased from 39.9% to 82.8%, whereas the adsorption capacity decreased from 25.22 mg/g to 5.84 mg/g. The increase of the removal efficiency can be ascribed to the increasing surface area where the adsorption occurs. However, the removal of ammonium ions increased slowly when the dosage exceeded 0.6 g. As the amount of dosage increased from 0.6 g to 0.7 g, the removal of ammonium increased from 81.35% to 82.8%. This may be attributed to the attainment of equilibrium between the adsorbate and the adsorbent under the operating conditions (Thirugnanasambandham, Sivakumar, & Prakash Maran, 2013). For better removal efficiency, more adsorbent was needed. Since the total treatment cost depended on the cost of the adsorbent, the compromise between removal efficiency and amount of adsorbent should be optimized for the treatment.

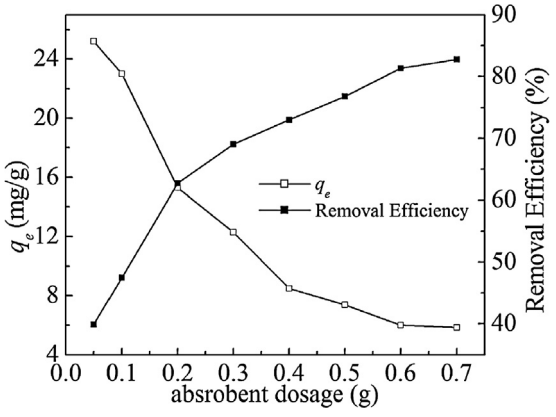

Fig. 4. Effect of adsorbent dosage for NH_4^+ adsorption on NaA zeolite/chitosan hybrid beads.

3.3. Effect of pH

The pH of the aqueous is an important controlling parameter in adsorption. The effect of pH on adsorption of ammonium onto NaA zeolite/chitosan hybrid beads was studied at pH range 3–10. The experiments carried out at 298 K with 50 mL 100 mg/L ammonium solution for a fixed dosage of 0.2 g. The results are shown in Fig. 5. As the pH values increased from 3 to 6, the adsorption increased from 8.96 mg/g to 15.78 mg/g. While kept on increasing the pH from 7 to 10, the adsorption decreased from 15.27 mg/g to 8.33 mg/g. The highest adsorption capacity was achieved at pH values of 5–6. It can be explained that pH can influence the character of the ammonium ions. At low pH values, the ammonium ions have to compete with hydrogen ions for the adsorption sites. When the pH is high, a portion of ammonium ions in solution are transformed to aqueous ammonia, which is unfavorable for adsorption on the surface of NaA zeolite (Wahab, Jellali, & Jedidi, 2010). As the initial pH of ammonium solution was near 6.8, the pH of the solution was not adjusted in the following experiments.

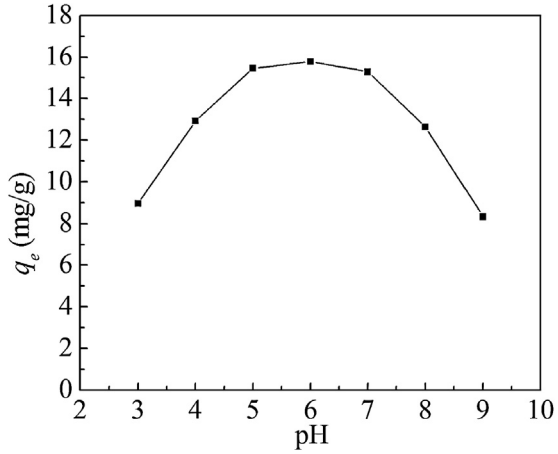

Fig. 5. Effect of initial pH for NH_4^+ adsorption on NaA zeolite/chitosan hybrid beads.

3.4. Effect of contact time and initial concentration

As shown in Fig. 6, for the different initial ammonium concentration, adsorption capacity of NaA zeolite/Chitosan beads increased quickly in the beginning. After 100 min, the rate of adsorption significantly reduced, and the adsorption equilibrium was reached after approximately 250 min. The change may be due to the fact that initially all adsorption sites are vacant and the solution concentration gradient is high. Afterwards the NH_4^+ ions uptake rate by the NaA zeolite/Chitosan beads decrease significantly due to decrease in adsorption sites (Du, Liu, Cao, & Wang, 2005). As initial concentration of ammonium ions solution increased from 50 to 300 mg/L, the amount of ammonium adsorbed at equilibrium increased from 9.28 to 35.03 mg/g. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial ammonium concentration in order to overcome all mass transfer resistance of ammonium ions between the aqueous and solid phases. Therefore, a higher initial concentration of ammonium ions may increase the adsorption capacity.

In addition, it can be observed that the halloysite almost had no adsorption of ammonium in Fig. 6. Meanwhile, compared with adsorption capacity (1.33 mg/g) of pristine HNTs at initial ammonium concentration of 100 mg/L, the adsorption capacity of the hybrid beads could reach as high as 15.27 mg/g, nearly 12 times higher than that on halloysite. The adsorption capacity of the hybrid beads is also higher than the previously reported similar absorbents, such as natural zeolite (6.30 mg/g), Chilean zeolite

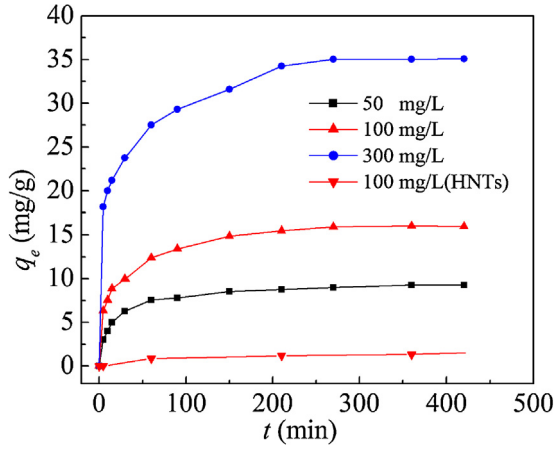

Fig. 6. Effect of time for batch adsorption of NH_4^+ on NaA zeolite/chitosan hybrid beads and HNTs. Condition: 50 mL solution; 0.2 g adsorbent; 298 K.

Table 1
Isothermal constants for batch adsorption of NH_4^+ on NaA zeolite/chitosan hybrid beads.

	Temperature (K)		
	288	298	308
Langmuir			
q_{max} (mg/g)	48.54	47.62	45.87
K_L (L/mg)	0.01643	0.01388	0.01260
r_1^2	0.970	0.982	0.992
Freundlich			
K_F ($mg^{1-1/n} L^{1/n} g^{-1}$)	2.824	2.023	1.931
$1/n$	0.5063	0.5592	0.5519
r_2^2	0.999	0.996	0.996

(12.3 mg/g) and Clinoptilolite(11.90 mg/g) (Widiastuti, Wu, Ang, & Zhang, 2011; Englert & Rubio, 2005; Ji, Yuan, & Li, 2007).

3.5. Adsorption isotherms

In order to describe the absorption process of ammonium uptake, two adsorption isotherms were used to evaluate the experiment results.

Langmuir isotherm is applicable under the following hypothesis: the adsorbent has a uniform surface; the absence of interactions between the adsorbent molecules; the adsorption process takes place in a single layer. The linear form of the Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} \cdot \frac{K_L + C_e}{q_{max}} \quad (6)$$

where q_e (mg/g) is the equilibrium amount of ammonium adsorption by NaA zeolite/chitosan hybrid beads, C_e (mg/L) is the equilibrium ammonium concentration in the solution, q_{max} (mg/g) is the maximum adsorption of ammonium, and K_L (L/mg) is the Langmuir constant related to the enthalpy of the process. K_L and q_{max} constants can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively.

The Freundich isotherm is the earliest known relationship describing the adsorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal adsorption that involves heterogeneous surface energy systems. The linear form of Freundlich isotherm is commonly given as:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \quad (7)$$

where K_F ($mg^{1-1/n} L^{1/n} g^{-1}$) and $1/n$ are Freundlich constant related to adsorption capacity and adsorption intensity, respectively. The higher value for K_F indicates higher affinity for adsorbate and the value of the empirical parameter $1/n$ lies between $0.1 < 1/n < 1$, indicating favorable adsorption. K_F and $1/n$ can be determined from the linear plot of $\log q_e$ versus $\log C_e$, respectively.

The two isotherm models are illustrated in Fig. 7. Parameters and correlation coefficients obtained from the two isotherm models are summarized in Table 1. As can be seen, Freundlich model was more adequate to describe the relationship between q_e and C_e values. The values of q_{max} decreased with increasing the temperature, indicating that the adsorption process was exothermic. The maximum of adsorption capacity reached 47.62 mg/g at 298 K according to Langmuir model. The Freundich value of $1/n$ was between 0.5063 and 0.5592, indicating favorable adsorption.

The NaA zeolite in the hybrid beads plays a critical role on the adsorption capacity of ammonium ions onto the hybrid beads. Zeolites are aluminosilicate framework porous structure generated by corner-sharing Al^{3+} and Si^{4+} oxygen tetrahedral (Zhao et al., 2010b). The small aluminum ions can occupy the position in the center of the tetrahedron of four oxygen atoms, and

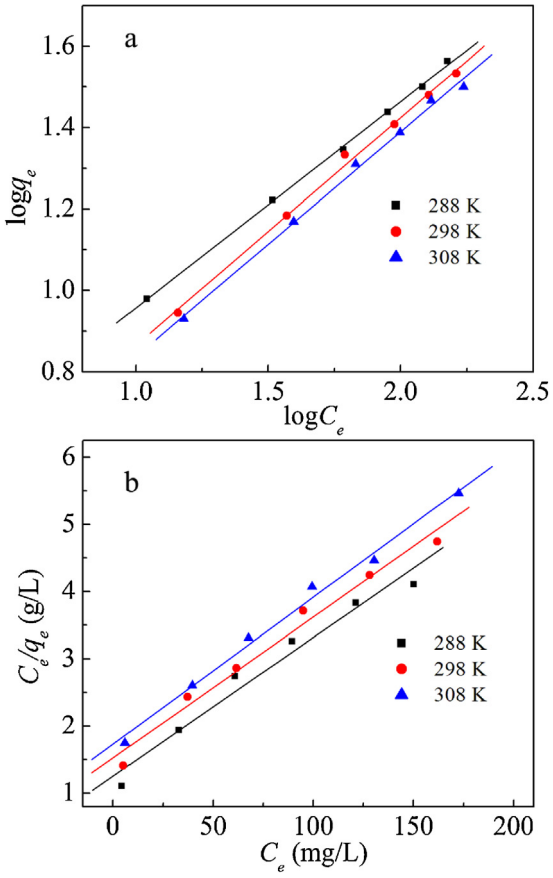

Fig. 7. Isotherm models for batch adsorption of NH_4^+ on NaA zeolite/chitosan hybrid beads: Langmuir model (a) and Freundlich model (b). Condition: 50 mL solution; 100 mg/L NH_4^+; 0.2 g adsorbent; 5 h contact time.

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^+. And the small mount of chitosan plays the role as the binding agent between the cubic particles of zeolites.

3.6. Effect of the competitive cations

In practical applications, wastewater usually contains some other cations (Na^+, Mg^{2+}, K^+, Ca^{2+}). These cations can compete with NH_4^+ for adsorption on the zeolite. Therefore, the adsorption of ammonium onto NaA zeolite/chotisan beads was carried out in the presence of other cations. As shown in Table 2, increasing of the concentration of K^+, Na^+, Ca^{2+}, Mg^{2+} from 0 (with NH_4^+ only) to 0.025 mol/L, the values of ammonium adsorbed decreased from 15.27 to 8.19, 9.58, 10.73, 11.98 mg/g, respectively. For the NaA zeolite/chitosan hybrid beads, it could be observed that the effect of competition had an order of K^+>Na^+>Ca^{2+}>Mg^{2+} at the same cations concentration, same with the selectivity order of natural zeolites (Sarioglu, 2005). In general, the hybrid beads can maintain a high adsorption capacity for ammonium ions in the case of competitive cations (Na^+, Mg^{2+}, K^+, and Ca^{2+}).

Table 2
Effect of competitive cations for NH_4^+ adsorption on NaA zeolite/chitosan hybrid beads.

NH_4^+ adsorption capacity (mg/g)				
NH_4^+ only	15.27			
Cations C (mol/L)	K^+	Na^+	Ca^{2+}	Mg^{2+}
0.01	11.00	12.40	13.15	13.53
0.025	8.19	9.58	10.73	11.98

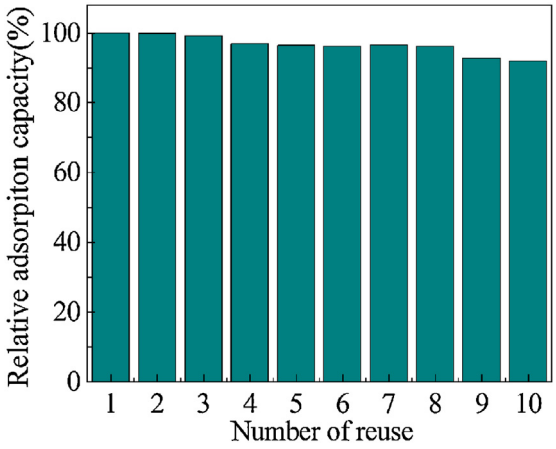

Fig. 8. The reusability of NaA zeolite/chitosan hybrid beads.

3.7. Regeneration and reuse

Reusability of an adsorbent is necessary for practical application. In this study, the adsorption was operated by using 0.2 g NaA zeolite/chitosan hybrid beads and 50 mL 100 mg/L ammonium solution shaking for 5 h at 298 K. And in the desorption process, the adsorption of adsorbed NH_4^+ onto NaA zeolite/chitosan hybrid beads were added into 100 mL 0.1 mol/L NaCl solutions (Widiastuti et al., 2011) which was used as the eluent shaking for 4.5 h at 298 K. The results are presented in Fig. 8. Compared with the first adsorption capacity 15.27 mg/g, there was slightly decrease after consecutive adsorption-desorption cycle 10 times. It is concluded that the adsorbent can be regenerated easily using NaCl as the eluent under normal condition. Consequently, it is believed that NaA zeolite/chitosan hybrid beads are a reusable adsorbent.

4. Conclusions

In conclusion, NaA zeolite/chitosan porous hybrid beads were successfully synthesized by the method of in-situ hydrothermal synthesis using natural halloysite as source. The cubic NaA zeolite particles with sizes of 6–8 μm in the hybrid beads were congregated by chitosan to form a porous and loose structure. The porous hybrid beads had exhibited a fast adsorption rate and a high adsorption capacity to NH_4^+. Both Langmuir and Freundlich models fitted well with the experimental data. The maximum adsorption capacity was 47.62 mg/g at 298 K according to Langmuir model. The regeneration of NaA zeolite/chitosan hybrid beads was realized by NaCl solution under mild conditions, and the recovered adsorbent could be used again for NH_4^+ removal. The results indicate that porous hybrid beads have the potential to be utilized as an environment-friendly adsorbent for NH_4^+ removal.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 21271158 and 20871105).

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