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[a] School of Chemical Engineering, Zhengzhou University, Zhengzhou, P.R. China [b] Henan Academy of Sciences, Zhengzhou, P.R. China

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Removal of Ammonium from Wastewater by Pure Form Low-Silica Zeolite Y Synthesized from Halloysite Mineral

Yafei Zhao,[1] Bing Zhang,[1,2] Yanwu Zhang,[1] Jinhua Wang,[1] Jindun Liu,[1] and Rongfeng Chen[2]
[1]*School of Chemical Engineering, Zhengzhou University, Zhengzhou, P.R. China*
[2]*Henan Academy of Sciences, Zhengzhou, P.R. China*

Pure form, single phase, and highly crystalline low-silica zeolite Y was synthesized from natural nanotubular halloysite mineral by the hydrothermal method. In the synthesis process, the halloysite consisted of SiO_2 and Al_2O_3 was used as starting material with adding supplementary silica and alumina sources. Ammonium adsorption properties of the as-synthesized zeolite Y were studied using batch experiments and the results revealed that its adsorption properties were strongly dependent on contact time, adsorbent dosage, pH, ionic strength, temperature, and initial concentration. The equilibrium data fit well with the Langmuir isotherm compared with the Freundlich isotherm. Kinetic studies showed that the adsorption followed the pseudo-second-order model. 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 of ammonium on zeolite Y was a spontaneous and exothermic process at ambient conditions. Due to its low cost, high adsorption capacity and fast adsorption rate, the zeolite Y synthesized from halloysite has the potential to be utilized for the cost-effective removal of ammonium from wastewater.

Keywords ammonium; halloysite; hydrothermal method; removal; zeolite Y

INTRODUCTION

Nitrogen pollution has recently attracted great attention for eutrophication, dissolved oxygen depletion, and fish toxicity in lakes and rivers. Ammonium is the inorganic ion form of nitrogen pollution arising from municipal sewage, industrial wastewater and agricultural wastes. Hence, removing ammonium from wastewater is of great importance in the control of nitrogen pollution. A variety of methods including physical, chemical, and biological methods (1–6) have been used for ammonium removal. 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, the adsorption technique employing solid adsorbents are well established. Currently, activated carbon (7,8) and resins (9) are the most popular adsorbents. However, both of them suffer from the drawback of the cost in production. Thus, there is a need to develop inexpensive and efficient adsorbents for substituting activated carbon and resins to perform the ammonium purification function.

Zeolites are most frequently proposed as ammonium collectors in wastewater treatment applications. Due to their highly developed porous structure and large specific surface area they exhibit a considerable adsorption capacity towards the ammonium pollutant. Several zeolites, such as chabazite, erionite, mordenite and clinoptilolite (10–16), and synthetic zeolites (17–19) have been identified as potential candidates for ammonium removal from wastewater. Synthetic zeolites are attractive because of their controlled and known physico-chemical properties compared with that for the natural zeolites.

Zeolite Y is one of the most important synthetic zeolites due to its extensive catalytic applications in the detergent, petroleum refining, and petrochemical industries. Increasing attention has been paid to zeolite Y for its high surface area, uniform pore size distributions, and high thermal stability. Zeolite Y is predominantly prepared from commercial reagents (20–22). However, commercial reagents usually are expensive and toxic, which greatly increase the cost of preparation and pollute the environment.

In order to obtain low-cost and environment-friendly adsorbent zeolite Y, many researchers have investigated the synthesis of zeolite Y from natural zeolite (23), rice husk ash (24), Kaolin (25), and fly ash (26,27). However, in many of these studies, the synthetic zeolite products still contained a significant amount of residual raw materials and other phases. The presence of non-zeolitic phases in the converted products limited the adsorption capacity of the products and greatly hindered the potential applications of zeolite Y.

Literature on using the synthetic zeolite Y for ammonium removal is limited. Wang et al. (23) synthesized

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Address correspondence to Bing Zhang, School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China. Tel.: 86-371-67781724; Fax: 86-371-67781724. E-mail: zhangb@zzu.edu.cn

pure zeolite NaY from the Chinese low-grade natural zeolite by fusion with sodium hydroxide prior to hydrothermal reaction. With lower Si/Al molar ratio and higher purity, the modified zeolite NaY had a much higher ion exchange capacity than the natural zeolite. Yusof et al. (28) used zeolite Y synthesized from rice husk ash to remove ammonium from aqueous solutions. The monolayer adsorption capacity for zeolite Y ($42.37\,\mathrm{mg \cdot g^{-1}}$) was found to be higher than that of powdered mordenite ($15.13\,\mathrm{mg \cdot g^{-1}}$) and granular mordenite ($14.56\,\mathrm{mg \cdot g^{-1}}$). Those studies indicated that synthetic zeolite Y was considered as a suitable candidate to replace other more expensive adsorbents available in the market.

The adsorption capacity of synthetic zeolites Y were strongly dependent on the properties of starting materials and synthesized conditions involved. Therefore, the starting premise of this paper was to develop an efficient and low-cost adsorbent based on zeolite Y for the removal of ammonium ions. Furthermore, the preparation method of zeolite Y should be environmentally friendly, as simple as possible, and no modification was performed onto the adsorbent.

Halloysite mineral is a kind of aluminosilicate clay with hollow nanotubular structure mined from natural deposits in countries such as China, America, Brazil, France, and so on. Halloysite is chemically similar to kaolinite and is usually used in the manufacture of high quality ceramic white-ware. Herein, we introduce halloysite mineral as a source material to synthesis zeolite Y under "mild" operating conditions. The as-synthesized zeolite Y is a pure, single phase, highly crystalline structure, and exhibits a fast adsorption rate and high adsorption capacity to ammonium ions.

EXPERIMENTAL AND METHODS

Raw Materials

Natural halloysite mineral used in this work was obtained from clay minerals in the Henan province, China. Halloysite mineral and supplementary silicon dioxide and aluminum hydroxide were used as Si and Al sources and sodium hydroxide (Solid white particle) as the sodium source for the synthesis.

All chemicals were of analytical reagent grade and were used without further purification. Ammonium chloride salt (NH_4Cl) and deionized water were used in the preparation of the ammonium solutions.

Synthesis of Zeolite Y

In the synthesis process, the halloysite was used as starting material and silicon dioxide and aluminum hydroxide were used as supplementary silica and alumina sources. The synthesis process was carried out using a reaction mixture with the following molar composition: $4Na_2O$:Al_2O_3:$8SiO_2$:$280H_2O$. For this experiment, 2.5 g of halloysite powder and 3.33 g sodium hydroxide were fused at 400°C for 2 h to promote their reactivity and larger amounts of aluminosilicates could be dissolved by employing alkaline fusion. The alkali fused mixture and the calculated amounts of silicon dioxide and aluminum hydroxide were dissolved in 50 mL of deionized water to form the reaction mixture. Then the reaction mixture was stirred by a magnetic stirrer for 30 min until the reaction gel was homogenized. The reaction gel was aged under 40°C for 12 h to rearrange the reactant for forming nuclei. Nuclei can be defined as the smallest viable system capable of forming an identifiable crystal phase that can induce crystal growth. It is expected that these nuclei become more abundant with longer time in the aged synthesis mixture and thus the reaction time for crystallization gets reduced (29). The crystallization was carried out in a Teflon-lined stainless steel reactor and kept in an oven under static condition at 95°C for 12 h. After hydrothermal treatment, the reaction mixture was filtered and washed with deionized water to remove excess alkali until the pH became around 9. Then, the sample was dried under a vacuum oven at 110°C for 12 h.

Instrumentation and Characterization

The raw halloysite material and the as-synthesized zeolite Y were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and high-resolution transmission electron microscopy (HRTEM). XRD was obtained using a Rigaku X-ray diffractometer operating at 35 kV and 25 mA with CuKα ($\lambda = 1.54\,\mathrm{\AA}$) radiation and a step width of 0.04°. The size and the morphology were examined by SEM, TEM, and HRTEM. The SEM experiment was performed on a JSM-6700 F electron microscope (JEOL, Japan) operating at an accelerating voltage of 20–30 kV and the sample was sputtered with a thin film of Pt. TEM and HRTEM were performed with a FEITECNAIG2 microscope operated at 200 kV.

Ammonium Adsorption Experiments

All the experiments were carried out in a stopper conical flask containing 25 mL varying initial concentration of ammonium and adsorbent dosage. On reaching equilibrium the adsorbent was eliminated by centrifugation at 3000 rpm in the laboratory. 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 amount of ammonium adsorbed by the zeolite Y (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e ($\mathrm{mg \cdot g^{-1}}$) is the amount of the total adsorbed ammonium, C_0 and C_e ($\mathrm{mg \cdot L^{-1}}$) are initial and equilibrium concentrations of ammonium in solution, respectively. V (L) is the solution volume and M (g) is the adsorbent weight.

RESULTS AND DISCUSSION

Characterization

Figure 1 displays the typical XRD pattern and TEM image of the natural halloysite mineral. Figure 1a shows that the diffraction peaks of the 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 = 5.133, b = 5.133 and c = 7.160 (JCPDS Card No. 29-1487). The significant broadening of the diffraction peaks are ascribed to the very small crystallite size. Figure 1b shows that the halloysite mineral has a tubular and a hollow structure with 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 $79.62\,m^2 \cdot g^{-1}$ that contributes to enhance reactivity.

Figure 2 shows the XRD pattern of the product. The typical diffraction peaks corresponding to halloysite remarkably disappear and all XRD peaks agree well with the characteristic peaks of low-silica zeolite Y ($Na_2Al_2Si_{4.5}O_{13} \cdot xH_2O$) with the lattice constants a = 24.676, b = 24.647, and c = 24.676 by comparing the d-values of the products obtained with JCPDS data of card No. 43-0168, and no additional peaks are observed. Notably, the product exhibits characteristic and strong XRD peaks of zeolite Y, indicating a pure phase of zeolite Y with high crystallinity.

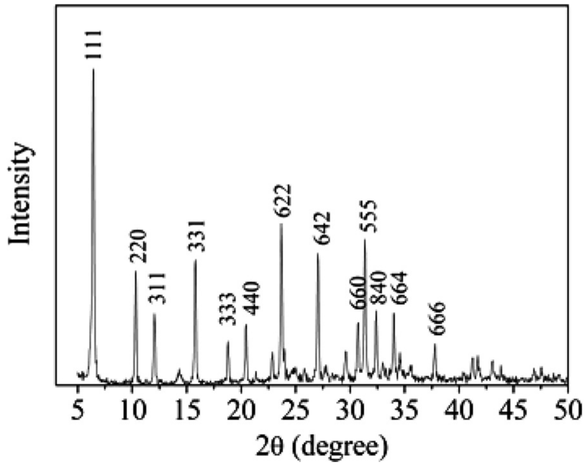


FIG. 2. XRD pattern of synthesized zeolite Y obtained by halloysite.

SEM images of zeolite Y are shown in Fig. 3. Well-defined octahedral crystals with eight equilateral triangles as faces of zeolite Y and size ranging from 1 to 2 μm are seen from the images. The octahedral crystals further confirmed the synthesis of a faujasite-type zeolite Y. Similar SEM images of zeolite Y were also reported by Karim et al. (20), Ferchiche et al. (21), Berger et al. (22), and Rayalu et al. (27).

TEM and HRTEM images of the sample are shown in Fig. 4. According to the TEM image (Fig. 4a), the particle size of the synthesized zeolite Y has been estimated between 1 and 2 μm and the morphology of the crystals resembles that of SEM (Fig. 3). The lattice fringe can be clearly seen from the HRTEM image (Fig. 4b), implying the good crystallization of the zeolite Y. The micropore size is calculated from HRTEM image about 0.9 nm, which corresponds to the pore diameter of zeolite Y (JCPDS card No. 43-0168). The symmetrical and uniform pore channels provide a huge surface and active sites, and thus ions can penetrate into the pore channels or be adsorbed onto the surface easily. So it can be used as a low-cost adsorbent for the adsorption of ammonium ions.

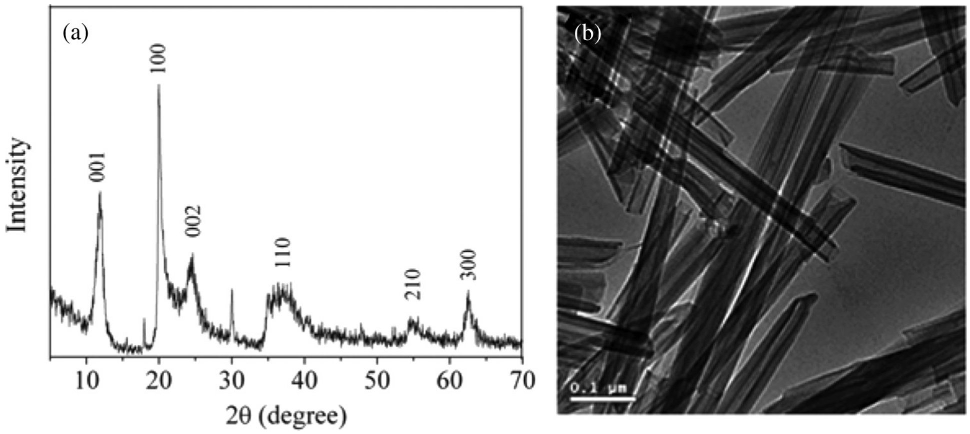


FIG. 1. The characterization of halloysite (a) XRD pattern (b) TEM micrograph.

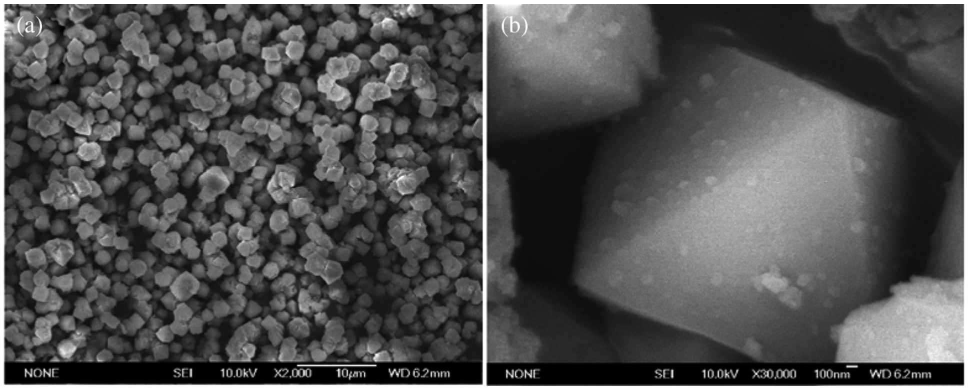


FIG. 3. SEM images of synthesized zeolite Y obtained by halloysite (a) ×2000 (b) ×30000.

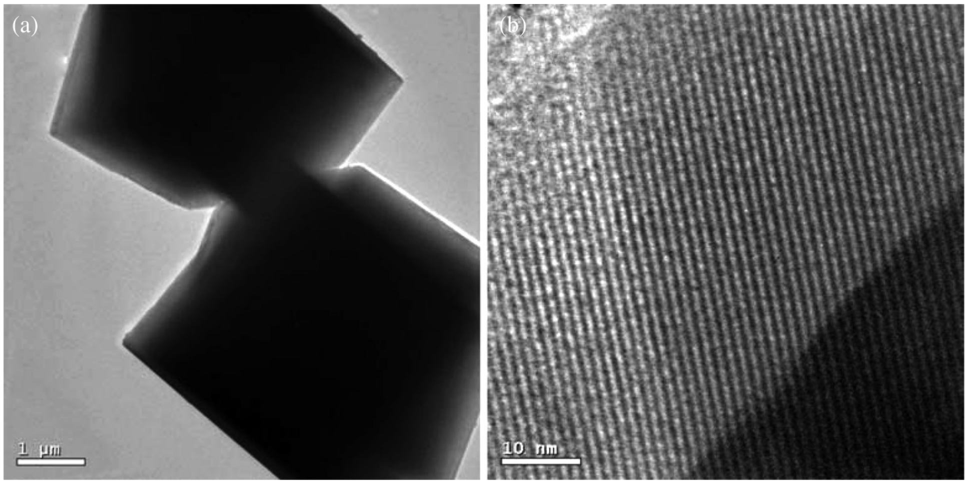


FIG. 4. TEM and HRTEM micrographs of synthesized zeolite Y obtained by halloysite mineral (a) TEM (b) HRTEM.

Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter in the determination of the adsorption capacity. The effect of the adsorbent dosage was investigated by the addition of various amounts of zeolite in 25 mL 100 $\mathrm{mg \cdot L^{-1}}$ ammonium ions aqueous solution at 25°C. The result is shown in Fig. 5. It was observed that with an increase in zeolite Y dosage from 0.025 to 0.30 g, the removal efficiency of ammonium ions increases from 30.84% to 85.68%, whereas the adsorption capacity decreases from 30.84 to 7.14 $\mathrm{mg \cdot g^{-1}}$. The increase in the removal efficiency can be explained by the increasing surface area where the adsorption takes place. However, a slower increase in the removal of ammonium ions is observed beyond the dosage of 0.10 g. When the dosage of zeolite increased from 0.20 to 0.30 g, the removal of ammonium ions increased from 83.63% to 85.68%. This may be attributed to the attainment of equilibrium between the adsorbate and the adsorbent under the operating conditions (30).

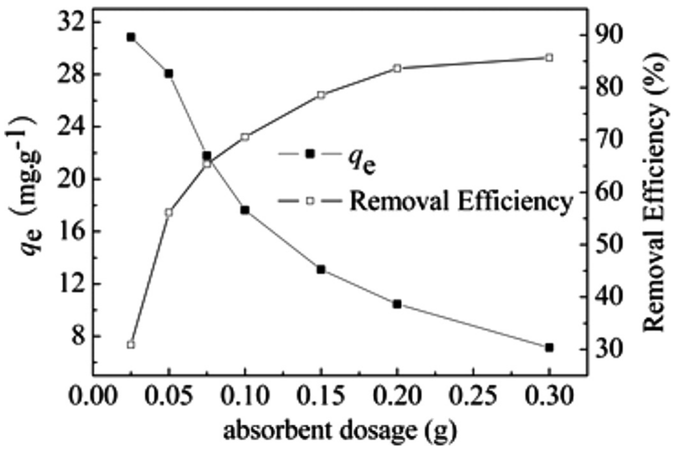


FIG. 5. Effect of adsorbent dosage for ammonium adsorption on synthesized zeolite Y at 25°C.

The adsorption process reaches a saturation point after which no further ammonium ions adsorption takes place. Thus, in all subsequent studies the amount of zeolite Y was chosen as 0.05 g. At this amount the adsorption is considered to be efficient and saves unnecessary use of excess adsorbent.

Effect of Initial pH

The effect of the initial pH on adsorption of ammonium onto zeolite Y was investigated at 25°C by varying the initial pH of 100 mg · L^{-1} of ammonium solution (25 mL) for a fixed zeolite dosage of 0.05 g. The pH of the solutions was adjusted to within 3–9 using 0.1 mol · L^{-1} HCl and 0.1 mol · L^{-1} NaOH solutions. The result is shown in Fig. 6. The highest adsorption capacity is achieved when operating at pH values of 6–7. pH is one of the most important parameters on ammonium removal by zeolite Y since it can influence the character of the ammonium ions. At lower pH, the ammonium ions have to compete with hydrogen ions among the adsorption sites; however, when the pH is higher, the ammonium ions are transformed to aqueous ammonia (3). Aqueous ammonia is unfavorable for adsorption on the surface of zeolite Y. As the initial pH of ammonium solution is near 6.8, the pH of the solution was not adjusted in the next experiments.

Effect of Temperature and Initial Ammonium Concentration

The temperature and initial ammonium concentration were studied at 25–45°C with 25 mL of ammonium solution of different initial ammonium concentrations in the range of 10–300 mg · L^{-1} and 0.05 g zeolite Y, respectively. The results are shown in Fig. 7. The results indicate that the amount of ammonium adsorption onto zeolite Y increases with a decrease in temperature, and this may be due to a tendency for the ammonium molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution. Lower temperature favors adsorption of ammonium onto zeolite Y, which proves that the adsorption process is exothermic. The ammonium adsorption capacity increases with increasing initial ammonium concentration in solution and this is the result of an increase in the driving force. The higher the ammonium concentration in solution is, the higher the solute concentration gradient is, and it provides the necessary driving force so that ammonium ions can be adsorbed on the surface of the micropores of zeolite Y within the given contact time.

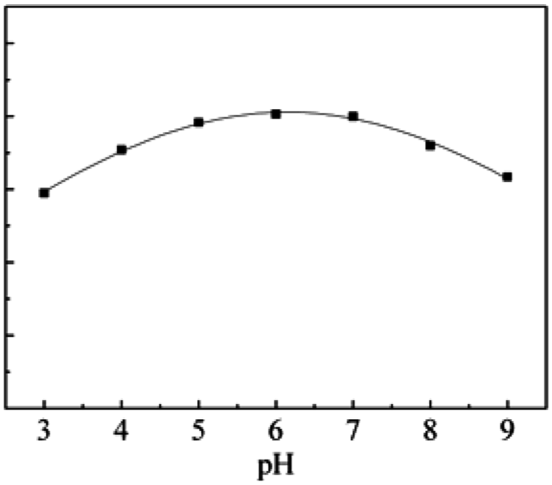


FIG. 6. Effect of pH values for ammonium adsorption on synthesized zeolite Y at 25°C.

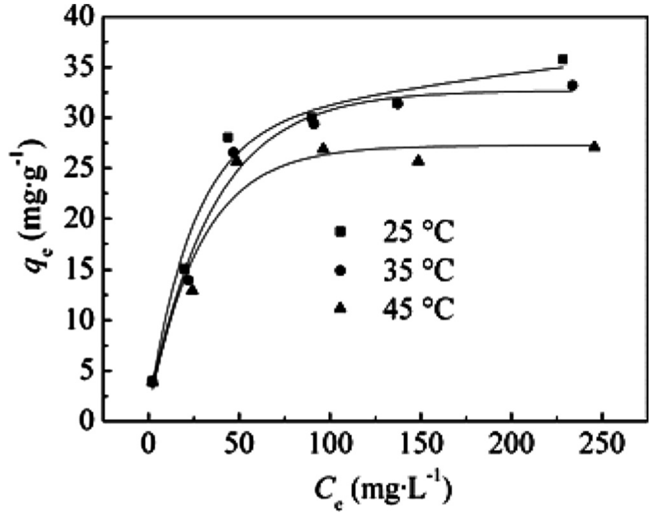


FIG. 7. Effect of initial concentration and temperature for ammonium adsorption on synthesized zeolite Y.

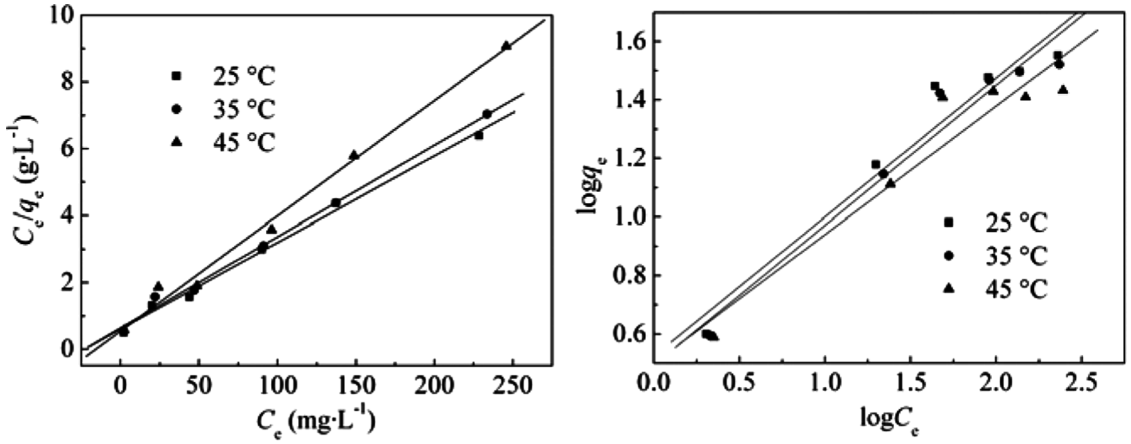
Adsorption Isotherms

Adsorption isotherm is essential for the description of how ammonium ions will interact with zeolite Y and is useful to optimize the use of zeolite Y as adsorbent. Therefore, the Langmuir and Freundlich adsorption isotherms were used for the evaluation of experimental results.

The 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:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad (2)$$

where q_e (mg · g^{-1}) is the equilibrium amount of ammonium adsorption by zeolite Y, C_e (mg · L^{-1}) is the equilibrium ammonium concentration in the solution, q_{max}



(a) (b)

FIG. 8. Isotherm models for ammonium adsorption on zeolite Y (a) Langmuir model (b) Freundlich model.

$(\mathrm{mg \cdot g^{-1}})$ is the maximum adsorption of ammonium, and K_L $(\mathrm{L \cdot mg^{-1}})$ is the Langmuir constant related to the enthalpy of the process. q_{max} and K_L constants can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively.

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F $(\mathrm{mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}})$ and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The higher value for K_F indicates higher affinity for adsorbate and the values of the empirical parameter $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption (31). K_F and $1/n$ can be determined from the linear plot of log q_e versus log C_e, respectively.

Both the two isotherm models are illustrated in Fig. 8, and parameters and correlation coefficients obtained from the two isotherm models are summarized in Table 1. It was found that the fitting to the Langmuir model gave higher values of correlation coefficients R than those for the Freundich model at the temperature investigated. The result showed that the Langmuir model is better than the Freundich model in describing the behavior of ammonium adsorption onto zeolite Y, implying that the adsorption process could be a homogeneous distribution onto the zeolite Y surface. The Freundlich values of $1/n$ between 0.439 and 0.475 $(0 < 1/n < 1)$ revealed the favorable removal conditions.

The values of q_{max} for zeolite Y decreased with increasing temperature, indicating the adsorption process is exothermic. The highest q_{max} value was found to be 38.64 mg · g^{-1} at 25°C from Langmuir model. A comparison of the ammonium adsorption capacity of various adsorbents is presented in Table 2. It is observed that our result is similar to Chinese natural zeolite synthesized NaP and rice husk ash synthesized zeolite Y, while higher than Chinese natural zeolite synthesized NaY and clinoptilolite prepared NaY and CaY, etc. This confirmed that halloysite synthesized zeolite Y had a comparable higher adsorption capacity for removing ammonium ions. Variation in ammonium ions' adsorption capacity was mainly attributed to the difference in the property of the adsorbent and the experimental condition involved.

Effect of Contact Time

Figure 9 shows the effect of contact time on the adsorption of ammonium ions by zeolite Y for different initial ammonium concentrations. The amount of ammonium adsorbed increased with the increase in contact time for any initial concentration and equilibrium was established

TABLE 1
Isotherm constants for ammonium adsorption on zeolite Y

	Temperature (°C)		
Isotherm models	25	35	45
Langmuir			
q_{max} $(\mathrm{mg \cdot g^{-1}})$	38.64	36.63	29.03
K_L $(\mathrm{L \cdot mg^{-1}})$	0.0157	0.0175	0.0189
R	0.997	0.997	0.996
Freundlich			
K_F $(\mathrm{mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}})$	3.351	3.115	3.171
$1/n$	0.475	0.478	0.439
R	0.971	0.974	0.954

TABLE 2
Comparison of adsorption capacity of ammonium onto various adsorbents

Adsorbents	Capacity ($mg \cdot g^{-1}$)	References
Halloysite synthesized zeolite Y (NaY)	38.64	This Study
Volcanic tuff	19.00	(3)
Transcarpathian clinoptilolite and Turkish clinoptilolite	11.50/8.121	(14)
New Zealand clinoptilolite and mordenite	6.588/9.479	(16)
MesoLite	49.00	(17)
Chinese natural zeolite synthesized NaP	39.06	(19)
Chinese natural zeolite and synthesized NaY	11.20/22.64	(23)
Rice husk ash synthesized zeolite Y, powdered mordenite and granular mordenite	42.37/15.13/14.56	(28)
Clinoptilolite prepared NaY and CaY	11.90/11.51	(32)

in 30 min. It was observed that the rate of ammonium removal by zeolite Y is high in the initial 10 min, but thereafter the rate significantly reduces and eventually equilibrates. The change in the rate of ammonium removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high (33). Afterwards the ammonium uptake rate by zeolite Y decreases significantly due to a decrease in adsorption sites. Karadag et al. (14) also found that ammonium ions uptake by natural Turkish clinoptilolite was a fast process that occurred with 40 min. It was also observed that the amount of ammonium adsorbed at equilibrium increased from 15.08 to 35.75 $mg \cdot g^{-1}$ with increasing initial concentration of ammonium ions solution from 50 to 300 $mg \cdot L^{-1}$. 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.

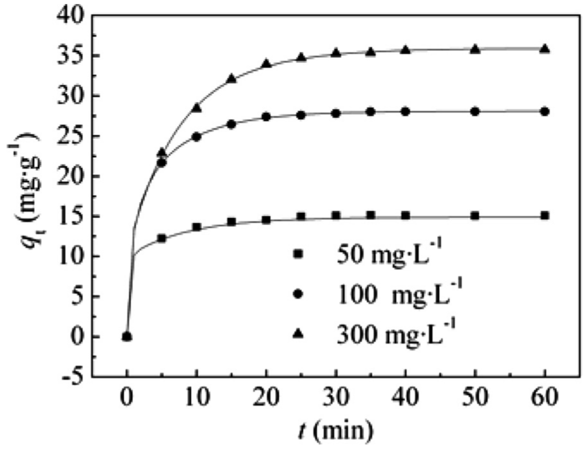


FIG. 9. Effect of contact time for ammonium adsorption on synthesized zeolite Y at 25°C.

Adsorption Kinetics

In order to examine the mechanism of the adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. The pseudo-first-order and pseudo-second-order kinetic models were employed to examine the experimental data.

The linear pseudo-first-order equation is given as follows:

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

where q_e and q_t ($mg \cdot g^{-1}$) are the amounts of ammonium adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption process. The parameters k_1 and q_e could be calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ versus t and are given in Table 3. The correlation coefficients R obtained at all the studied concentrations are low, in the range 0.8281–0.9661. Furthermore, the experimental values of $q_{e,exp}$ ($mg \cdot g^{-1}$) are far from the calculated $q_{e,cal}$ ($mg \cdot g^{-1}$). These suggest that the pseudo-first-order kinetic model is not suitable for describing the adsorption process.

The linear form of pseudo-second-order equation is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

where k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the rate constant of the pseudo-second-order. The q_e and k_2 values can be obtained from the slope and intercept of plots of t/q_t versus t. Figure 10 shows typical plots of the pseudo-second-order equation for the ammonium-zeolite Y system as t/q_t versus t. The straight lines in the plot of the linear pseudo-second-order equation show good agreement of experimental data with the pseudo-second-order kinetic model for different initial ammonium concentrations.

TABLE 3
Kinetic parameters for ammonium adsorption onto zeolite Y

Kinetic models	Ammonium concentration ($mg \cdot L^{-1}$) 50	100	300
$q_{e,exp}$ ($mg \cdot g^{-1}$)	15.32	28.29	35.94
Pseudo-first-order			
$q_{e,cal}$ ($mg \cdot g^{-1}$)	1.894	4.536	12.20
k_1 (min^{-1})	0.0469	0.0626	0.0800
R	0.8281	0.9157	0.9661
Pseudo-second-order			
$q_{e,cal}$ ($mg \cdot g^{-1}$)	15.44	28.86	37.75
k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	0.0598	0.0259	0.0099
R	0.9999	0.9999	0.9996

The values of the pseudo-second-order equation parameters together with correlation coefficients are listed in Table 3. The correlation coefficients for the pseudo-second-order equation were greater than 0.9996 for all concentrations. The calculated $q_{e,cal}$ values also agree very well with the experimental data. This strongly suggests that the adsorption of ammonium onto zeolite Y follows the pseudo-second-order kinetic model.

Effect of Ionic Strength

Since industrial effluents are always contaminated with various additives such as inorganic salts, it is important to study the effect of these ions on the adsorption property of ammonium solutions. Therefore, the adsorption of ammonium in the presence of salt was carried out at 0.001–0.100 $mol \cdot L^{-1}$ NaCl salt concentrations, 0.05 g adsorbent and constant initial ammonium concentration of 100 $mg \cdot L^{-1}$ at 25°C. The adsorption of ammonium on zeolite Y is significantly affected by the presence of NaCl (Fig. 11). With an increase of the ion strength from 0.001 to 0.1 $mol \cdot L^{-1}$, the value of the ammonium absorbed decreased from 23.85 to 1.63 $mg \cdot g^{-1}$. This may be due to the ion exchange reaction between ammonium ions from aqueous solutions and sodium ions from zeolite Y, which can be expressed as (9):

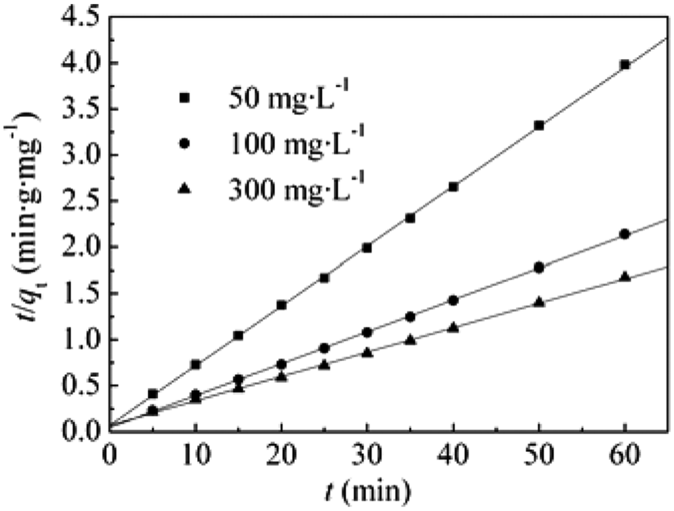


FIG. 10. Pseudo-second-order kinetic plots for ammonium adsorption on synthesized zeolite Y at 25°C.

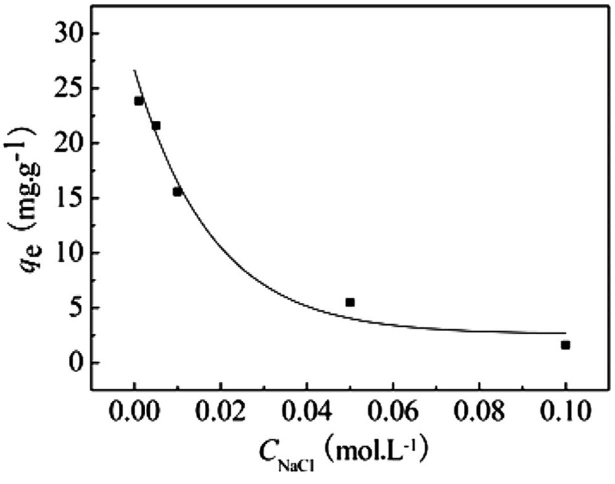


FIG. 11. Effect of ionic strength for ammonium adsorption on synthesized zeolite Y at 25°C.

$$Z^- - Na^+ + NH_4^+ \rightleftharpoons Z^- - NH_4^+ + Na^+ \tag{6}$$

where Z^- symbolizes the negatively charged functional group of the zeolite. As the Na^+ in the solution was increased, the reaction would be shifted from the right to the left, resulting in the reduction of ammonium adsorption. Similar results were found in the literature on the adsorption of ammonium by natural clinoptilolite and modified zeolite NaY, which also concluded that NaY has a much bigger aperture than clinoptilolite and the ionic strength in the solution turns into the principal factor in ion exchange (23).

Thermodynamic Parameters

In order to gain an insight into the mechanism involved in the adsorption process, thermodynamic parameters for the present system are calculated. The adsorption free energy (ΔG^0), adsorption enthalpy (ΔH^0), and adsorption entropy (ΔS^0) at different temperatures (25, 35, 45°C) are calculated using the following equations:

$$\Delta G^0 = -RT \ln K_c \tag{7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

TABLE 4
Thermodynamic parameters for ammonium adsorption on zeolite Y

Temperature (°C)	25	35	45
ΔG^0 ($\mathrm{kJ \cdot mol^{-1}}$)	−0.609	−0.317	−0.130
ΔH^0 ($\mathrm{kJ \cdot mol^{-1}}$)		−7.735	
ΔS^0 ($\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$)		−0.0240	

$$K_c = \frac{C_{Ae}}{C_{Se}} \tag{9}$$

where K_c is the equilibrium constant, C_{Ae} ($\mathrm{mg \cdot L^{-1}}$) is the amount of ammonium adsorption on the zeolite Y per L of the solution at equilibrium, C_{Se} ($\mathrm{mg \cdot L^{-1}}$) is the equilibrium concentration of the ammonium in the solution. T (K) is the solution temperature and R ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) is the gas constant and is equal to 8.31.

ΔH^0 and ΔS^0 are calculated from the intercept and slope of the linear plot of ΔG^0 versus T. The values of ΔG^0, ΔH^0, and ΔS^0 parameters are summarized in Table 4. Change in the standard free energy ΔG^0 have negative values, −0.609, −0.317, and $-0.130\,\mathrm{kJ \cdot mol^{-1}}$ at 25, 35, 45°C, respectively. These results indicate that ammonium adsorption by zeolite Y is spontaneous and has physical characteristics. A change in the standard enthalpy ΔH^0 value is $-7.73\,\mathrm{kJ \cdot mol^{-1}}$, indicating that ammonium adsorption is an exothermic process. The negative value of the standard entropy change ΔS^0 ($-0.024\,\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$) suggests that randomness decreases the removal of ammonium on zeolite Y.

CONCLUSIONS

In conclusion, pure form, single phase, and highly crystalline zeolite Y was successfully synthesized from natural halloysite mineral by hydrothermal reaction. It exhibits a fast adsorption rate and high adsorption capacity to ammonium ions. High initial concentration and low temperature favor the ammonium ions adsorption on the zeolite Y. The isotherm study indicates that experimental data fits better with the Langmuir than the Freundlich model. The maximum adsorption capacity is $38.64\,\mathrm{mg \cdot g^{-1}}$ at 25°C. It has a comparable higher adsorption capacity for removing ammonium ions than many other low-cost absorbents yet reported in the previous work. The kinetic study at different initial concentrations reveals that the pseudo-second-order model yields a much better fit than that of the pseudo-first-order model. The negative values of ΔG^0 and ΔH^0 show that the adsorption is a spontaneous and exothermic process. The results indicate that zeolite Y synthesized from halloysite mineral could be used as an effective adsorbent for ammonium removal. However, further research into the practical use needs to be carried out prior to the application of zeolite Y obtained from halloysite mineral in ammonium wastewater treatment.

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