

ADSORPTION OF LOW-CONCENTRATION AMMONIUM ONTO VERMICULITE FROM HEBEI PROVINCE, CHINA

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Abstract—Vermiculite is a common layered silicate clay mineral which has good adsorption and ion-exchange properties, and which is used to remove pollutants from groundwater. The adsorption by vermiculite from Hebei Province, China, of low-concentration ammonium in water was assessed here to evaluate the effects of adsorption time, particle size, adsorbent dose, pH, and temperature. Using Fourier-transform infrared spectroscopy, the concentration of NH_4^+ at 1430 cm^{-1} was evaluated after ammonium was adsorbed by vermiculite. Based on Langmuir-model analysis, the adsorption capacity of the Chinese vermiculite (in the particle-size range $0.025\text{--}0.075\text{ mm}$) for ammonium was 18 mg/g after 3 h of equilibration. Optimal adsorption occurred at pH 6–7 and 60°C , which is different from that at high ammonium concentrations. Smaller particle-size fractions showed greater degrees of adsorption. Increase in Mg^{2+} , K^+ , or Na^+ concentrations influenced ammonium adsorption and, therefore, indicated that cation exchange was the mechanism for ammonium uptake from low-concentration solutions.

Key Words—Adsorption, Ammonium, China, Vermiculite.

INTRODUCTION

Contamination of groundwater by ammonium is a widespread environmental problem with the ammonium originating from industrial wastewater and urban sewage, dissolution of solid waste, and from excessive use of nitrogen fertilizers in agriculture. Reaction of ammonium with microorganisms can generate nitrite and decompose nitrate. Proteins in the human body can further combine with nitrite, thereby forming nitrosamines, a kind of carcinogen (Boumer and Crowe, 1988). The amount of ammonium discharged to the environment is regulated strictly: the maximum limit for drinking water according to the World Health Organization is 10 mg/L of nitrate. Removal of ammonium from groundwater is of great importance in controlling nitrite and ammonium pollution.

Research on treatment of groundwater contaminants began in the 1970s. Many treatment technologies, such as the “pump and treat” system (Fetter, 1993), “air sparging” (Nicholas, 2000), and biological remediation (Langwaldt and Puhakka, 2000) have been developed. However, these technologies have several constraints, e.g. pump and treat systems need a long-period cycle and they generate secondary pollution; in biological remediation, degradation of contaminants is incomplete; and air sparging only works for pollution by petroleum hydrocarbons. Permeable reactive barriers (PRB) are used in the *in situ* removal of groundwater contaminants

(Arun, 1999). The PRB consists of a water-permeable material which facilitates adsorption, oxidation-reduction, precipitation, and biological degradation. The main advantage of PRB is the passive nature of the treatment, i.e. for the most part, its operation does not depend on any external labor or energy inputs. Once installed, the barrier takes advantage of the *in situ* groundwater flow to bring the contaminants into contact with the reactive material. The technology is effective at removing heavy metals and organic contaminants which are poorly soluble in water. James and Judith (2006) used Apatite II[®] [$\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$], where $x < 1$, in a subsurface PRB. The study treated successfully Zn, Pb, Cd, Cu, SO_4 , and NO_3 released during acid-mine drainage over a five-year period. Vogan *et al.* (1997) installed a PRB consisting of granular iron to evaluate the possible remediation of chlorinated volatile organic compounds (VOCs) in groundwater. The VOC degradation rates were stable and similar to laboratory results, and the system was apparently free from microbial fouling over the monitoring period.

The examples above also demonstrate that remediation materials must be inexpensive, accessible, free of the possibility of secondary pollution, and have high permeability to be suitable for use in a PRB. Because of its particle size and cation exchange capacity (CEC), vermiculite may be an ideal material for this purpose. Several studies have focused on the adsorption of heavy metals (Marinos, 2007; Gilberto and Jorge, 2005; Panuccio, 2009) and organics (Gilberto and Jorge, 2003; Socías-Viciana *et al.*, 1998) onto vermiculite but studies on the adsorption of ammonium by vermiculite have been few in number. Scott *et al.* (1958) studied the influence of pH on NH_4 -saturated vermiculite extracted

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by 1 N Na, 1 N K, and 0.1 N acid solutions. The results showed that the removal of NH_4 by solution was strongly correlated to the pH of the solution. Evangelou and Lumbanraja (2002) investigated ammonium-potassium-calcium exchange on vermiculite and hydroxy-aluminum vermiculite. The results demonstrated a cation-exchange selectivity in vermiculite which is dependent on the number and type of cations present. Several studies have also focused on construction of wetlands for removal of ammonium from wastewater (Reddy and Smith, 1987; Mitsch and Cronk, 1992). Both of these studies used vermiculite as a medium for microbial growth and formation, and the ammonium was then removed *via* direct microbial biochemical nitrification. The studies focused on the removal of high concentrations of ammonium. Studies of the removal of low concentrations of ammonium have not been reported. In the present study, adsorption of low-concentration ammonium on vermiculite is reported. Factors affecting the adsorption of ammonium included contact time, particle size, pH, vermiculite dose, and temperature.

MATERIALS AND METHODS

Materials

Vermiculite was obtained from a mining operation (Mining Co., Ltd., Lingshou) in Hebei Province, China (38.3° north, 114.4° east). The average particle sizes of 2–4 mm were first separated by sieving. Phase analysis indicated that the main minerals were Mg-vermiculite ($d_{001} = 14.68 \text{ \AA}$) and Na-vermiculite ($d_{001} = 12.91 \text{ \AA}$). Qualitative X-ray diffraction (XRD) analysis showed that vermiculite, hydrobiotite, magnesiohornblende, calcite, and quartz were present (Figure 1).

A stock solution was prepared by dissolving NH_4Cl in distilled water to achieve a concentration of 10 mg/L of NH_4^+ (0.56 mmol). The initial pH was adjusted by addition of NaOH or HCl.

Adsorption experiments

The batch experiments were conducted using glass bottles containing 100 mL of ammonium solution (10 mg/L) with pH values of 2, 4, 6, 7, and 9; temperatures of 15, 20, 30, 40, 48, 60, and 70°C; initial vermiculite amounts of 1, 2, 3, 4, 5, 7, 9, and 10 g; and particle-size ranges of 0.025–0.074 mm, 0.074–0.25 mm, 0.25–0.4 mm, 0.4–0.8 mm, 0.8–1.5 mm, and 1.5–2 mm. The bottles were stirred in an air bath at a speed of 170 rpm. The solutions were centrifuged at 7000 rpm in an HC-3515 Sharpies centrifuge obtained from Zhongke Technology Co., Anhui, China (relative centrifugal force = $7119 \times g$) for 20 min and filtered through paper of pore size 30–50 μm . The filtrates were analyzed immediately for NH_4^+ concentration. The removal efficiency (%) and the amount of ammonium adsorbed, q_t , (mg/g) were

calculated at time t by the following formulae where the analysis error was $\pm 0.5\%$.

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 is the initial concentration of ammonium (mg/L), C_e is the ammonium solution concentration at any time t (mg/L), V is the solution volume (L), and m is the mass of the adsorbent (g).

Methods of analysis

The ammonium was measured using a T6 Series UV/Vis Spectrophotometer (Puxi Co., Beijing, China) at 420 nm by Nessler's reagent method, in which ammonium and mercury potassium iodide reagent produce a yellow-brown complex in an alkaline medium. The absorbance of the complex, which is proportional to the concentration of ammonium ions, was measured using the spectrophotometer. The solution pH was measured using a pH meter (pHS-3C, Shanghai Leici Instrument Factory, China). X-ray diffraction analyses were performed using a Rigaku D/Max-rA/rB X-ray Diffractometer with 1.5406 nm $\text{CuK}\alpha$ radiation at 40 kV and 100 mA. Samples were scanned from 2 to $80^\circ 2\theta$ at $4^\circ/\text{min}$ and with a step size of $0.02^\circ 2\theta$. Vermiculite powder was dispersed ultrasonically in ethyl alcohol, and then a preferentially oriented sample was prepared by dropping some of the solution onto a glass slide and drying in air. Fourier-transform infrared spectra (FTIR) were acquired on a Nicolet 750 infrared spectrometer using the KBr (the ratio of sample to KBr was 1:100 by weight) pellet method at room temperature. Ion concentrations were measured using an AFS3100 Atomic fluorescence spectrometer (Kechuang Haiguang Instrument Co., Beijing, China).

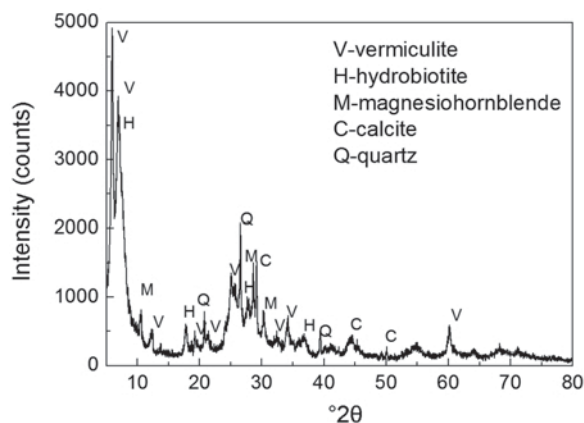


Figure 1. XRD pattern of raw vermiculite ($\text{CuK}\alpha$; $\lambda = 1.5406 \text{ nm}$, 2° – $80^\circ 2\theta$, $0.02^\circ/\text{step}$, 40 kV, 100 mA).

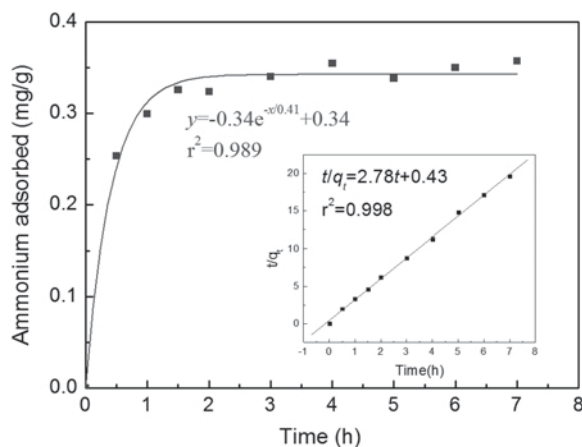


Figure 2. Adsorption of ammonium on vermiculite as affected by time (stirring speed = 170 rpm, temperature = 20°C, pH = 7.0, vermiculite dose = 2 g, concentration of ammonium = 10 mg/L, vermiculite particle-size range = 1.5–2 mm). Insert is the linear plot of equation 3; the solid line is the pseudo second-order fit to the observed data.

RESULTS AND DISCUSSION

Adsorption times

Adsorption of ammonium typically increased rapidly for the first 60 min and slowed gradually with time as shown in the 20°20 example in Figure 2. With an equilibrium time of 3 h, the removal efficiency was 75%. The kinetic data were fitted to various kinetic models, with the best fits found to follow a pseudo second-order kinetics model which describes chemisorption and is applied widely to the adsorption of contaminants from aqueous solutions (e.g. Zheng *et al.*, 2008). The form of this model was given as:

$$q_t = \frac{kq_e^2}{1 + kq'_t} \tag{3}$$

where k (g/mg h) is the rate constant of adsorption, t is the adsorption time, q_e (mg/g) is the amount of ammonium adsorbed at equilibrium, and q_t (mg/g) is the amount of ammonium adsorbed at any time t . Equation 3 can be rearranged into a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{4}$$

where kq_e^2 is the initial rate (mg/g h). The plots of t/q_t vs. t for the adsorption of ammonium on vermiculite showed good agreement with experimental data, the coefficient of correlation r^2 was 0.998, and q_e was 0.34 mg/g. The adsorption system obeyed the pseudo second-order kinetic model for the entire adsorption period.

Effect of particle size on adsorption

Results (Figure 3) revealed that different particle sizes yielded different adsorption trends over time. In all cases, for the first 60 min, adsorption was rapid. After a further 60 min, the adsorption slowed gradually. The time to reach adsorption equilibrium decreased with decreasing particle size. The smallest particle size (0.074 mm) reached equilibrium in <60 min. For larger particle sizes, the equilibrium time was longer, e.g. for particle size >1.5 mm, the equilibrium time was 5 h. Particle sizes <0.074 mm and >1.5 mm revealed removal efficiencies of 91% and 72%, respectively. Taking into consideration the need for high permeability of materials for PRB, the 1.5 mm vermiculites were used in the following experiments.

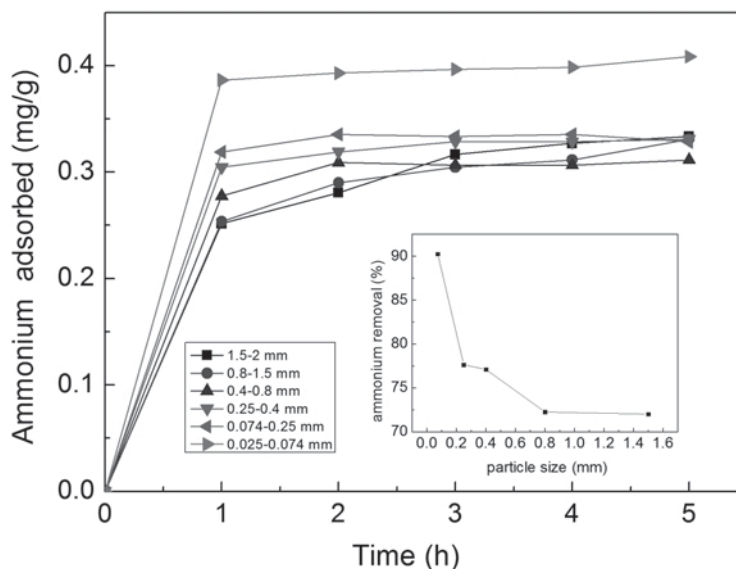


Figure 3. Effect of vermiculite particle-size on the adsorption of ammonium for different times (stirring speed = 170 rpm, vermiculite dose = 2 g, temperature = 20°C, pH = 7.0, concentration of ammonium = 10 mg/L).

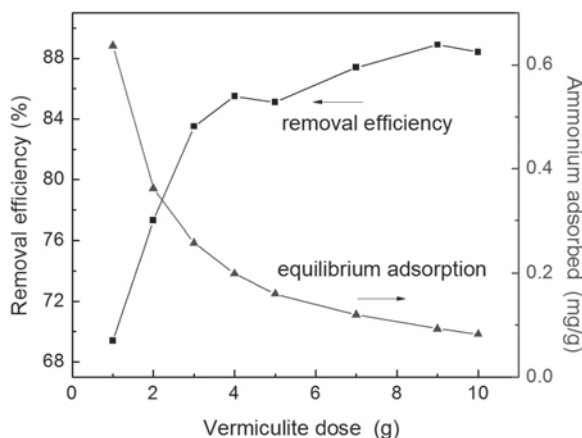


Figure 4. The effect of vermiculite dose on ammonium adsorption (stirring speed = 170 rpm, stirring time = 24 h, temperature = 20°C, pH = 7.0, concentration of ammonium = 10 mg/L, vermiculite particle-size range = 1.5–2 mm).

Effect of vermiculite dosage on adsorption

Using initial amounts of vermiculite of 1, 2, 3, 4, 5, 7, 9, and 10 g, ammonium-removal efficiencies of 69%, 77%, 84%, 86%, 85%, 87%, 89%, and 88% were noted (Figure 4).

Effect of pH on adsorption

Solution pH had a significant impact on the adsorption process (Figure 5). The removal efficiencies of acid solutions (pH = 2) were poor, with values of ~20%. As pH values increased, adsorption of ammonium on vermiculite increased significantly, reaching a maximum at pH 6–7 with a maximum removal efficiency of 80%. However, as pH increased to alkaline values, the adsorption capacity decreased slightly. Solution pH affected equilibrium between the soluble NH_4^+ ions and

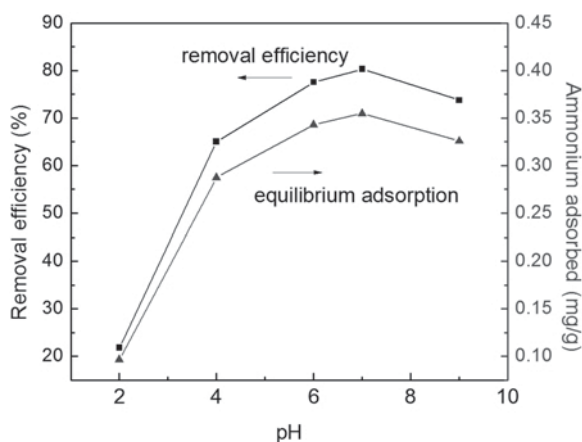
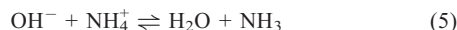


Figure 5. Effect of pH on the amount of ammonium adsorbed by vermiculite (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle-size range = 1.5–2.0 mm, concentration of ammonium = 10 mg/L, vermiculite dose = 2 g, temperature = 20°C).

dissolved molecular ammonia, NH_3 , in water (Lin *et al.*, 2007). The reaction was



In an acidic environment, ammonium was present as NH_4^+ . The solution H^+ competed with NH_4^+ to adsorb on the vermiculites, so that the adsorption of NH_4^+ on vermiculites decreased. When the pH increased to alkaline values, the non-volatile NH_4^+ ion paired with OH^- in the solution, which led to the formation of molecular ammonia. As the number of exchangeable ions in the interlayer increased, the removal of ammonium increased. At pH 7, the capacity of adsorption reached a maximum.

Effect of temperature on adsorption

The removal efficiency of ammonium increased with increasing temperature (Figure 6) and the greatest efficiency was achieved at 333 K. Higher temperatures appeared unfavorable to exothermic reaction once equilibrium has been attained.

The amount of ammonium adsorbed at equilibrium at different temperatures – 288, 293, 303, 313, 321, 333, and 343 K – was used to calculate the thermodynamic state functions, standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), from the following equations (Zheng *et al.*, 2008):

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (6)$$

$$\Delta G^0 = -RT \ln K_c \quad (7)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where K_c is the equilibrium constant, C_{Ae} is the amount of adsorbate on the adsorbent per L of the solution at

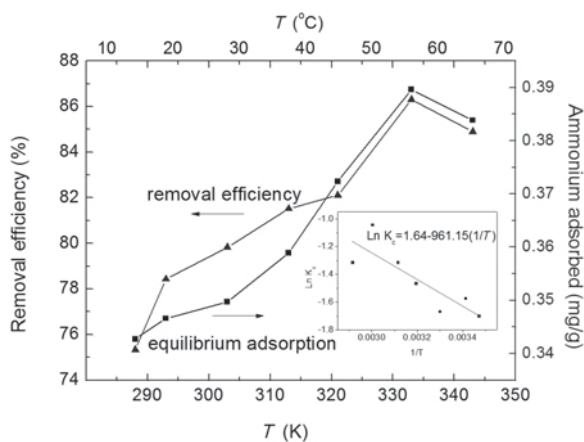


Figure 6. The effect of temperature on the amount of ammonium adsorbed by vermiculite (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle-size range = 1.5–2.0 mm, concentration of ammonium = 10 mg/L, vermiculite dose = 2 g, pH = 7.0).

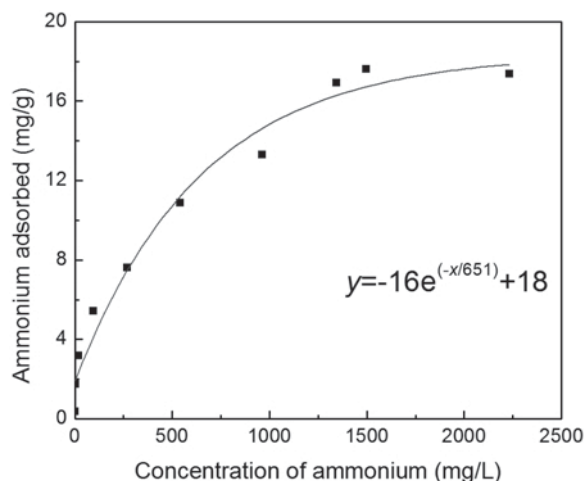


Figure 7. Adsorption isotherm of ammonium adsorbed by vermiculite (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle-size range = 0.025–0.074 mm, vermiculite dose = 2 g, temperature = 20°C, pH = 7.0).

equilibrium (mg/L), and C_{Se} is the equilibrium concentration of adsorbate in the solution (mg/L). T is the solution temperature (K) and R is the universal gas constant (8.314 J/mol K⁻¹). The relationship between $\ln K_c$ and $1/T$ are inserted in Figure 7, and the enthalpy and entropy were calculated by line fit of the curve. In the ion-adsorption reaction, ΔG^0 cannot be used as a fundamental parameter to justify the spontaneity of a reaction. According to the laws of thermodynamics, the criterion for spontaneity is that the real change in Gibbs free energy of the reaction be less than zero ($\Delta G < 0$). The following equation (Wu *et al.*, 2009) was used to calculate ΔG of adsorption of various cations, including ammonium, onto vermiculite (Table 1):

$$F = \Delta G/(RT) = [A_0 \ln(1 - x/y) + (W_0 \beta) \ln(1 - x/\beta)]/M \quad (9)$$

where A_0 is the initial adsorbate concentration; x is the ratio of the equilibrium concentration of the ion adsorbed onto the solid surface; W_0 is the concentration (mol/L) of adsorbent in the solution at equilibrium; y is the ratio of A_0 to W_0 ; β is the ratio of the maximum

adsorption capacity of the initial system to the concentration of adsorbent; and M , the molecular weight of adsorbate (in this case 18.03 g/mol for NH₄⁺).

The negative F values (Table 1) indicated attractive interaction between ammonium and vermiculite, thus the adsorption of ammonium on vermiculite was spontaneous and exergonic. The positive values for ΔH^0 indicated that ammonium adsorption onto vermiculite was an endothermic process. The positive ΔS^0 indicated that the adsorption was spontaneous due to an increase in system randomness as ammonium molecules moved themselves from water onto the solid surface. The result is opposite to an exothermic process of ammonium adsorption on zeolite (Zheng *et al.*, 2008; Karadag *et al.*, 2006).

Adsorption isotherm

Freundlich and Langmuir adsorption models were applied to fit the experimental data (Figure 7). The maximum adsorption capacity was 18.4 mg/g, similar to the value of 20.8 mg/g found by Hu *et al.* (2004). The linear form of the Langmuir model is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_0} C_e + \frac{1}{q_0 k} \quad (10)$$

where q_e is the amount of adsorbate adsorbed (mg) at equilibrium per unit mass of adsorbent (g), C_e is the concentration of adsorbate in equilibrium solution (mg/L), and the values of q_0 (mg/g) and k (L/mg) are the maximum adsorption capacity of adsorbent and the adsorption energy coefficient, respectively (Table 2).

The linear form of the Freundlich model is expressed as follows:

$$\log q_e = \log K_f + 1/n \log C_e \quad (11)$$

where K_f is the Freundlich constant (mg/g), the measure of the adsorption capacity of the adsorbent; and $1/n$ is the heterogeneity factor, a constant relating to adsorption intensity or surface heterogeneity (Table 2). Comparing the correlation coefficient value of the linear plot of the Langmuir and Freundlich isotherms indicated that the Langmuir model gave a better statistical fit.

Table 1. Calculated thermodynamic properties of NH₄⁺ adsorption onto vermiculite at various temperatures (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle-size range = 1.5–2.0 mm, initial NH₄⁺ concentration = 10 mg/L, vermiculite dose = 2 g, pH = 7.0).

Temperature (°C)	$\ln K_c$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/K mol)	F
15	0.0023	-5.5			-2.53
20	0.0024	-5.9			-2.66
30	0.0023	-5.9			-2.56
40	0.0025	-6.5	8.0	13.6	-2.78
48	0.0027	-7.1			-2.84
60	0.0029	-8.0			-3.12
70	0.0027	-7.6			-2.84

Table 2. Parameters from the Langmuir and Freundlich models.

	Parameter	Value
Langmuir model	$1/q_0$	0.054
	K ($L\ mg^{-1}$)	5.35×10^{-3}
	r^2	0.99
Freundlich model	K_f (mg/g)	2.57
	n	0.45
	r^2	0.97

FTIR analyses

The IR spectra of the vermiculite (Figure 8), with characteristic bands at $1000\text{--}1010\text{ cm}^{-1}$ and $440\text{--}460\text{ cm}^{-1}$ (assigned to Si–O bending modes) and at $1630\text{--}1640\text{ cm}^{-1}$ and $3400\text{--}3450\text{ cm}^{-1}$ (bending and stretching vibrations of O–H, respectively (Farmer, 1974; Wu, 2005)), before and after NH_4^+ adsorption showed no distinct change, indicating that the adsorption of NH_4^+ did not alter the structure of the vermiculite. The characteristic band for NH_4^+ at 1430 cm^{-1} (Schroeder and Ingall, 1994), however, did appear in the spectrum after adsorption (Figure 8).

Ion-concentration analyses

Changes in the ionic concentration of the solution (Table 3) revealed that after adsorption of NH_4^+ , the

concentration of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in the solution increased to ~ 391.5 , 143.8 , 56.4 , and 147.9 mmol/L (Table 3). The total charge exchange of Mg^{2+} , K^+ , and Na^+ was $\sim 492\text{ mmol/L}$, which corresponds closely to the amount of NH_4^+ (500 mmol/L) lost from the solution, measured by Nessler's reagent method, suggesting that the adsorption of NH_4^+ on vermiculite is mainly through ion exchange for the inter-layer Mg^{2+} , K^+ , and Na^+ of vermiculite. The results show a selectivity of vermiculite by adsorption of cations from solution (Sawhney, 1970; Saha *et al.*, 2001). The concentration of Ca^{2+} increased greatly (Table 3), possibly due to the existence of calcite (Figure 1). After adsorption of NH_4^+ , the pH of solution became more acidic (~ 4.56) and poorly crystalline calcite dissolved.

CONCLUSIONS

The maximum adsorption capacity of ammonium on the 1.5 mm particle-size fraction of vermiculite from Hebei Province, China, was 18 mg/g , with an equilibrium time of 3 h. Maximum adsorption occurred at pH 6–7 at 60°C . Ammonium adsorption was greater with smaller particle sizes. After adsorption of ammonium, the FTIR of vermiculite showed an IR adsorption band of NH_4^+ at 1430 cm^{-1} . The ionic concentration of Mg^{2+} , K^+ , and Na^+ in the solution increased, consistent with the decrease of NH_4^+ in the solution, suggesting that at low ammonium concentrations, the adsorption of ammonium on

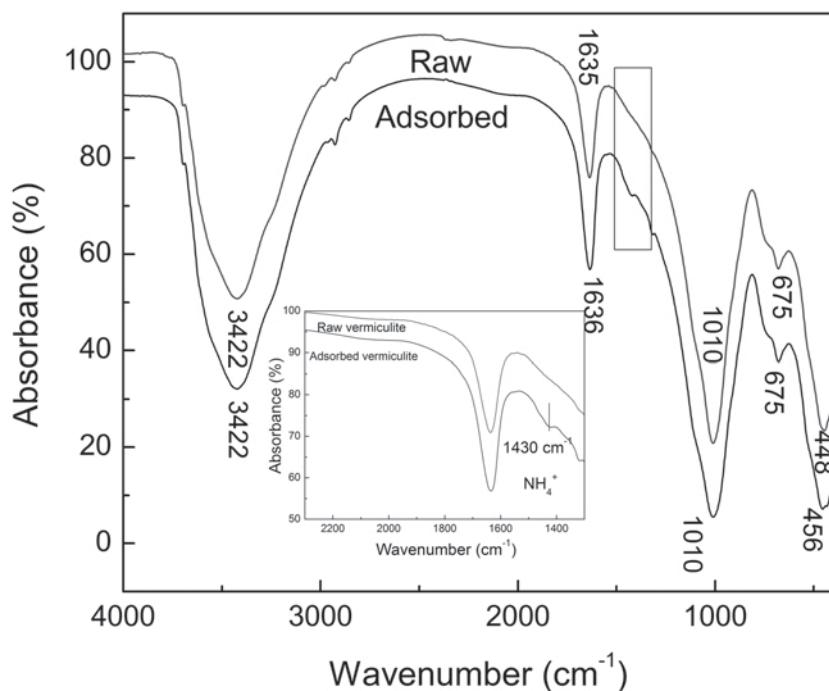


Figure 8. FTIR spectra of raw vermiculite and vermiculite with adsorbed ammonium (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle-size range = $0.025\text{--}0.074\text{ mm}$, ammonium concentration = 10 mg/L , vermiculite dose = 2 g , temperature = 20°C , pH = 7.0).

Table 3. Ionic-concentration changes of stock solution and adsorbed solution (stirring speed = 170 rpm, stirring time = 24 h, vermiculite particle size range of 0.025–0.074 mm, concentration of ammonium = 10 mg/L, vermiculite dose = 2 g, temperature = 20°C, pH = 7.0).

	Concentration of solution (mmol/L)		Concentration of exchanged ion (mmol/L)	Concentration of charge exchange (mmol/L)
	Before adsorption	After adsorption		
NH ₄ ⁺	588.9	88.9	500	500
Ca ²⁺	3.5	395	391.5	783
Mg ²⁺	2.1	145.89	143.8	287.6
K ⁺	0	56.49	56.5	56.5
Na ⁺	13.09	160.9	147.9	147.9

vermiculite depended mainly on the ion exchange of NH₄⁺ for the interlayer cations of vermiculite.

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