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Ammonium removal from water by natural and modified zeolite: kinetic, equilibrium, and thermodynamic studies

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ABSTRACT

Zeolite is commonly used to remove ammonium from water. To improve its adsorption performance, natural zeolite (N-Z) was modified by NaCl immersion and calcination. Batch experiments were used to investigate the adsorption performance of N-Z, immersion zeolite (M-Z-1), and immersion-calcination zeolite (M-Z-2). Kinetic studies showed that the adsorption rate followed the sequence M-Z-2 > M-Z-1 >> N-Z. The pseudo-second-order model fitted the N-Z, M-Z-1, and M-Z-2 data well. The k_s values of the two types of modified zeolite were considerably larger than that of N-Z; the k_s of M-Z-2 was slightly larger than that of M-Z-1. These results indicate that the adsorption rate of M-Z-2 is only slightly faster than that of M-Z-1, which agrees with the experimental results. Equilibrium studies showed that the adsorption capacities of M-Z-1 and M-Z-2 were 1.4–1.5 times higher than that of N-Z. Adsorption isotherms fitted the Freundlich model well. The k_F and $1/n$ values of the modified zeolites were similar, which indicates that M-Z-2 does not exhibit significant improvements compared with M-Z-1. Thermodynamic studies showed that the ΔG°, ΔH°, and ΔS° of all zeolite samples were negative, which indicates that adsorption was spontaneous, exothermic, and orderly. The ΔG° values of both types of modified zeolites were similar and more negative than that of N-Z. This similarity suggests that NaCl modification effectively improves the adsorption potential of zeolite.

Keywords: Ammonium removal; Zeolite; Modification; Adsorption

1. Introduction

Nitrogen is an essential element for animals, plants, and micro-organisms [1]. In excess, however, nitrogen in lakes and rivers can cause eutrophication. The presence of this element in drinking water can also cause human diseases. Given that increasing amounts of nitrogen are loaded into water over time, nitrogen removal from water bodies is a very important undertaking.

Ammonium is a nitrogen compound commonly found in wastewater. Several methods, including air stripping, biological nitrification–denitrification, and ion-exchange are used for ammonium removal. Among these methods, ion-exchange using zeolite is effective, environment-friendly, competitive, and fairly temperature-insensitive [1–4]. N-Z, an abundant cation exchange material, represents a class of hydrated aluminosilicates that possess a 3D framework structure [5,6]. Substitution of silicon by aluminum atoms in the crystal framework engenders extra negative charges

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that are balanced by surrounding exchangeable cations [7]. These cations, which are normally alkali or alkaline-earth metal cations (e.g. Na^+, K^+, Mg^{2+}, and Ca^{2+}), are easily exchanged by other surrounding cations in a contact solution resulting in the wide applicability of zeolite in ion-exchange adsorption [7,8], especially in ammonium removal [7,9,10]. The removal capacity of ammonium on N-Z is mainly determined by the ion-exchange process and mobile cations. Thus, water molecules and organics in the pore channels can negatively influence the ion-exchange capacity of zeolite [11]. In this case, N-Z must be modified to improve its adsorption performance prior to use [12,13].

N-Z can be modified by calcination [14], NaCl immersion [7,15,16], NaCl immersion plus calcination [6], and so on [8,13]. The removal efficiency of calcined zeolite is only 5% higher than that of N-Z [14]. Studies [7,15] have shown that the ammonium adsorption capacities of NaCl-modified zeolite are 58 and 40% higher than those of N-Z at initial ammonium concentrations of 1,000 and 1,500 mg/L, respectively. Vassileva [16] also used NaCl-modified zeolite for ammonium removal and the calculated maximum adsorption capacity of modified zeolite was 12.29 mg/g, which is about 1.6 times higher than that of N-Z. The ammonium uptake of NaCl immersion plus calcination-modified zeolite is about 1.4 times larger than that of N-Z at an initial ammonium concentration of 25 mg/L [11]. Microwave treatment and NaOH fusion plus hydrothermal treatment [8,13] also effectively improved the adsorption capacity of N-Z. The ammonium adsorption capacities of the modified zeolites obtained from these treatments are about 1.7 and 1.8 times higher than those of N-Z at initial ammonium concentrations of 50 and 250 mg/L, respectively. However, microwave treatment and NaOH fusion + hydrothermal treatment involve complicated procedures; thus, NaCl immersion and NaCl immersion plus calcination are preferred methods for modifying N-Z.

This study aims to determine whether NaCl immersion or calcination is the more effective step for modifying N-Z by investigating the adsorption kinetics, equilibrium isotherms, and thermodynamic properties of modified zeolite samples.

2. Materials and methods

2.1. Materials

The N-Z samples obtained from Henan Province, China had a diameter between 1 and 2 mm. The samples were washed with deionized water and dried in an oven at 105℃ for 24 h prior to use. M-Z-1 was prepared by immersing 10 g of N-Z in 100 mL of 10% (wt) NaCl solution at 25℃ for 24 h. M-Z-2 was obtained [11] by calcining M-Z-1 in a muffle furnace at 300℃ for 1 h.

2.2. Experimental methods

Batch experiments were conducted to investigate the kinetics, isotherms, and thermodynamics of the modified samples. Adsorption experiments were conducted with zeolite (0.1 g/L) + ammonium (NH_4Cl, 1 g/L) working solutions using a shaker (HZQ-X100) at 90 r/min and 25℃. Samples were filtered through a micro-filtration membrane (0.45 μm) and the ammonium concentration was analyzed using a spectrophotometer (JH-721) based on the standard salicylate method [17]. Each sample was examined in triplicate, and the average values were used. The adsorption amount (q) was calculated using Eq. (1):

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of ammonium in solution (mg/L), respectively, V is the volume of the solution (L), and m is the adsorbent mass (g).

2.3. Analysis

ICP-MS (7700X; Agilent Technologies) analysis was conducted to measure the cation concentrations in solutions. The microstructure of the zeolite samples was observed by SEM (S-4700; HITACHI). BET surface area, pore size, and pore volume were determined by an automated surface area and pore size analyzer (AS-IC-YP; Quantachrome).

3. Results and discussion

3.1. Adsorbent characterization

ICP-MS was used to analyze two kinds of solutions. Solution 1 was the filtrate of the NaCl solution obtained after immersion of N-Z and Solution 2 was the filtrate of deionized water obtained after immersion of N-Z. The results are shown in Table 1. The Na^+ concentration in the NaCl solution before modification was 1709.4 mM/L and no other cations were found. After modification, the concentration of Na^+ decreased to 1629.54 mM/L; thus, 0.7986 mM Na^+ increased per 1 g of zeolite after modification. Based on the concentrations of other cations, 0.2956 mM Na^+ was virtually exchanged with other cations

Table 1
Concentrations of cations in the modifying solution and immersion liquid

	Na^+ (mM/L)	Mg^{2+} (mM/L)	K^+ (mM/L)	Ca^{2+} (mM/L)	Ba^{2+} (mM/L)
Solution 1	1629.54	2.54	6.42	10.08	0.045
Solution 2	90	0.016	0.12	1.02	0.0015

(Mg^{2+}, K^+, Ca^{2+}, and Ba^{2+}) as equal valence per 1 g of zeolite. The other 0.503 mM Na^+ may adhere to the zeolite surface as NaCl. Lin et al. [7] reported that Na^+ is the dominant cation exchanged with ammonium under low initial concentration conditions (<500 mg/L). Therefore, the more Na^+ in the zeolite, the larger the amount of ammonium removed. Fig. 1 shows that the M-Z-2 surface became rougher and developed more pores (mainly mesopores and macropores) than N-Z and M-Z-1 samples. This result implies that calcination renders zeolite with a multi-pore structure. The M-Z-1 surface was similar to the N-Z surface; this finding differs from the results reported by Lin et al. [7]. Table 2 presents the BET surface areas, average pore sizes, and total pore volumes of N-Z and M-Z-2. Average pore sizes and total pore volumes increased but BET surface areas decreased after modification. These findings are attributed to pore blockage after modification and contrasts a report by Liang and Ni [11]; discrepancies may be attributed to differences in the zeolites used between studies.

3.2. Adsorption kinetics

Fig. 2 shows that the adsorption amounts on N-Z, M-Z-1, and M-Z-2 increases as the contact time increases. However, no significant differences in adsorption amounts were observed between N-Z after 300 min, M-Z-1 after 180 min, and M-Z-2 after 120 min. The adsorption rates of M-Z-1 and M-Z-2 were much higher than that of N-Z, although M-Z-2 adsorption was bit faster than M-Z-1 adsorption. Increased adsorption rates may be attributed to the presence of more exchangeable Na^+ in M-Z-1 and M-Z-2 than in N-Z and the larger average pore size and total pore volume of M-Z-2 compared with those of M-Z-1. These results indicate that NaCl immersion produces more effect on the adsorption rate of zeolite.

To investigate the adsorption kinetics of the zeolite system, which is critical in designing new treatment systems, pseudo-first-order and pseudo-second-order models, given by Eqs. (2) and (3), respectively, were applied to fit the kinetic data:

$$\ln (q_e - q_t) = \ln q_e - k_f t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_t (mg/g) is the amount of ammonium adsorbed at time t (min), q_e is the equilibrium adsorption amount (mg/g), k_f is the rate constant of the pseudo-first-order model (min^{-1}), and k_s is the rate constant of the pseudo-second-order model [g/(mg min)]. Fig. 3(A) and (B) illustrate the pseudo-first-order and pseudo-second-order kinetic plots for N-Z, M-Z-1, and M-Z-2. As shown in Table 3, the pseudo-second-order model provides a better fit for all zeolite data as the determination coefficient (R^2) value approached to 1. The k_s values of N-Z, M-Z-1, and M-Z-2 were 6.67×10^{-3}, 7.61×10^{-3}, and 7.93×10^{-3}, respectively. The k_s of M-Z-2 and M-Z-1 were much larger than that of N-Z, which indicates that the adsorption rates of M-Z-1 and M-Z-2 are faster than

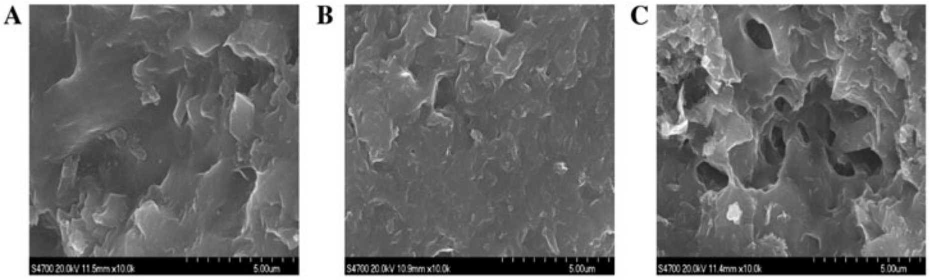

Fig. 1. SEM patterns of N-Z (A), M-Z-1 (B), and M-Z-2 (C).

Table 2
Results of BET surface area, pore size, and pore volume

	BET surface area (m^2/g)	Average pore size (nm)	Total pore volume (cm^3/g)
N-Z	61.10	14.34	0.2191
M-Z-2	24.76	64.08	0.3967

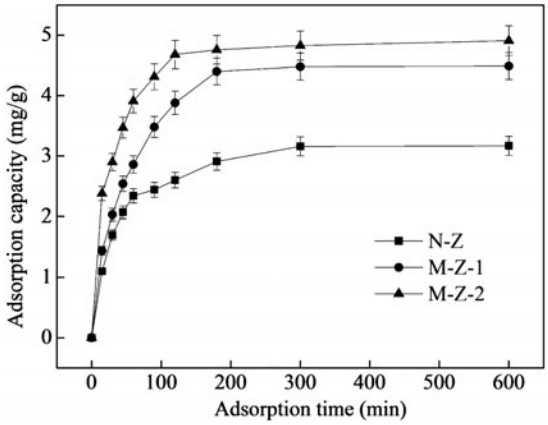

Fig. 2. Effect of adsorption time on ammonium removal (initial concentration: 100 mg/L).

that of N-Z. These findings are coincident with those of Lei et al. [8], who showed that the k_s and adsorption rate of microwave-treated zeolite are larger than those of N-Z. The k_s values of M-Z-2 and M-Z-1 were similar, which indicates that the adsorption rates of M-Z-1 and M-Z-2 are also similar. The equilibrium adsorption capacities of all zeolites calculated by the pseudo-second-order model were very close to the experimental data.

3.3. Adsorption isotherms

Fig. 4 shows the adsorption isotherms of N-Z, M-Z-1, and M-Z-2. M-Z-2 exhibited only about 10% higher adsorption capacity than M-Z-1, which increased significantly compared with that of N-Z. The adsorption capacities of M-Z-1 and M-Z-2 were about 1.4 and 1.5 times larger than that of N-Z, respectively, when the equilibrium ammonium concentration exceeded 50 mg/L.

Isotherm investigation was performed according to the Langmuir and Freundlich models. The Langmuir model assumes a monolayer adsorption, homogenous adsorption surface, and homogenous adsorption sites. The Freundlich model is an empirical equation that is valid for heterogeneous surfaces. These models were tested to describe the experimental data and are given by Eqs. (4) and (5):

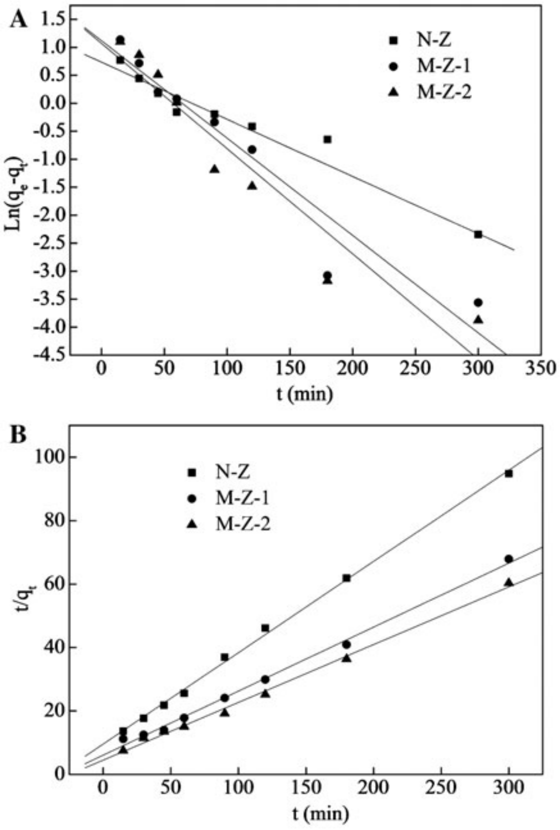

Fig. 3. (A) Pseudo-first-order and (B) pseudo-second-order kinetic plots of N-Z, M-Z-1, and M-Z-2.

Table 3
Kinetic parameters for ammonium removal

	Kinetic models					
	Pseudo-first-order			Pseudo-second-order		
	k_f	q_e	R^2	k_s	q_e	R^2
N-Z	0.0102	2.09	0.9453	6.67×10^{-3}	3.47	0.9980
M-Z-1	0.0174	2.92	0.9247	7.61×10^{-3}	4.75	0.9960
M-Z-2	0.0188	3.47	0.9206	7.93×10^{-3}	5.09	0.9954

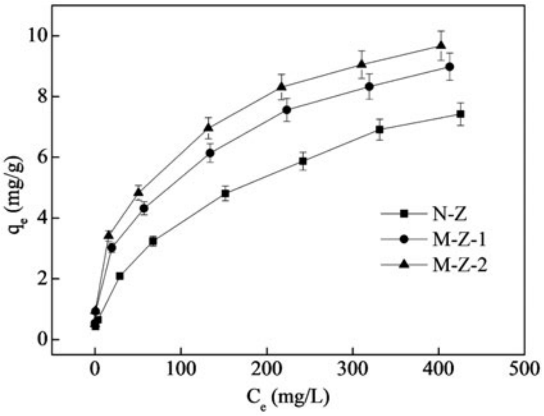

Fig. 4. Adsorption isotherms of N-Z, M-Z-1, and M-Z-2 at 25℃ (initial concentration: 5–500 mg/L; contact time: 300 min for N-Z 180 min for M-Z-1, and 120 min for M-Z-2).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4}$$

$$q_e = k_F C_e^{\frac{1}{n}} \tag{5}$$

where q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of ammonium in solution (mg/L), b is the Langmuir constant (L/mg), which is related to the temperature and nature of the adsorbent and adsorbate, k_F is an empirical constant related to the adsorption capacity and affinity between the adsorbent and adsorbate, and $1/n$ is also an empirical constant related to adsorption intensity or surface heterogeneity [18].

Fig. 5(A) and (B) illustrates plots of the Langmuir and Freundlich models. The R^2 values and calculated parameters are shown in Table 4. The R^2 values showed that the adsorption isotherms of all zeolites are better fitted by the Freundlich model than by the Langmuir model because of the heterogeneous surfaces of N-Z, M-Z-1, and M-Z-2. The k_F values were 0.5818, 1.387, and 1.629 for N-Z, M-Z-1, and M-Z-2, respectively. The k_F values of M-Z-1 and M-Z-2 were much higher than that of N-Z, which indicates that M-Z-1 and M-Z-2 have higher affinity for ammonium. This result agrees well with that of Wang et al. [13]. Wang et al. reported that the Freundlich model provides a better fit to the data compared with the Langmuir model and that the k_F of the modified zeolite is larger than that of N-Z; this finding indicates the higher sorption capacity of modified zeolite compared with that of ordinary zeolite. The k_F of M-Z-2 was only slightly higher than that of M-Z-1, which indicates that the adsorption capacities of M-Z-2 and M-Z-1 are similar. Moreover, the $1/n$ values of all zeolites ranged from of 0.1 to 1, which demonstrates favorable adsorption. The $1/n$ values of M-Z-1 and M-Z-2 were close to 0; thus, adsorption is highly favorable on these samples [18].

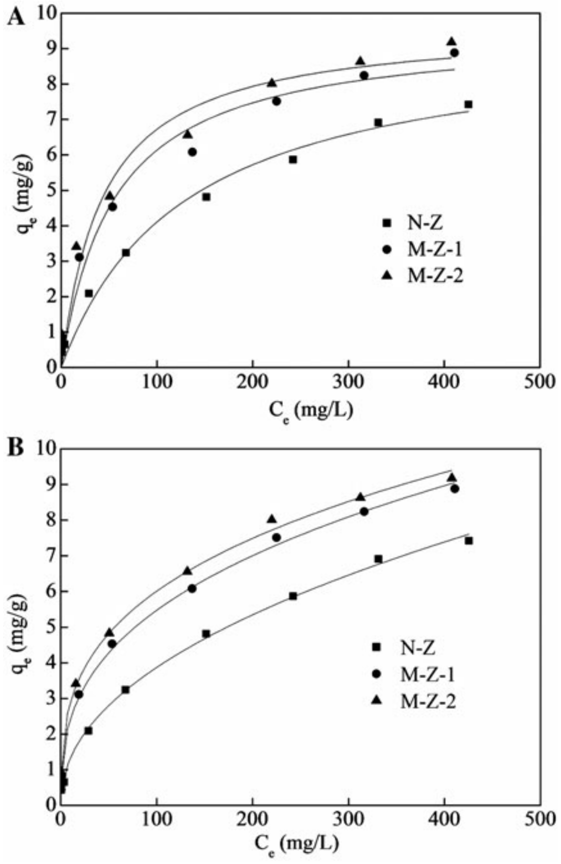

Fig. 5. (A) Langmuir and (B) Freundlich fitting plots for N-Z, M-Z-1, and M-Z-2.

Table 4
Langmuir and Freundlich constants for ammonium removal

	Isotherm models					
	Langmuir			Freundlich		
	b	q_m	R^2	k_F	$1/n$	R^2
N-Z	0.0144	6.346	0.9736	0.5818	0.3803	0.9967
M-Z-1	0.0389	6.8803	0.9672	1.387	0.2916	0.9981
M-Z-2	0.0451	6.995	0.9601	1.629	0.2460	0.9978

3.4. Thermodynamic study

Thermodynamic data, such as Gibbs free energy change ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), were calculated. The distribution constant (K_d) was used to determine ΔG°. K_d was computed at temperatures of 298, 318, and 338 K by Eq. (6), and ΔG° was calculated by Eq. (7):

$$K_d = \frac{q_e}{C_e} \tag{6}$$

$$\Delta G^\circ = -RT \ln K_d \tag{7}$$

where K_d was obtained from the slope of q_e vs. C_e plot (Fig. 6) (mL/g), C_e is the equilibrium concentration of ammonium in solution (mg/mL), R is the universal gas constant (J/mol K), and T is the absolute temperature (K). The relationship of ΔG° to ΔH° and ΔS° is expressed as follows:

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

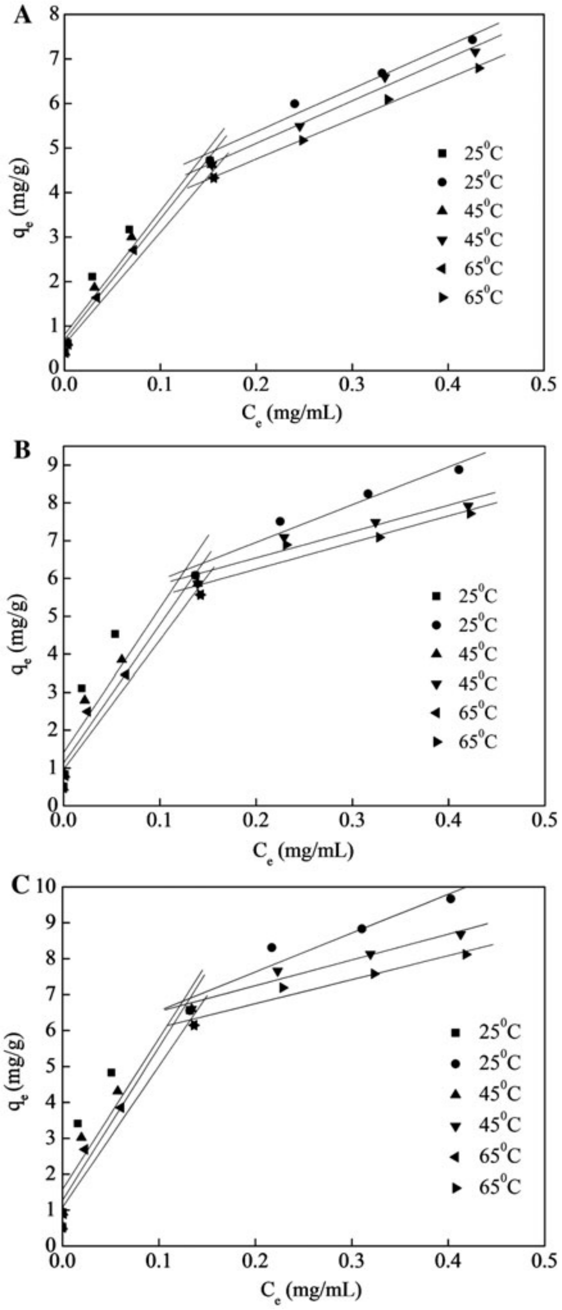

Fig. 6. q_e vs. C_e plots for N-Z (A), M-Z-1 (B), and M-Z-2 (C).

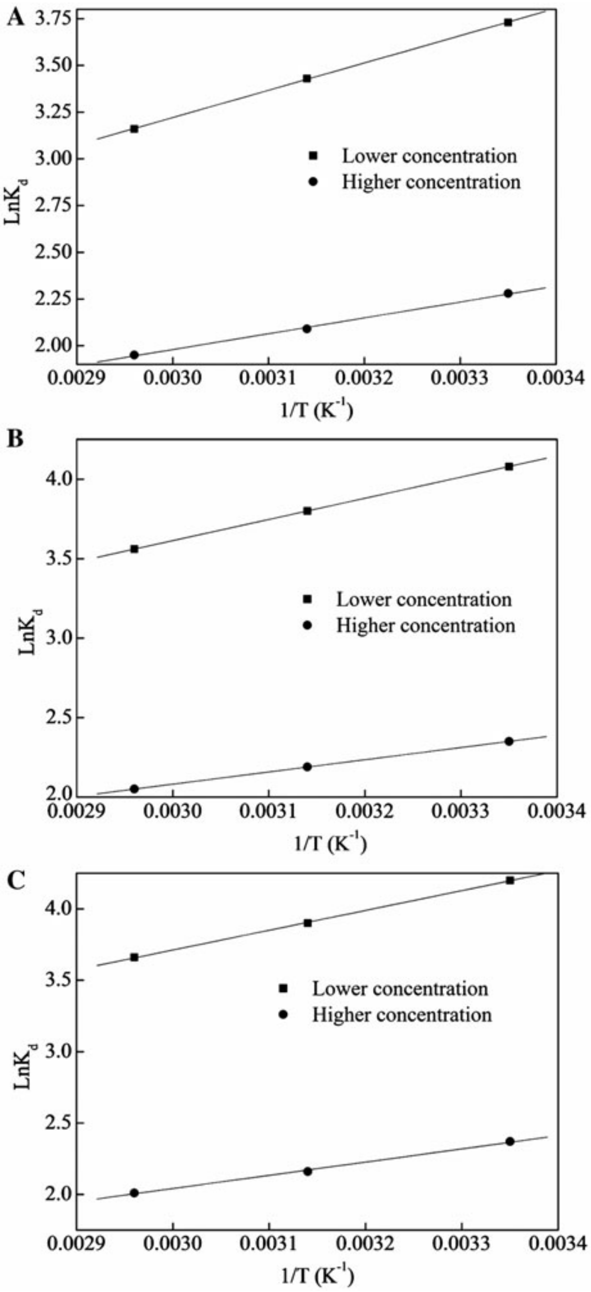

Fig. 7. LnK_d vs. $1/T$ plots for N-Z (A), M-Z-1 (B), and M-Z-2 (C).

Table 5
The thermodynamic results of N-Z, M-Z-1, and M-Z-2

	Initial ammonium concentration (mg/L)	T (K)	K_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
N-Z	Less than 200	298	41.81	−9.25	−12.14	−9.64
		318	32.79	−9.22		
		338	26.05	−9.17		
	More than 200	298	9.75	−5.64	−7.05	−4.66
		318	8.08	−5.53		
		338	7.03	−5.48		
M-Z-1	Less than 200	298	58.95	−10.10	−11.09	−3.24
		318	44.70	−10.06		
		338	35.16	−10.01		
	More than 200	298	10.48	−5.82	−6.39	−1.91
		318	8.85	−5.77		
		338	7.77	−5.75		
M-Z-2	Less than 200	298	66.57	−10.40	−11.52	−3.66
		318	52.40	−10.31		
		338	48.86	−10.29		
	More than 200	298	10.67	−5.87	−7.69	−6.07
		318	9.12	−5.84		
		338	7.92	−5.81		

Substituting Eq. (7) into Eq. (8) yields:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

ΔH° is approximately considered as constant when the temperature does not change. ΔH° and ΔS° can be calculated from the slope and intercept of $\ln K_d$ vs. $1/T$ plot (Fig. 7).

The calculation results are presented in Table 5. The ΔG° of all zeolites was negative, which indicates that the adsorption process is spontaneous. Adsorption was much more energetically favorable in M-Z-1 and M-Z-2 than in N-Z because of the more negative ΔG° of the former compared with that of the latter. The ΔG° of M-Z-2 was only slightly more negative than that of M-Z-1. The less negative ΔG° obtained at higher temperatures implies that higher temperatures lead to lower adsorption capacities. ΔG° was much more negative when the initial ammonium concentration was less than 200 mg/L, which may be ascribed to the higher abundance of adsorption sites in relatively lower concentrations of ammonium solutions. The negative values of ΔH° and ΔS° indicate that the adsorption process is exothermic and that the degree of freedom decreases during adsorption in all zeolites. Contrasting with our findings, Vassileva and Voikova [16] reported that higher temperatures lead to more negative ΔG° and ΔS° is positive. Discrepancies among these results are attributed to the different N-Z and modification conditions used between studies.

4. Conclusions

M-Z-1 and M-Z-2 exhibited about 40 and 50% higher ammonium adsorption capacities, respectively, and faster adsorption rates than N-Z. The adsorption capacity of M-Z-2 was only about 1.1 times larger than that of M-Z-1, and the adsorption rate of the former was only slightly faster than that of the latter. The adsorption kinetic data were better approximated by the pseudo-second-order model and the Freundlich model fitted the equilibrium data of all zeolites well. The negative values of ΔG°, ΔH°, and ΔS° indicate the spontaneous and exothermic nature of adsorption, and the degree of freedom decreased during adsorption. The ΔG° of M-Z-1 and M-Z-2 were much more negative than that of N-Z, which indicates that adsorption is much more energetically favorable in these zeolites. The ΔG° of M-Z-1 was slightly more negative than that of M-Z-2. Thus, compared with calcination, NaCl immersion was the more effective modification step for zeolite.

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