

Article

A further investigation of NH₄⁺ removal mechanisms by using natural and synthetic zeolites in different concentrations and temperatures

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Abstract: We investigate the ammonium removal abilities of natural and synthetic zeolites, which have distinct Si/Al ratios and various surface areas, to study how adsorption and ion-exchange processes in zeolites perform under different ammonium concentrations and different temperatures. Five zeolites including natural mordenite, chabazite, erionite, clinoptilolite and synthetic merlinoite were immersed in 20 mg/kg, 50 mg/kg and 100 mg/kg ammonium solutions. The results demonstrate that zeolites under high ammonium concentrations (100 mg/kg) possess higher physical adsorption capacity (0.398-0.468 meq/g), whereas those under lower ammonium concentrations (20 mg/kg) possess greater ion-exchange property (64-99%). The ion-exchange ability of zeolites are extremely dependent on the cation content of the zeolites, and the cation content is affected by the Si/Al ratio. The surface area of zeolites also has a partial influence on its physical adsorption ability. When the surface area is less than 100 m²/g, the adsorption ability of zeolite increases obviously with surface area; however, adsorption ability is saturated as the surface area becomes larger than this critical value of 100 m²/g. When we carried out the zeolites in 50 mg/kg ammonium concentration at different temperatures (5~50°C), we found that zeolites exhibit the highest ammonium removal ability at 30°C and the potassium release was enhanced at 30~40°C.

Keywords: zeolite; ion-exchange; adsorption; ammonium; Si/Al; temperature.

1. Introduction

Natural zeolites are microporous aluminosilicate minerals with high cation exchange capacities and high ammonium selectivity properties [1]. More than 50 different species of this mineral have been identified. Previous researchers have studied the ammonium removal ability of zeolites in the purification of livestock wastewater, landfill wastewater, and aquaculture water [2,3]. In polluted systems, toxic NH₃ will be transformed to NH₄⁺ under the NH₄⁺-reducing condition. Zeolites can effectively remove NH₄⁺ in water and waste products in order to weaken the virulence of NH₃. Natural zeolites including clinoptilolite [1], mordenite [4], erionite [5], and chabazite [6] have been widely utilized in water purification. Previous studies revealed the mechanisms of removing NH₄⁺ through ion-exchange and adsorption in different zeolites [7,8]. Mordenite and clinoptilolite have frequently been employed to remove ammonium [9]. Many previous investigations have been primarily concerned with equilibrium isothermal and kinetic models of ammonium adsorption on zeolites at different temperatures, pH, or initial concentrations [10-13]. We want to compare wider range of Si/Al ratio of zeolites in

this study, so we analyzed the chemical compositions of zeolites. In order to understand the effect on adsorption and ion-exchange capacities, we also measured the cation concentration of the reaction solutions. Moreover, we can understand the concentration and temperature effect on ion-exchange and adsorption mechanism. Cation release ability should be regarded as an important issue that can be advantageously applied in ecosystems and environmental treatments.

2. Materials

Different natural zeolites often grow together or coexist with other minerals, so the identification of zeolite composition is an imperative work. Natural zeolites used in this study include chabazites and erionites from Arizona, U.S.A., clinoptilolites were acquired from China, and mordenites were from Japan. Furthermore, we deliberately synthesized pure merlinoite to manually create a zeolite composition with lower Si/Al ratio than that of natural zeolites. The synthetic method was based on our previous studies by employing glass materials [14,15]. The five samples were identified by X-ray Diffraction (XRD, MAC, Science Mxp 3), which used a Cu target with Cu $k\alpha$ wavelength through a 1° divergent slit. Operative conditions were established as 45 kV and 40 mA, the scanning step size was $0.0083556^\circ/\text{s}$, and a per time step of 1.27 s in the range of 2θ between $3^\circ\sim80^\circ$. Mineral identifications by XRD are shown in Fig. 1. Most zeolites are very pure, and only chabazite has little amount ($\sim 5\%$) of quartz.

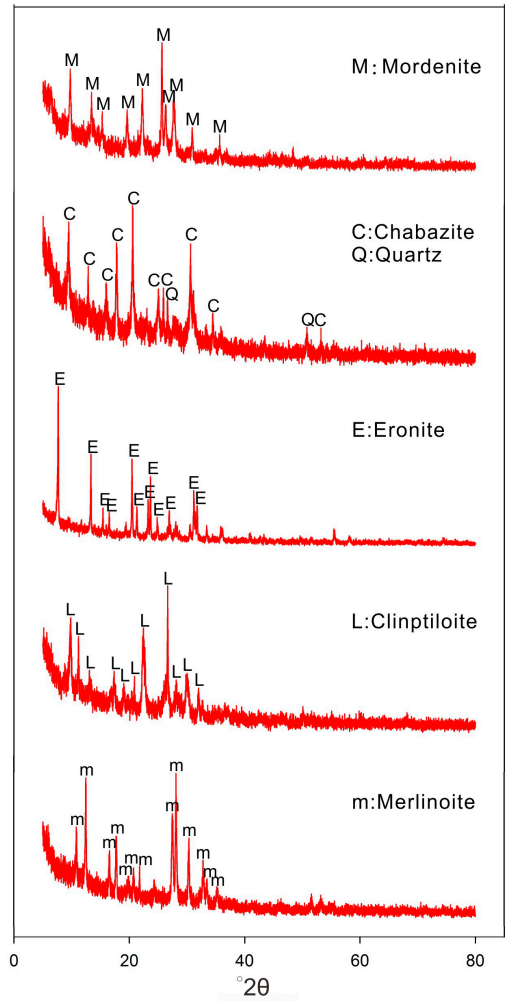


Figure 1. XRD results of each zeolite sample.

All morphology of zeolites shown in Fig. 2 are identified by the Scanning Electron Microscopy (SEM, Hitachi, model S-4800). It reveals good crystal forms and crystallinity of all the samples used in this study. In this case, we adopted the Electron Probe Microanalyses (EPMA, JEOL, model JXA-8900 R) as a method for analyzing each grain of zeolite [16]. The results of the chemical compositions of zeolites are shown in Table 1. Operating conditions are established with an accelerating voltage of 15 kV, the electronic current was set at 5 nA. The two electron beam sizes were less than 5 μm and 10 μm , and the detection time was set at 10 s and 15 s, respectively. Albite and silicate glass were chosen as the chemical standards. Average data of each sample were acquired from more than four individual grains, and each grain was repeatedly tested three times. Table 1 presents the averaged weight percentage of the chemical composition, the Si/Al molar ratios, and the moles of $2\text{Ca}+2\text{Mg}+\text{Na}+\text{K}$ based on 96 oxygen molecules for each zeolite. The Si/Al ratios of these zeolites range between 2.19 and 5.73.

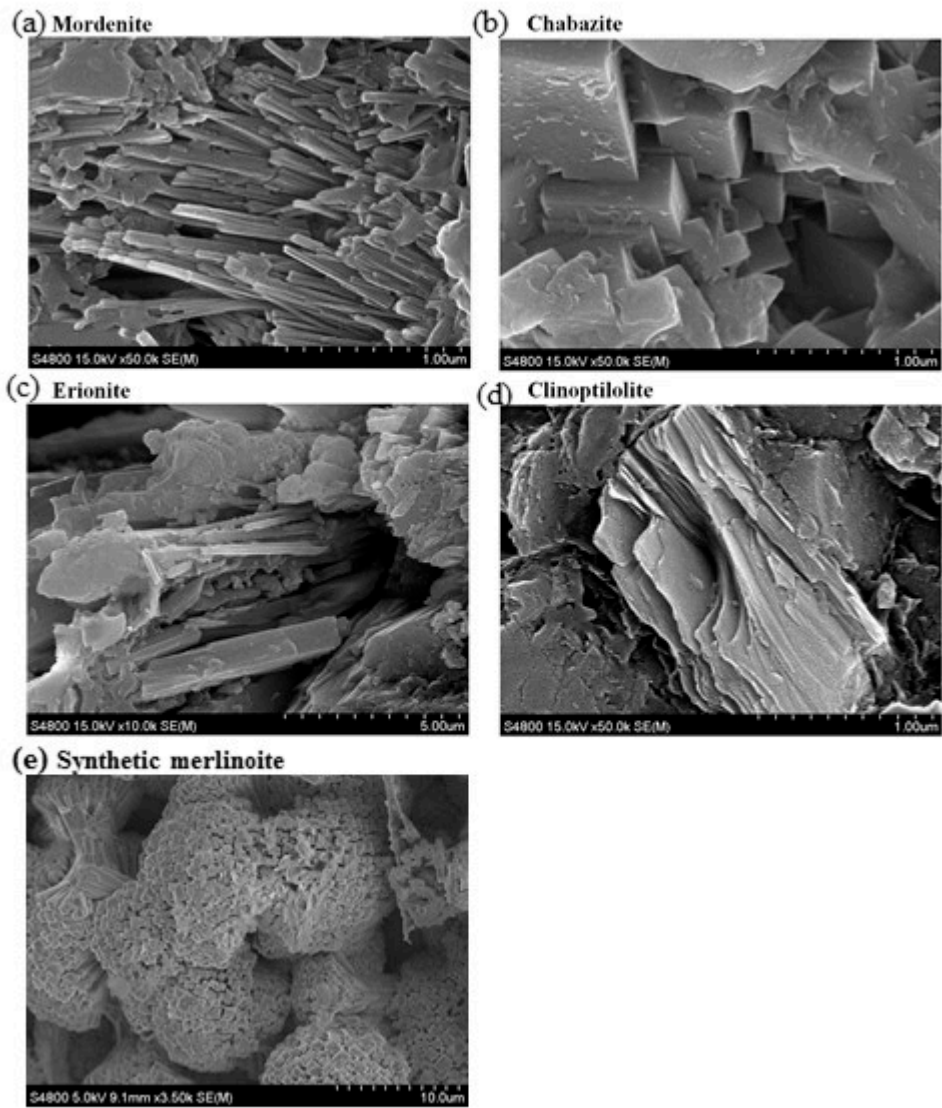


Figure 2. Morphology of the zeolites by the Scanning Electron Microscopy. (a) mordenite; (b) chabazite; (c) erionite; (d) clinoptilolite; and (e) synthetic merlinoite.

Table 1. Weight percentages of chemical composition of zeolites by the EPMA (n: means analytic grain numbers; Si/Al and 2Ca+Mg+Na+K based on 96 oxygen in molar ratio). Specific surface area was determined by the BET method.

	n	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Total (wt %)	Si/Al	2Ca+2Mg+ Na+K	Specific surface area (m ² /g)
Mordenite	26	71.36	10.58	0.04	3.33	1.12	1.98	88.42	5.73	6.8	85.1468
Chabazite	5	54.51	14.98	1.27	2.23	3.41	3.42	79.95	3.09	12.9	378.5544
Erionite	4	61.45	14.38	1.04	3.57	0.52	4.40	85.37	3.63	10.6	395.2574
Clinoptilolite	14	69.14	12.82	0.05	3.70	1.58	1.94	89.38	4.58	7.7	22.0504
Merlinoite	13	52.15	20.19	0.04	0.42	2.61	13.07	88.53	2.19	13.8	3.4623

3. Experimental Methods

In order to understand the ion-exchange and the adsorption proportions of zeolites, we first removed excess impurities in zeolites. To achieve this, the zeolites were washed in pure water and ultrasonically cleaned for 3 times to remove salts and excess adsorbed cations since many of our zeolite samples were collected from natural saline lakes [17]. The zeolites were then oven-dried at 110°C for 24 hours. The samples were then ground to powder and sieved through an 80 mesh sieve. A standard solution of 1000 mg/kg NH₄⁺ (Merck Chemistry, NH₄Cl) was diluted for our experiment. 5 g of zeolite powder was applied to 500 mL NH₄⁺ solution (solid/liquid=1/100). A blank experiment was conducted in correlation with the above experiments. Zeolites were immersed individually in different ammonium concentrations of 20 mg/kg, 50 mg/kg, and 100 mg/kg; and the temperature was held at 30°C. In the temperature controlled experiments, we only used mordenite, chabazite, and erionite in NH₄⁺ solutions of 50 mg/kg at different temperatures, i.e., 5°C, 15°C, 30°C, 40°C, and 50°C. All experiments were carried out in a thermostatic water bath.

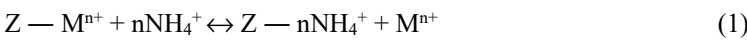
After commencing the experiments, 5 ml of solution (test samples) was removed from the container each time with a 6-h interval over a 7-day time span for measuring the cation concentrations. Each test sample was diluted to measure the concentration of NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺. Released cations Na⁺, K⁺, Ca²⁺, and Mg²⁺ were determined by a Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Ultima II type). Ammonium concentrations were measured by a UV-VIS Spectrophotometer (Metretech, SP 8001 type) at a transparent wavelength of 640±1 nm. The equilibrium concentration of each cation was collected within the 7-day long experiment, and the final result was determined.

The specific surface area of each zeolite sample was measured by a Specific Surface Area and Pore Size Distribution Analyzer (SSA, Micromeritics, model ASAP2020). The samples were pretreated in a vacuum environment at 393.15 K overnight to clean their surface, and then were analyzed at 77 K liquid nitrogen boiling temperature. The surface area value was determined by using the BET equation to fit the relative pressure curve that ranges from 0.06 to 0.2. The test results were calculated by averaging the values of the six measurements (Table 1).

4. Results and Discussion

4.1 Percentage of ion-exchange and adsorption in different concentrations

As one cation invades a zeolite structure, it can be adsorbed in channels of the zeolite or exchanged cation already occupying on zeolite lattice. According to the fundamentals of ion exchange between solid and liquid phases [7,8], ion exchange between a zeolite frame and the aqueous ammonium solution can be expressed by the following equation (1):



where Z and M represent zeolite and bonding cations in zeolite, respectively; and n is the number of the electric charge. Accordingly, we assume that total ammonium removal (NH₄⁺_{total}) from the solution equals the sum of ion-exchange (NH₄⁺_{ion}) and adsorption (NH₄⁺_{ads}) of ammonium of zeolites according to equation (2) below:

$$\text{NH}_4^+_{\text{ion}} + \text{NH}_4^+_{\text{ads}} = \text{NH}_4^+_{\text{total}} \quad (2)$$

Based on equation (1), we assume that released cations are equal to ion-exchange capacity ($\text{NH}_4^+_{\text{ion}}$) [8,18], which can be determined by equation (3). Finally, the adsorption capacity of zeolite can be derived from equations (2) and (3). Adsorption capacity ($\text{NH}_4^+_{\text{ads}}$) is given by equation (4):

$$\text{NH}_4^+_{\text{ion}} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] \quad (3)$$

$$\text{NH}_4^+_{\text{ads}} = \text{NH}_4^+_{\text{total}} - \text{NH}_4^+_{\text{ion}} \quad (4)$$

In Table 2, when we changed the ammonium concentration, we observed that the proportions of ion-exchange and adsorption capacities for each zeolite alter. In the 20 mg/kg ammonium solution, most zeolites have higher ion-exchange capacities, and more than 90% of ammonium removal is dependent on the ion-exchange mechanism. Only mordenite and erionite show lower than 70% ammonium removal by ion-exchange. The results of Table 2 imply higher ammonium concentration leads to higher proportion of adsorption by zeolites. The percentage of ion-exchange capacity ranges between 64–99 % at an initial concentration of 20 mg/kg, and declines to 54–85 % at a higher concentration of 50 mg/kg. In the highest ammonium concentration of 100 mg/kg, this percentage decreases to 52–70 %. This phenomenon has also been proven in other studies [19]. Comparing the ammonium-removal capacity of clinoptilolite between ours and Liu et al. [8] under the same conditions for 100 mg/kg, we found that total ammonium-removal capacity for their clinoptilolite mixing with heulandite and quartz is approximately 0.3 meq/g and ion-exchange capacity is approximately 0.2 meq/g [8]. In this study, total ammonium-removal capacity of our zeolites is higher than 0.4 meq/g, and ion-exchange capacity is higher than 0.2 meq/g (Table 2).

Table 2. Results of zeolite removal of NH_4^+ , and the proportion of ion-exchange and adsorption in different initial NH_4^+ concentrations.

NH_4^+ concentration	Zeolites	$\text{NH}_4^+_{\text{ion}}$ (meq/g)	Ion-exchange (%)	$\text{NH}_4^+_{\text{ads}}$ (meq/g)	Adsorption (%)	$\text{NH}_4^+_{\text{total}}$ (meq/g)
20 mg/kg	Mordenite	0.062	64%	0.034	36%	0.096
	Chabazite	0.103	97%	0.003	3%	0.106
	Erionite	0.073	68%	0.034	32%	0.108
	Clinoptilolite	0.087	90%	0.010	10%	0.097
	Merlinoite	0.091	99%	0.001	1%	0.092
50 mg/kg	Mordenite	0.128	54%	0.110	46%	0.238
	Chabazite	0.163	65%	0.088	35%	0.251
	Erionite	0.134	56%	0.104	44%	0.238
	Clinoptilolite	0.120	55%	0.097	45%	0.217
	Merlinoite	0.194	85%	0.034	15%	0.228
100 mg/kg	Mordenite	0.234	55%	0.189	45%	0.423
	Chabazite	0.277	59%	0.190	41%	0.467
	Erionite	0.238	52%	0.219	48%	0.457
	Clinoptilolite	0.240	58%	0.172	42%	0.412
	Merlinoite	0.277	70%	0.120	30%	0.398

4.2 The relationship between ion-exchange and adsorption with zeolite composition

Each zeolite possesses a different structure and composition. Theoretically, numbers of exchangeable cations in zeolites will influence the ion-exchange capacity, and the channel pore size of zeolites will impact the adsorption capacity. The pore size and numbers of channels in zeolites are somewhat dependent on the Si/Al ratio. Substitution of silicon by aluminum atoms in the crystal framework leads to additional negative charge,

requiring balancing by IA and IIA cations (e.g., Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) [17]. Therefore, we must compare cation numbers and Si/Al ratios of zeolites with the ammonium-removal ability.

Fig. 3(a) presents the relationship between the ammonium ion-exchange capacity and the Si/Al ratio of zeolites under initial NH_4^+ concentrations of 20 mg/kg, 50 mg/kg, and 100 mg/kg. The trend indicates that zeolites of lower Si/Al ratios (merlinoite, chabazite) have slightly higher ion-exchange capacities ($\text{NH}_4^+_{\text{ion}}$). This may be somewhat influenced by the more exchangeable IA and IIA cations in lower Si/Al ratio zeolites [14,15]. On the other hand, the adsorption capacity of zeolite is primarily controlled by the zeolite structure. Therefore, we calculated the ammonium adsorption capacity and compared it with the zeolite Si/Al ratio relationship (Fig. 3(b)). We discovered that zeolites of higher Si/Al ratios have slightly higher ammonium adsorption capacities ($\text{NH}_4^+_{\text{ads}}$). Leyva-Ramos et al. [10, 20] compared the ion-exchange capacities of chabazite and clinoptilolite, and also reported that natural chabazite has a higher ion-exchange capacity, similar to our result shown in Fig. 3(a).

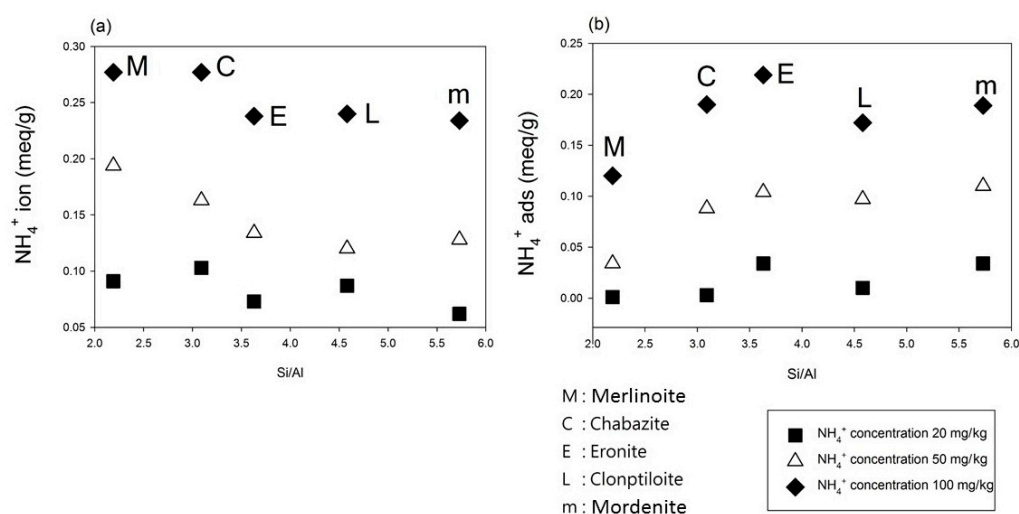


Figure 3. Relationship between (a) ion-exchange and (b) adsorption capacities with the Si/Al ratio of zeolites for different ammonium solutions.

Our previous studies proved that phillipsite and merlinoite of lower Si/Al ratios accompany higher IA and IIA cation contents [14,15]. Therefore, we attempted to calculate the five zeolites in this case, and show the same trend in Fig. 4. We compared the adsorption capacity ($\text{NH}_4^+_{\text{ads}}$) and the ion-exchange capacity ($\text{NH}_4^+_{\text{ion}}$) with the sum of IA and IIA cations in zeolites. Mordenite, clinoptilolite, and erionite have lower ion-exchange capacities due to lower cation contents (Fig. 4), while chabazite and synthetic merlinoite of higher cation contents lead to higher ion-exchange capacities (Fig. 5). The results indicate a positive correlation between the cation content and the ion-exchange capacity in all concentrations (Fig. 5).

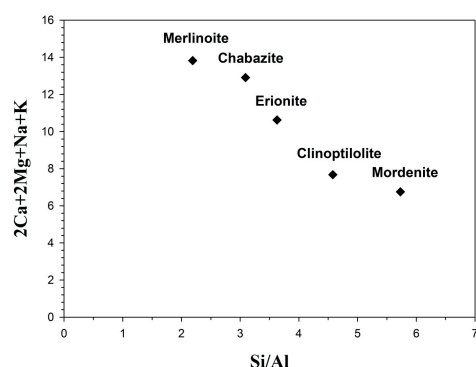
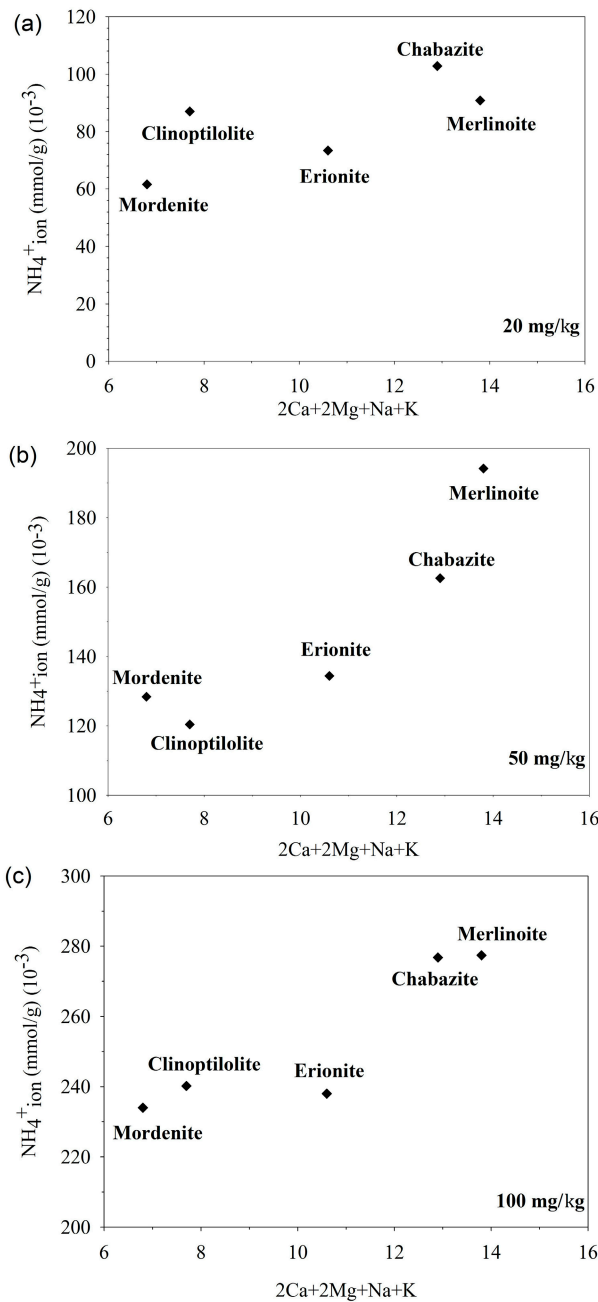


Figure 4. Relationship between Si/Al ratio with IA and IIA cation content in zeolite compositions.

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170

171 **Figure 5.** Relationship between IA and IIA cation content and ion-exchange capacity in initial concentration of (a) 20 mg/kg,
172 (b) 50 mg/kg, and (c) 100 mg/kg.

173 Zeolites of higher Si/Al ratios have larger channel apertures in their zeolite structures [17]. Low Si/Al
174 zeolites (merlinoite, chabazite, and erionite) have eight-ring channels and a smaller aperture size, but high Si/Al
175 zeolites (clinoptilolite and mordenite) have 8-ring, 10-ring, and 12-ring channels and a larger aperture size.
176 Adsorption capacity of zeolites may be affected by the aperture size of channels because larger apertures
177 facilitate the passing through of cations. Therefore, Fig. 3(b) shows that the higher Si/Al zeolites have larger
178 aperture sizes [17], and lead to slightly higher adsorption capacities than others. When we only consider the
179 behavior of ion exchange, the diameter of NH₄⁺ is approximately 2.96 Å [21], which passes through zeolite
180 channels very easily. On the other hand, the diameter of a hydrated NH₄⁺ ion is approximately 6.62 Å [21],
181 which is larger than the aperture of most zeolites, and thus the hydrated ion cannot freely enter such small pores.
182 Although the aperture size of zeolite only reflects an average result of an ideal crystal, the specific surface area

of zeolites may also affect the adsorption results.

4.3 Specific surface area of zeolites

We attempted to measure the specific surface area (SSA) of zeolites in order to investigate its role in adsorption and ion exchange capacities. Erionite and chabazite have larger SSAs, which are 395.26 and 378.55 m²/g, respectively (Table 1), while mordenite and clinoptilolite show SSAs of 85.15 and 22.05 m²/g, respectively. Synthetic merlinite is only 3.46 m²/g, which constitutes the smallest SSA.

SSA reveals no relationship with ion-exchange capacity in all concentrations (Fig. 6 (b)(d)(f)). The SSA results from Fig. 6(a)(c)(e) show that higher SSA in zeolites (i.e., erionite, chabazite, mordenite, and clinoptilolite) have higher adsorption capacity than synthetic merlinoite, especially at high concentrations of 50 mg/kg and 100 mg/kg (Fig. 6(c)(e)) with a non-linear relationship. As the SSA increases to 100 m²/g, the adsorption capacity exhibits an obviously positive trend with the SSA. Interestingly, however, as the SSA rises above a critical value of 100 m²/g, the adsorption capacity no longer increases. It implicates that the adsorption capacity has saturated.

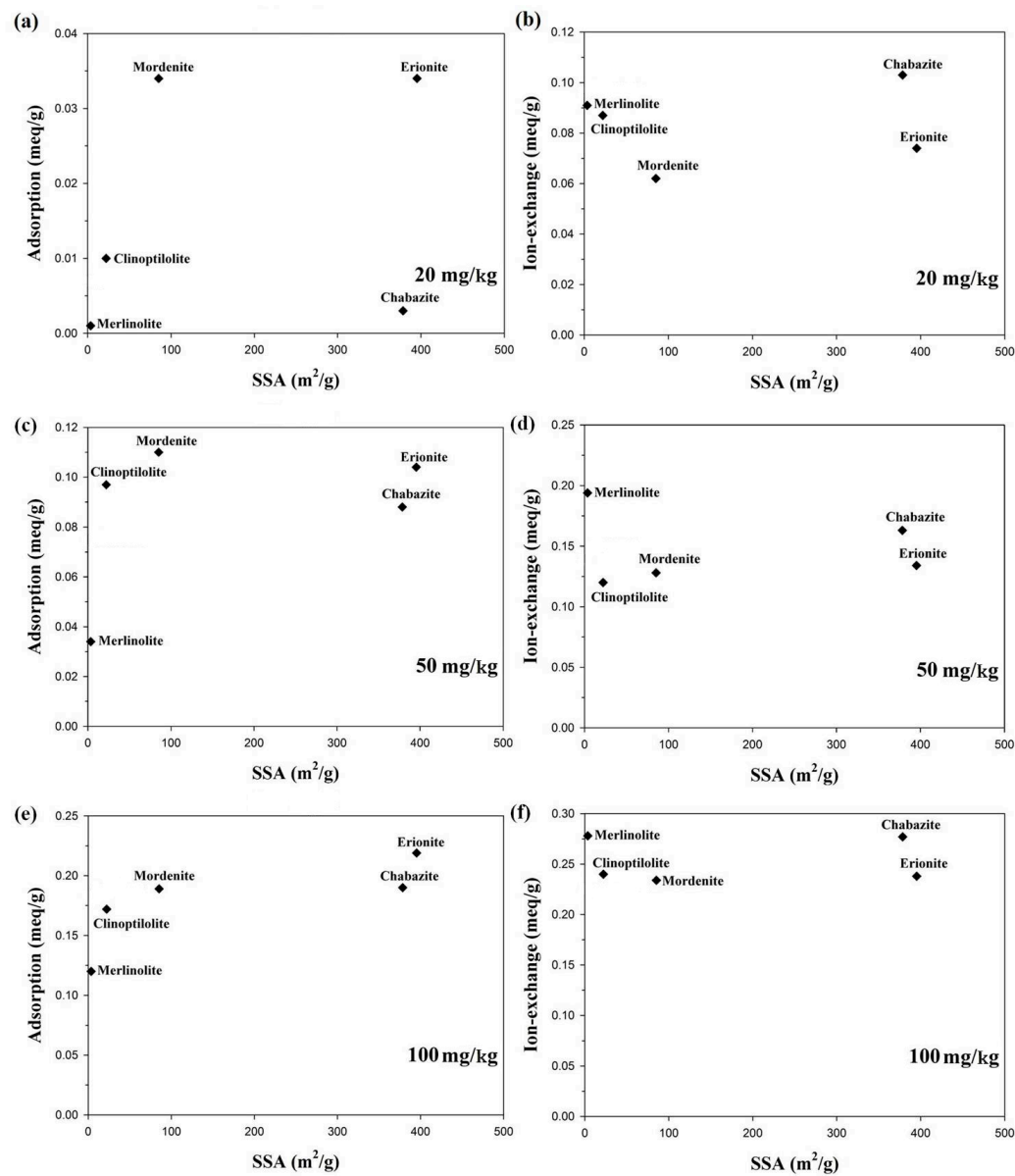


Figure 6. Relationship between SSA and (a) adsorption capacity in concentration of 20 mg/kg; (b) ion-exchange capacity in concentration of 20 mg/kg; (c) adsorption capacity in concentration of 50 mg/kg; (d) ion-exchange capacity in

concentration of 50 mg/kg; (e) adsorption capacities in concentration of 100 mg/kg; and (b) ion-exchange in concentration of 100 mg/kg.

4.4 Temperature effect

4.4.1 Total ammonium removal at different temperatures

In order to examine the effect of temperature on zeolite ammonium-removal, we selected three of the more effective ammonium-adsorbing zeolites (i.e., mordenite, chabazite, and erionite) to immerse in 50 mg/kg NH_4^+ solution under 5°C, 15°C, 30°C, 40°C, and 50°C, respectively. We calculated the percentage of total NH_4^+ removal under different temperatures (Fig. 7). This experiment reveals that the percentage of NH_4^+ removal reaches its highest at 30°C for these zeolites. The percentages of NH_4^+ removal are 77.91% for mordenite, 81.96% for chabazite, and 75.94% for erionite. However, when the temperature is higher or lower than 30°C, the ammonium removal ability decreases rapidly. This result agrees well with previous research [10, 11, 22–24], which also demonstrated that the highest ammonium removal efficiency occurs at room temperature (25°C~35°C). At low temperatures of 5°C and 15°C, only chabazite and erionite have better removal abilities than mordenite (Fig. 7). It is really interesting that the ammonium removal ability of mordenite drops extremely as the temperature reaches lower than 20°C. We know the rate of ion-exchange should decrease as the temperature drops and the adsorption ability should decrease as the temperature goes up. Therefore, 30°C is the best temperature for the ammonium removal process to reach its maximum capacity. The exchangeable cation (2Ca+2Mg+Na+K) of Mordenite is only 6.8, but that of erionite and chabazite are 10.6 and 12.9, respectively (Table 1). The major reason for the sudden decline in ion-exchange ability of mordenite under lower temperature is due to its lower amount of exchangeable cation.

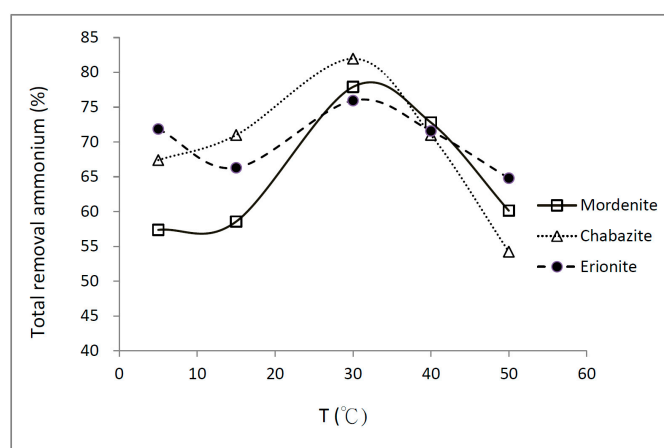


Figure 7. Percentage of total ammonium removal for zeolites at initial NH_4^+ concentration of 50 mg/kg at different temperatures.

4.4.2 Zeolite selectivity at different temperatures

In order to compare ion-exchange mechanisms, it is necessary to understand the cation selectivity of zeolites. We calculated the content of cations in solution and in zeolites at equilibrium. The equilibrium constant K_i of element i follows equation (5):

$$K_i = (C_i)_z / (C_i)_s \quad (5)$$

where $(C_i)_s$ is the concentration of element i in the solution; and $(C_i)_z$ represents the concentration of element i in the zeolite. A higher K_i value indicates that cations tend to adsorb easier onto zeolite at equilibrium. Therefore, the reciprocal $1/K_i$ can be regarded as the cation-release ability of element i from zeolite. Table 3 presents each cation's release ability among zeolites at different temperatures. Interestingly, our results demonstrate that the release-ability ($1/K_i$) of all elements change with temperature. This implies that zeolite-selectivity changes with temperature and zeolite type. Moreover, most conditions reveal that ion release

priority follows: Na > Ca > K for mordenite, chabazite and erionite; however, when the temperature approached 30–40°C, the release ability of all elements rose and the release ability of K increased markedly in mordenite and erionite. This result reveals that the ion-exchange ability of zeolite reaches a maxima at 40°C (Table 3). The irregular release of Mg may be due to the zeolite structure controlling the release sequence of Mg. Mordenite possesses less Mg content than chabazite and erionite (Table 1), but the release ability of Mg in mordenite is prior to chabazite and erionite (Table 3). Although chabazite has more potassium content (Table 1), its potassium was never released into the solution in our experiments (Table 3). This indicates that zeolite type also influences the ion release ability.

Previous studies often use clinoptilolite to explore the ranking of cation selectivity [22, 25, 26]. Their results suggest the order: K > Na > Ca > Mg. However, Lin et al. [8] found different cation selectivity of clinoptilolite following the sequence: Mg > K > Ca > Na. This result is congruent with our results. Our result also shows K > Ca > Na under most conditions, but the selectivity sequence of K and Ca changes at 40°C for mordenite and erionite. This phenomenon gives us a hint that higher temperature promotes large cation to exchange with ammonium ion. Regular selectivity may directly reflect the ionic diameter of cations. The ionic diameter of K (2.66 Å) is larger than Ca (1.98 Å); that of Ca is larger than Na (1.9 Å); that of Na is larger than Mg (1.3 Å) [21]. This result indicates that the release ability of cations is mainly controlled by the cation size. Larger cations favor being conserved in the zeolite structure, but smaller ones are released more readily into solution. In addition, as temperature changes, the selectivity sequence may vary slightly. However, the reason why Mg has a solely different release sequence among different zeolites needs to be further investigated.

Table 3. Release ability of each cation in zeolites and zeolite selectivity under different temperatures.

Mordenite	1/K _{Mg}	1/K _{Ca}	1/K _{Na}	1/K _K	Release priority	Zeolite selectivity
5°C	0.554	0.082	0.169	0	Mg > Na > Ca	Mg < Na < Ca < K
15°C	0.768	0.055	0.112	0	Mg > Na > Ca	Mg < Na < Ca < K
30°C	0.961	0.096	0.343	0.040	Mg > Na > Ca > K	Mg < Na < Ca < K
40°C	1.256	0.100	0.344	0.111	Mg > Na > K > Ca	Mg < Na < K < Ca
50°C	0.919	0.057	0.247	0	Mg > Na > Ca	Mg < Na < Ca < K
Chabazite	1/K _{Mg}	1/K _{Ca}	1/K _{Na}	1/K _K		
5°C	0	0.012	0.176	0	Na > Ca	Na < Ca < Mg = K
15°C	0.008	0.005	1.951	0	Na > Mg > Ca	Na < Mg < Ca < K
30°C	0.007	0.004	0.310	0	Na > Mg > Ca	Na < Mg < Ca < K
40°C	0	0	0.133	0	Na	Na < Ca = Mg = K
50°C	0	0	0.158	0	Na	Na < Ca = Mg = K
Erionite	1/K _{Mg}	1/K _{Ca}	1/K _{Na}	1/K _K		
5°C	0	0.019	8.339	0	Na > Ca	Na < Ca < K = Mg
15°C	0	0.008	1.605	0	Na > Ca	Na < Ca < K = Mg
30°C	0	0.008	1.915	0.006	Na > Ca > K	Na < Ca < K = Mg
40°C	0	0.009	4.026	0.011	Na > K > Ca	Na < K < Ca = Mg
50°C	0	0	1.028	0	Na	Na < Ca = K = Mg

5. Conclusions

In this study, we controlled several experimental factors including the initial ammonium concentration, the zeolite composition, and the temperature. We also discussed the mechanisms governing ammonium removal by zeolites to study zeolite adsorption and ion-exchange capacity. The results of applying various initial concentrations of NH_4^+ show that zeolites possess greater adsorption capacity under higher ammonium concentrations. In addition, it is found that ion-exchange capacity is mainly controlled by the cation content in zeolites, while adsorption capacity is mainly influenced by the Si/Al ratio and the SSA of zeolites. We discovered that mordenite has the highest adsorption capacity due to its sufficient SSA of nearly $100 \text{ m}^2/\text{g}$ and the largest Si/Al ratio. On the other hand, synthetic merlinoite possesses the lowest Si/Al ratio and the highest $2\text{Ca}+2\text{Mg}+\text{Na}+\text{K}$ content, and it also accompanies a higher ion-exchange capacity. Moreover, when we performed removal experiments at 5°C , 15°C , 30°C , 40°C , and 50°C , we found that 30°C benefits ammonium adsorption among all zeolites. Furthermore, the cation selectivity of mordenite, chabazite, and erionite shows the sequence of: $\text{K} > \text{Ca} > \text{Na}$. This phenomenon involves the diameter of cations. The release of Mg is primarily controlled by zeolite structure, and there is no specific trend among different zeolites. Finally, it was found that temperature changes the ion-exchange ability among all zeolites, and also slightly affects the release sequence of cations. .

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Conflicts of Interest: The authors declare no conflict of interest.

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