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Mechanism of the Adsorption of Ammonium Ions from Aqueous Solution by a Chinese Natural Zeolite

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Abstract: The adsorption of ammonium ions onto a Chinese natural zeolite in an agitated batch adsorber was studied. A trial-and-error non-linear method was developed to examine two widely used isotherms, the Langmuir and Freundlich. The data gained from the adsorption system fitted the Freundlich isotherm better. An ion exchange model, describing the relationship among the total metal ions in the solution, NH_4^+ removed from the solution, and ions initially released from the zeolite, was developed for the adsorption system. In addition, a parameter of the ion exchange potential was defined to describe the adsorption mechanism. Ion exchange was the main mechanism that accounted for the adsorption of ammonium ions onto the Chinese natural zeolite.

Keywords: Natural zeolite, adsorption, isotherm, ion exchange

INTRODUCTION

Since the 1970s, natural zeolites have been valued as low-cost adsorbents and ion-exchangers for water pollution control (1, 2). Indeed, zeolite-based systems have been advocated as potential solutions to a wide range of problems. Previous researchers have applied natural zeolites for the removal of ammonium from domestic wastewater (3, 4) as well as from industrial

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wastewaters such as tannery wastewater (5), aquaculture wastewater (6), and piggery wastewater (7, 8). In addition, a number of studies have focused on the application of natural zeolites to treat heavy-metal-contaminated wastewaters for the removal of lead (9, 10), cadmium (11, 12), and other heavy metals (13, 14).

Good performance of a zeolite in pollution control is based on its physical and chemical traits. Natural zeolite is a porous mineral described chemically as aluminosilicate. Zeolites have large variance of specific surface area. The specific surface of most of Chinese natural zeolites range from 70 to 340 m²/g (15). Natural zeolites also possess special ion exchange property due to their crystal structure (16). Differing from the regular structure of silicate, a few crystal lattices of zeolite are occupied by aluminium ions, so an additional surplus charge is generated. The charge is balanced by ions of alkali or alkaline-earth metals, which are reversibly fixed in the cavities of the structure and can easily be exchanged by other cations. According to their composition, natural zeolites are of different sorts, of which clinoptilolite was regarded as the best ion-exchanger for ammonium (17–19). The ion exchanging selectivity of clinoptilolite is as follows: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{Ag}^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ (16).

For removing ammonium from aqueous solution using zeolite, it was suggested that both physical adsorption and ion exchange play roles (19). Physical adsorption of zeolite is essentially the same as other porous materials by dispersive force. While the process of ion exchange in the zeolite-solution system is quite similar to the physical adsorption process except that the ion exchange process is highly selective (20, 21). In the research of removing ammonium from wastewater by a zeolite, the micro-cosmic mechanism can be ignored and all forces of the zeolite effecting on NH_4^+ in the aqueous solution can be regarded wholly as “adsorption” (3, 18, 22–25). To fit the data of NH_4^+ variation in the zeolite-solution system, it was feasible to use adsorption isothermal equations, for example, the Langmuir isotherm (4, 23, 25–27), the Freundlich isotherm (22) or both isotherms (28–30).

However, for the selection of zeolite material, optimization of the operational parameters and regeneration conditions, it is better to distinguish the relationship of the ion exchange from the physical adsorption in wastewater treatment.

In this study, the mechanism of the adsorption of NH_4^+ in aqueous solution by a Chinese natural zeolite was studied. A non-linear method was applied to compare two widely used isotherms, the Langmuir and Freundlich isotherms, in a mathematical fitting of the experimental data. A trial-and-error procedure was used for the non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. In addition, an ion exchange model was presented to describe the relationship among the total metal ions in the solution, NH_4^+ removed from the solution, and ions initially released from the zeolite.

MATERIALS AND METHODS

Zeolite Material

A kind of natural zeolite, mainly clinoptilolite combined with mordenite and heulandite produced in Jinyun, Zhejiang Province, China, was used as the experimental material. Jinyun clinoptilolite ore has higher levels of Na and Ca, so it shall be categorized as Na-Ca-type or Na-type zeolite which is a rare source in China (31).

In the experiment, two different sizes of the zeolite particles are screened, 1.0–3.2 mm and 8–15 mm. With an electron microscope, the internal structure of the zeolite can be observed (Fig. 1). The physical properties and chemical ingredients of the zeolite are listed in Tables 1 and 2 respectively. The cavity structure of the zeolite mainly consists of mesopores and macropores, resulting in a lower specific surface area. Therefore, it is disadvantageous for physical adsorption, but advantageous for ion exchange since the diffusion resistance within the pores is reduced.

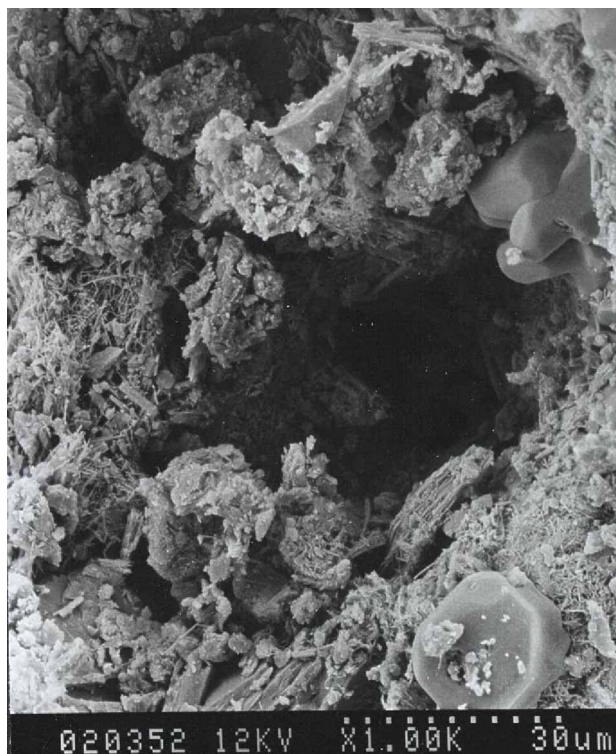


Figure 1. Natural clinoptilolite produced in Jinyun, Zhejiang Province, China.

Table 1. Major physical properties of the zeolite produced in Jinyun, Zhejiang Province, China

Item	Value
Density	2.16
Hardness	3–4
Silicaon/aluminum ratio	4.25–5.25
Thermal stability	750°C
Specific surface area	6.95 m ² /g
Cavity volumn	0.0191 ml/g
Average diameter of pores	112.44 Å

EXPERIMENTAL METHOD

Static condition was adopted as the following procedure: prepare NH₄Cl solution by deionized water, in which only NH₄⁺ cation exists; add zeolite, *m* (g), and NH₄Cl solution, *V* (dm³), into a 250 ml flask; seal the flask and put it on an orbital shaker; set the rotation rate and temperature of the shaker and let the zeolite-solution system contact sufficiently until equilibrium is reached; examine the equilibrium concentration of NH₄⁺ as well as the concentrations of other cations, i.e. Na⁺, K⁺, Ca²⁺, and Mg²⁺ in the solution.

The monitoring method of NH₄⁺ is by spectrophotometry for NH₃-N with Shimadzu 2401 UV-VIS spectrophotometer; and method for detecting cations of Na⁺, K⁺, Ca²⁺, and Mg²⁺ is by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) with Leeman-Profile ICP spectrometer.

RESULTS AND DISCUSSION

Adsorption Isotherm

Under a static condition, we changed the initial concentration of NH₄⁺, *C*_i, and conducted the adsorption experiment under a constant temperature (25°C). In the zeolite and ammonium brine system, the adsorption process reached a balance under the equilibrium concentration of NH₄⁺, *C*_e, in the solution and the equilibrium quantity of NH₄⁺ adsorbed on the zeolite, *q*_e. A set of *C*_e and *q*_e data were acquired and fitted to the Langmuir and Freundlich isotherms, the widely used adsorption isotherms. Linear regression is frequently used to determine the best-fitting isotherm, however, non-linear regression is rather dependable than linear regression after several comparative studies were made (32). In the case of the non-linear method, a trial-and-error procedure, which is applicable to computer operation, was

Table 2. Major chemical ingredients of the zeolite produced in Jinyun, Zhejiang Province, China

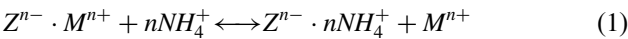
Sample	Zeolite concentration	Chemical ingredient ^a (%)											Ignition loss
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	
1#	65%	66.21	0.13	10.99	0.96	—	0.04	0.53	2.98	2.22	0.92	6.45	13.83
2#	70%	69.58	0.14	12.20	0.87	0.11	0.07	0.13	2.59	2.59	1.13	11.9	—
3#	71%	69.50	0.14	11.05	0.08	0.11	0.08	0.13	2.59	2.95	1.13	—	11.00

^aBesides, the zeolite also contains microelements such as Cu, Pb, As, Be, Zr, Ni, P, Mo, Sn, Ga, Cr, V, Yb, Y, Nb, La, etc.

developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The abilities of two commonly used isotherms, the Langmuir and Freundlich isotherms, to model the equilibrium adsorption data were examined. Table 3 lists the values of the parameters and the coefficient of determinations, r^2 , of the two isotherms using the non-linear method. The coefficient of determinations, r^2 , indicates that the adsorption of NH_4^+ onto zeolite follows the Freundlich isotherm better. Figure 2 shows the non-linear Langmuir and Freundlich isotherms with the experimental data for the adsorption of NH_4^+ onto the zeolite with two particle sizes.

Ion Exchange Model

Within the zeolite-ammonium brine system, the ion exchange process can be expressed as the following chemical transfer:



where Z is zeolite, M is metal ions in the zeolite, for example Na^+ , Ca^{2+} , K^+ , and Mg^{2+} , and n is the number of electric charge.

If the ion exchange predominates over the process of adsorption in the liquid-solid system, the electric charge shall be balanced between the number of NH_4^+ adsorbed onto the zeolite and the total number of the metal ions emitted from the zeolite.

By the non-linear Freundlich equation, Fig. 3 shows the relationship of the equivalent concentrations between the total metal ions emitted from the zeolite and NH_4^+ remained in the aquatic solution, C_e , with two particle sizes. It is clear that ion exchange increased with decreasing particle size of the zeolite. The total ion exchange fits the Freundlich model well, implying that the adsorption of the ammonium from the solution onto zeolite depends on ion exchange to a great extent. An ion exchange model can be set up to describe the relationship among the total emitted metal ions in the solution, NH_4^+ removed from the solution, and ions initially released from the zeolite

Table 3. Isotherm parameters obtained by using the non-linear method

	Langmuir			Freundlich		
	q_m (meq/g)	K_a (dm ³ /mg)	r^2	$1/n$	K_F (meq/g) (dm ³ /mg) ^{1/n}	r^2
1.0–3.2 mm	108	1.30	0.986	0.445	54.1	0.995
8–15 mm	97.1	1.02	0.986	0.450	44.0	0.993

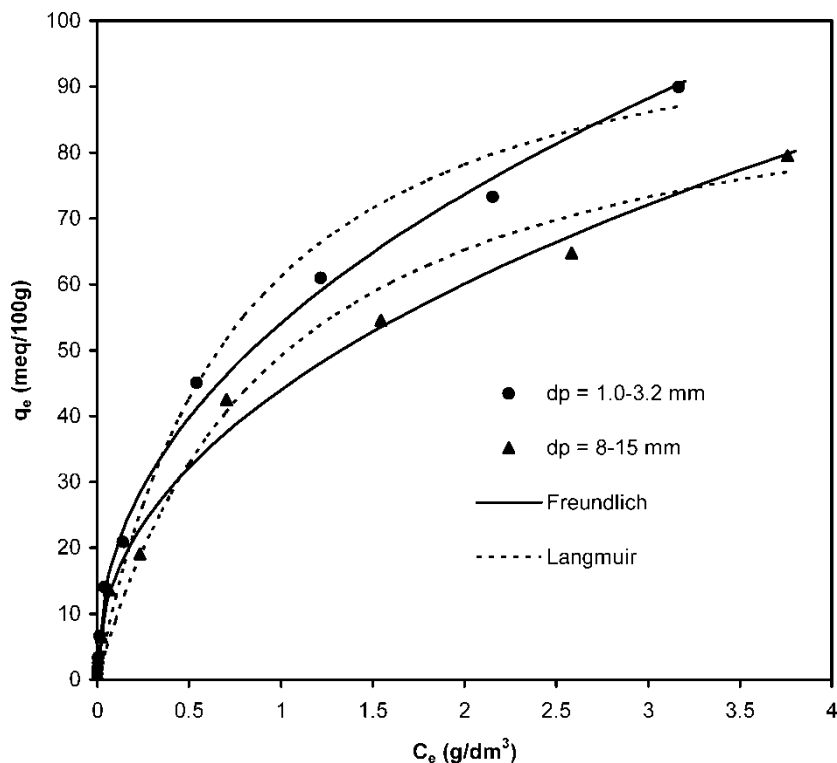


Figure 2. Adsorption of NH_4^+ onto the zeolite fitted by the Langmuir and Freundlich isotherms.

due to re-distribution between the liquid and solid phases. There is a linear relationship with a high coefficient of determination as shown in Fig. 4. The model can be expressed as:

$$I_T = I_E + I_R \quad (2)$$

$$I_E = PR_N \quad (3)$$

$$I_T = PR_N + I_R \quad (4)$$

where I_T is the concentration of total metal ions (here refers Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) emitted from the zeolite, meq/dm^3 ; I_E is the metal ions exchanged from the zeolite in I_T , meq/dm^3 ; and I_R is the metal ions initially released from the zeolite in I_T , meq/dm^3 ; P is an indicator constant; and R_N is the concentration of NH_4^+ removed from the solution, meq/dm^3 . Table 4 lists the parameters (P and I_R) of the ion exchange model.

It can be seen from Fig. 4 and Table 4 that more ions released from the zeolite when the smaller particle size was used as adsorbent (intercept, I_R is

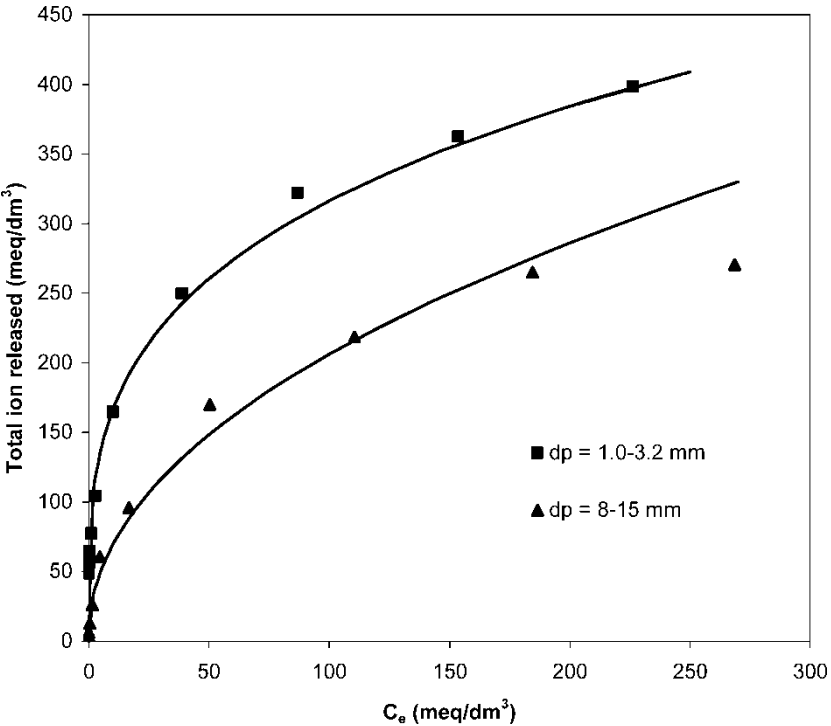


Figure 3. Desorption of total metal ions from the zeolite fitted by the Freundlich isotherm.

55.0 meq/dm³ for the smaller zeolite, and 7.63 meq/dm³ for the larger zeolite). This is to be expected because, for a fixed adsorbent dose, decreasing adsorbent particle size provides greater surface area so that more ions can be released from the liquid-solid interface at the initial stage. The indicator of the ion exchange potential, P , is a measure of how much ion exchange occurred between NH_4^+ in the aqueous solution and metal ions (i.e. Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) in the zeolite. In general, ion exchange shall be an equivalent process to keep electric neutralization of the system, i.e. when the adsorption reaches equilibrium, P shall be 1 if ion exchange is the sole adsorption mechanism for the zeolite effecting on aquatic NH_4^+ . This is confirmed by the case of the smaller particle size ($d_p = 1.0-3.2$ mm, $P = 1.03$). But in the case of the larger particle size, ions in the zeolite exchanged less with NH_4^+ in the solution ($d_p = 8.0-15$ mm, $P = 0.916$). The reason shall not be attributed to physical adsorption of NH_4^+ since no physical adsorption mechanism occurred even in the smaller particle size of the same zeolite. It is also due to different particle sizes of the adsorbent that affected the ion exchange potential.

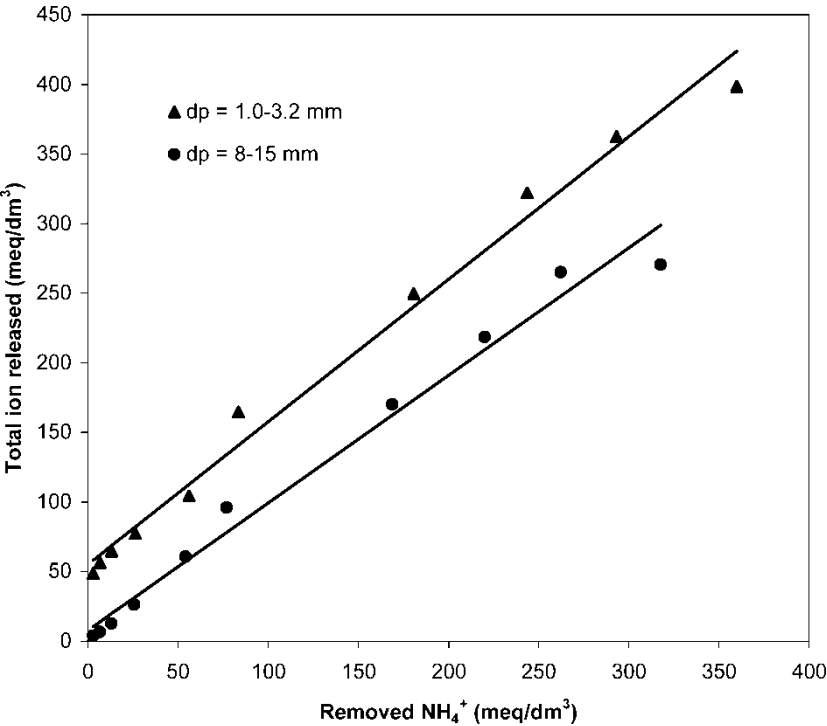


Figure 4. Ion exchange model for the zeolite-ammonium brine system.

Adsorption is a dual-rate process comprised of two phases, i.e. the rapid diffusion phase and the slow diffusion phase (rate-restricted phase). For a larger particle size, after the rapid diffusion phase, the ions in the zeolite encounter much greater resistance for further diffusing from the pore-canals of the crystal. When the adsorption does not reach the ultimate equilibrium, less ions have been diffused from the larger particle size of the zeolite while equilibrated quantity of NH_4^+ have already been adsorbed onto the zeolite as the result. But if more time is allowed the, P value should be improved to approach 1 for the larger particle size of the zeolite.

Analyzing the possibility of the adsorption mechanism in the zeolite-ammonium brine system, it can be predicted from the ion exchange model

Table 4. Parameters of the ion exchange model

d_p mm	P	I_R (meq/dm ³)	r^2
1.0–3.2	1.03	55.0	0.989
8–15	0.916	7.63	0.984

Table 5. Analysis of the zeolite adsorption mechanism by the ion exchange model

Model equation: $I_T = PR_N + I_R$			Type of adsorption (when equilibrium is reached)
Values of P	$P > 1$	(impossible)	
	$P = 1$	Ion exchange only	
	$0 < P < 1$	Ion exchange plus physical adsorption	
	$P = 0$	Non-ion exchange, only physical adsorption	
Values of I_R	$I_R < 0$	Used zeolite releases NH_4^+ (often happens in the desorption or regeneration of zeolite)	
	$I_R = 0$	No ions release from zeolite (reaches ultimate equilibrium)	
	$I_R > 0$	Fresh or unbalanced zeolite releases metal ions (often happens in the adsorption of zeolite)	

as shown in Table 5. For the natural zeolite produced in Junyun, Zhejiang Province, the adsorption of ammonium from the aquatic solution is predominated by ion exchange, and physical adsorption has little influence on the process.

For distinguishing the contribution from different metal ions in the total ion exchange, Fig. 5 describes the case of the smaller zeolite particle showing equivalent concentrations of Mg^{2+} , Ca^{2+} , K^+ , and Na^+ , respectively under various equilibrium concentrations of NH_4^+ , and Fig. 6 describes the case of the larger zeolite particle. The cases of Mg^{2+} and K^+ are similar for both particle sizes. Concentration of Mg^{2+} is the lowest and has little emission from the zeolite in equilibrium. Thus Mg^{2+} is hardly involved in the ion exchange. Concentration of K^+ is lower in the solution, but increases a little in equilibrium. The reason shall be the re-distribution of K^+ between the liquid and solid phases instead of ion exchange because K^+ is prior to NH_4^+ in the ion exchange sequence of clinoptilolite (16).

Ion exchange occurs mainly between Na^+ and Ca^{2+} in the zeolite and NH_4^+ in the aquatic solution. In the cases of Na^+ and Ca^{2+} in Figs. 5 and 6, it is found that the ion exchange is affected by different particle sizes. For the smaller zeolite particle, exchanging-degree is approximately similar for Na^+ and Ca^{2+} replaced by NH_4^+ . However, the tendency indicates that Na^+ is prior to be exchanged at lower concentration of NH_4^+ ($C_e < 80 \text{ meq/dm}^3$), while more Ca^{2+} is selected for ion exchange at higher concentration of NH_4^+ ($C_e > 80 \text{ meq/dm}^3$). For the larger zeolite particle, Ca^{2+} is much more preferable to be exchanged when C_e is more than 15 meq/dm^3 . The ion size of Na^+ is smaller than that of Ca^{2+} , so Na^+ is easier to emit from zeolite, especially from the zeolite with smaller particle size under lower concentration difference, while higher concentration difference is necessary for Ca^{2+} emitting from the pore-canals of zeolite. However, calcium ion has two electric charges whereas

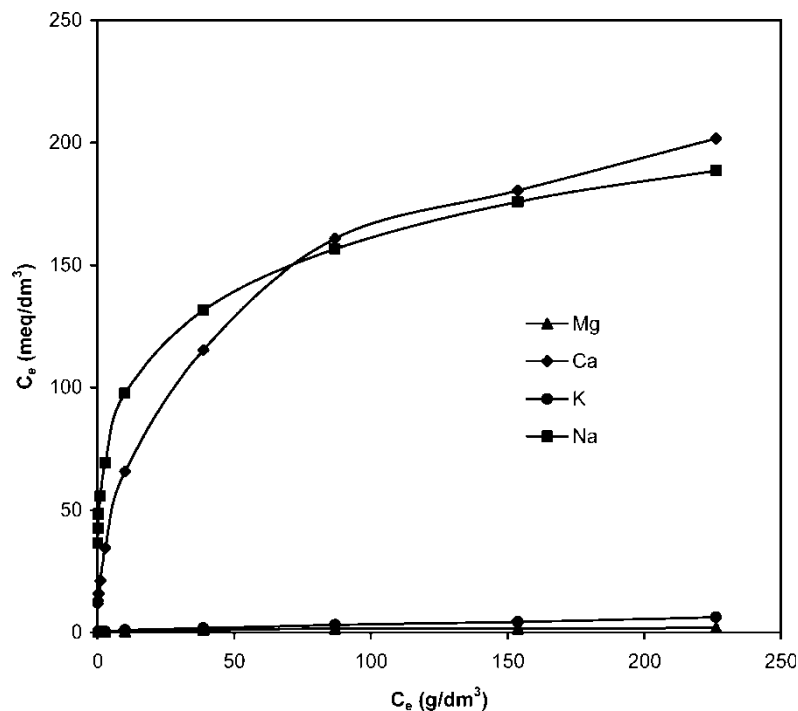


Figure 5. Equivalent concentrations of different metal ions under various equilibrium concentrations of NH_4^+ for the smaller zeolite particle ($d_p = 1.0\text{--}3.2$ mm).

sodium ion has only one electric charge, the equivalent concentration of Ca^{2+} increases rapidly with the increasing concentration pressure, and will definitely exceed the equivalent concentration of Na^+ in the solution.

CONCLUSIONS

For a Chinese natural zeolite, the mechanism of its adsorption of NH_4^+ from aqueous solution was studied. Based on the experimental data of either the adsorbed ammonium ion or the total emitted metal ions, the adsorption fits the Freundlich isotherm better. An ion exchange model, describing the relationship among the total metal ions in the solution, NH_4^+ removed from the solution, and ions initially released from the zeolite, can reveal the adsorption mechanism. The parameter of the ion exchange potential, P , is about 1, indicating that the adsorption of ammonium from the aquatic solution by the natural zeolite is predominated by ion exchange whereas physical adsorption has little influence. More ions are released from the zeolite with the

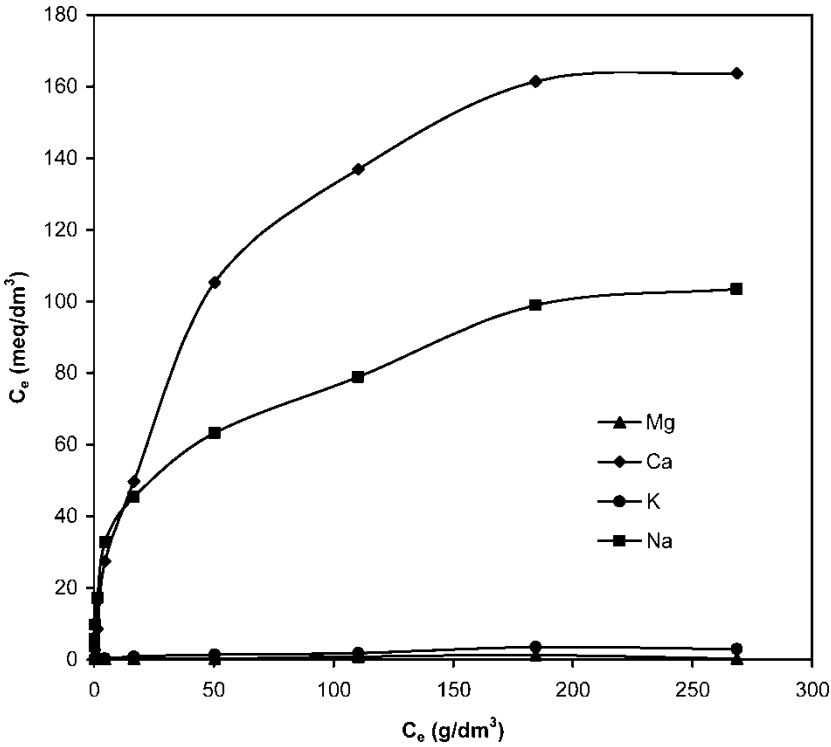


Figure 6. Equivalent concentrations of different metal ions under various equilibrium concentrations of NH_4^+ for the larger zeolite particle ($d_p = 8\text{--}15\text{ mm}$).

decreasing of the particle size at the initial stage, as reflected from the parameter I_R . Tracking the different ions, ion exchange mainly occurs between Na^+ and Ca^{2+} in the zeolite and NH_4^+ in the aquatic solution. Na^+ is prior to be exchanged at lower concentration difference, but Ca^{2+} is much more preferable to be exchanged under higher pressure of concentration difference. Mg^{2+} is hardly involved in the ion exchange and K^+ is released from the zeolite by the re-distribution between the liquid and solid phases.

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