

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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

Donghui Wen<sup>a</sup>; Yuh-Shan Ho<sup>a</sup>; Shuguang Xie<sup>a</sup>; Xiaoyan Tang<sup>a</sup>

<sup>a</sup> Department of Environmental Sciences, College of Environmental Sciences, Peking University, Beijing, People's Republic of China

**To cite this Article** Wen, Donghui , Ho, Yuh-Shan , Xie, Shuguang and Tang, Xiaoyan(2006) 'Mechanism of the Adsorption of Ammonium Ions from Aqueous Solution by a Chinese Natural Zeolite', *Separation Science and Technology*, 41: 15, 3485 – 3498

**To link to this Article:** DOI: 10.1080/01496390600854636

URL: <http://dx.doi.org/10.1080/01496390600854636>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

Donghui Wen, Yuh-Shan Ho, Shuguang Xie,  
and Xiaoyan Tang

Department of Environmental Sciences, College of Environmental Sciences, Peking University, Beijing, People's Republic of China

**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,  $\text{NH}_4^+$  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

Received 21 February 2006, Accepted 16 May 2006

Address correspondence to Xiaoyan Tang, Department of Environmental Sciences, College of Environmental Sciences, Peking University, Beijing 100871, People's Republic of China. Tel./Fax: 86 10 6275 1925; E-mail: xytang@pku.edu.cn

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 m<sup>2</sup>/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 theirs 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: Cs<sup>+</sup> > Rb<sup>+</sup> > K<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Pb<sup>2+</sup> > Ag<sup>+</sup> > Ba<sup>2+</sup> > Na<sup>+</sup> > Sr<sup>2+</sup> > Ca<sup>2+</sup> > Li<sup>+</sup> > Cd<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> (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 microcosmic mechanism can be ignored and all forces of the zeolite effecting on NH<sub>4</sub><sup>+</sup> in the aqueous solution can be regarded wholly as “adsorption” (3, 18, 22–25). To fit the data of NH<sub>4</sub><sup>+</sup> 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.

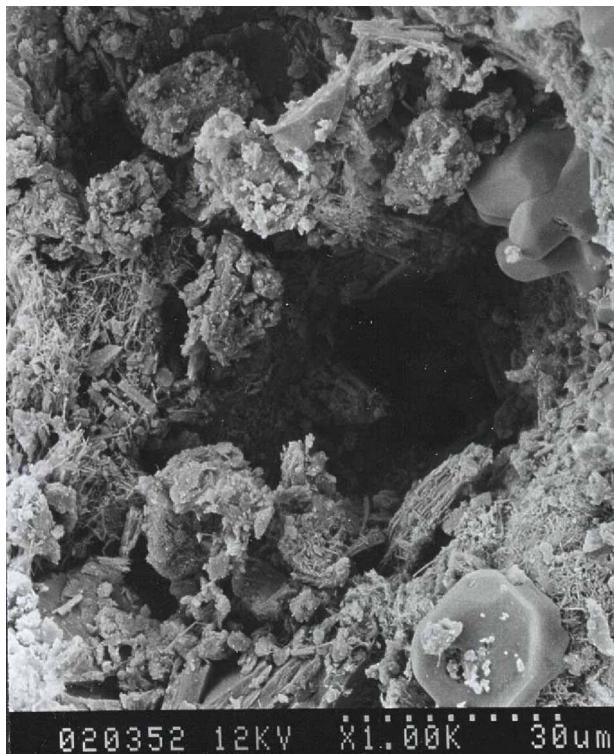
In this study, the mechanism of the adsorption of NH<sub>4</sub><sup>+</sup> in aqueous solution by a Chinese natural zeolite was studied. A non-linear method was applied to compare two widely used isotherms, the Langmuir and Freundlich isotherms, in a mathematical fitting of the experimental data. A 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<sub>4</sub><sup>+</sup> 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 <sup>2</sup> /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 NH<sub>4</sub>Cl solution by deionized water, in which only NH<sub>4</sub><sup>+</sup> cation exists; add zeolite, *m* (g), and NH<sub>4</sub>Cl solution, *V* (dm<sup>3</sup>), 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 NH<sub>4</sub><sup>+</sup> as well as the concentrations of other cations, i.e. Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> in the solution.

The monitoring method of NH<sub>4</sub><sup>+</sup> is by spectrophotometry for NH<sub>3</sub>-N with Shimadzu 2401 UV-VIS spectrophotometer; and method for detecting cations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> is by inductively coupled plasma-atomic emission spectroscope (ICP-AES) with Leeman-Profile ICP spectrometer.

## RESULTS AND DISCUSSION

### Adsorption Isotherm

Under a static condition, we changed the initial concentration of NH<sub>4</sub><sup>+</sup>, *C<sub>i</sub>*, 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 NH<sub>4</sub><sup>+</sup>, *C<sub>e</sub>*, in the solution and the equilibrium quantity of NH<sub>4</sub><sup>+</sup> adsorbed on the zeolite, *q<sub>e</sub>*. A set of *C<sub>e</sub>* and *q<sub>e</sub>* 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

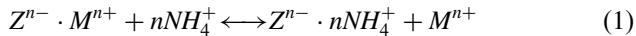
Sample	Zeolite concentration	Chemical ingredient <sup>a</sup> (%)										Ignition loss	
		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O		
1#	65%	66.21	0.13	10.99	0.96	—	0.04	0.53	2.98	2.22	0.92	6.45	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

<sup>a</sup>Besides, 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  $\text{NH}_4^+$  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  $\text{NH}_4^+$  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  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ , 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  $\text{NH}_4^+$  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  $\text{NH}_4^+$  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,  $\text{NH}_4^+$  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 <sup>3</sup> /mg)	$r^2$	$1/n$	$K_F$ (meq/g) (dm <sup>3</sup> /mg) <sup>1/n</sup>	$r^2$
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

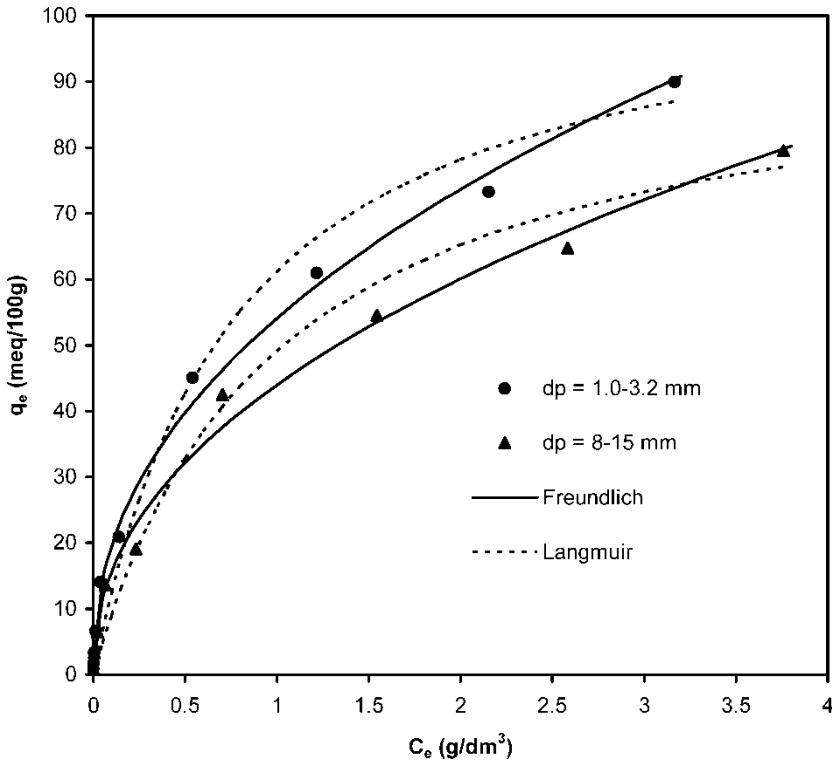


Figure 2. Adsorption of  $\text{NH}_4^+$  onto the zeolite fitted by the Langmuir and Freundlich isotherms.

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  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) emitted from the zeolite, meq/dm<sup>3</sup>;  $I_E$  is the metal ions exchanged from the zeolite in  $I_T$ , meq/dm<sup>3</sup>; and  $I_R$  is the metal ions initially released from the zeolite in  $I_T$ , meq/dm<sup>3</sup>;  $P$  is an indicator constant; and  $R_N$  is the concentration of  $\text{NH}_4^+$  removed from the solution, meq/dm<sup>3</sup>. 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

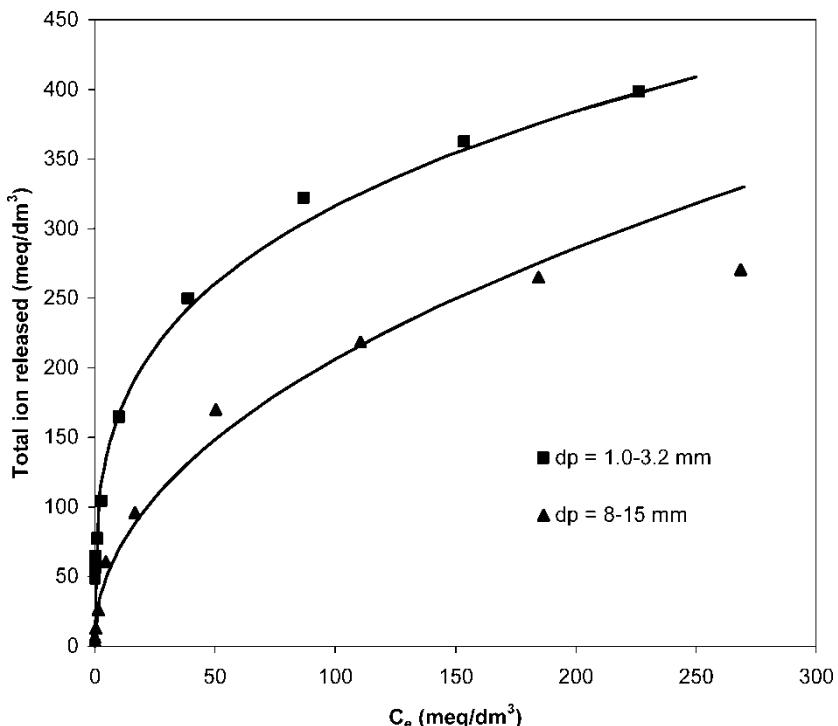


Figure 3. Desorption of total metal ions from the zeolite fitted by the Freundlich isotherm.

55.0 meq/dm<sup>3</sup> for the smaller zeolite, and 7.63 meq/dm<sup>3</sup> 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  $\text{NH}_4^+$  in the aqueous solution and metal ions (i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) 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  $\text{NH}_4^+$ . 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  $\text{NH}_4^+$  in the solution ( $d_p = 8.0-15$  mm,  $P = 0.916$ ). The reason shall not be attributed to physical adsorption of  $\text{NH}_4^+$  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.

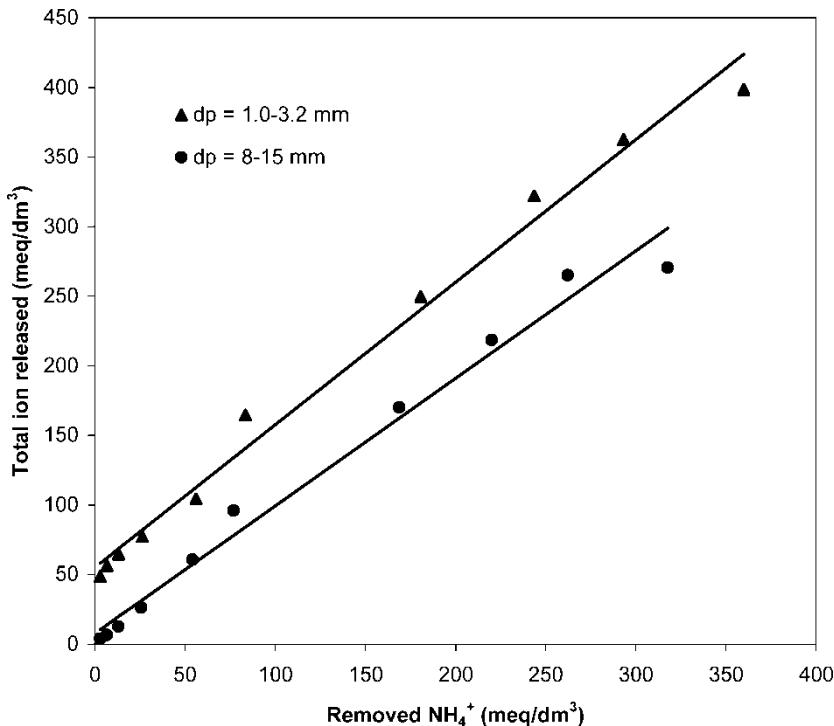


Figure 4. Ion exchange model for the zeolite-ammonium brine system.

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  $\text{NH}_4^+$  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 <sup>3</sup> )	$r^2$
1.0–3.2	1.03	55.0	0.989
8–15	0.916	7.63	0.984

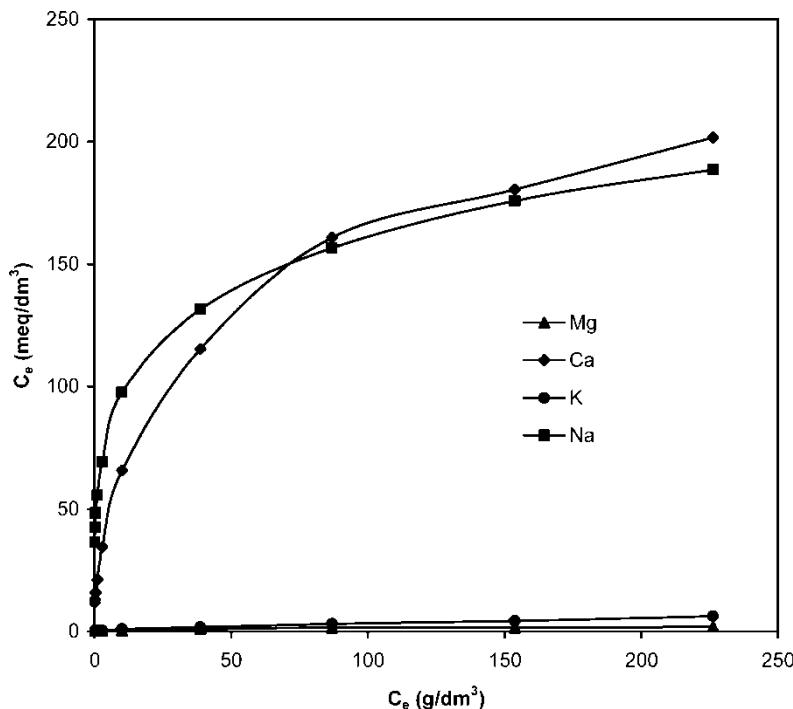
**Table 5.** Analysis of the zeolite adsorption mechanism by the ion exchange model

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 $\text{NH}_4^+$ (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  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ , respectively under various equilibrium concentrations of  $\text{NH}_4^+$ , and Fig. 6 describes the case of the larger zeolite particle. The cases of  $\text{Mg}^{2+}$  and  $\text{K}^+$  are similar for both particle sizes. Concentration of  $\text{Mg}^{2+}$  is the lowest and has little emission from the zeolite in equilibrium. Thus  $\text{Mg}^{2+}$  is hardly involved in the ion exchange. Concentration of  $\text{K}^+$  is lower in the solution, but increases a little in equilibrium. The reason shall be the re-distribution of  $\text{K}^+$  between the liquid and solid phases instead of ion exchange because  $\text{K}^+$  is prior to  $\text{NH}_4^+$  in the ion exchange sequence of clinoptilolite (16).

Ion exchange occurs mainly between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the zeolite and  $\text{NH}_4^+$  in the aquatic solution. In the cases of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  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  $\text{Na}^+$  and  $\text{Ca}^{2+}$  replaced by  $\text{NH}_4^+$ . However, the tendency indicates that  $\text{Na}^+$  is prior to be exchanged at lower concentration of  $\text{NH}_4^+$  ( $C_e < 80 \text{ meq}/\text{dm}^3$ ), while more  $\text{Ca}^{2+}$  is selected for ion exchange at higher concentration of  $\text{NH}_4^+$  ( $C_e > 80 \text{ meq}/\text{dm}^3$ ). For the larger zeolite particle,  $\text{Ca}^{2+}$  is much more preferable to be exchanged when  $C_e$  is more than  $15 \text{ meq}/\text{dm}^3$ . The ion size of  $\text{Na}^+$  is smaller than that of  $\text{Ca}^{2+}$ , so  $\text{Na}^+$  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  $\text{Ca}^{2+}$  emitting from the pore-canals of zeolite. However, calcium ion has two electric charges whereas

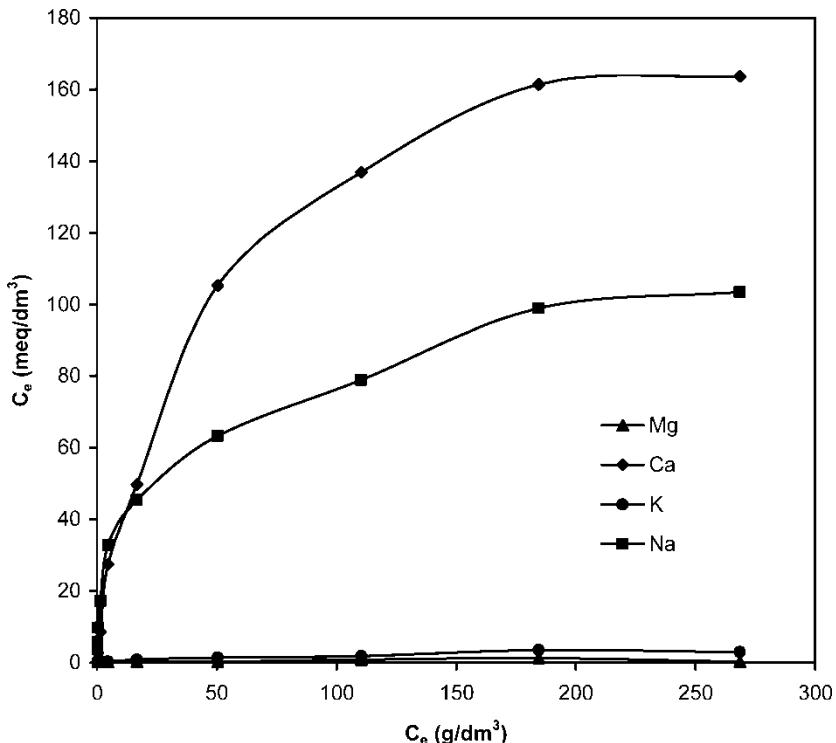


**Figure 5.** Equivalent concentrations of different metal ions under various equilibrium concentrations of  $\text{NH}_4^+$  for the smaller zeolite particle ( $\text{dp} = 1.0\text{--}3.2 \text{ mm}$ ).

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

## CONCLUSIONS

For a Chinese natural zeolite, the mechanism of its adsorption of  $\text{NH}_4^+$  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,  $\text{NH}_4^+$  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  $\text{NH}_4^+$  for the larger zeolite particle ( $dp = 8-15$  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  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the zeolite and  $\text{NH}_4^+$  in the aquatic solution.  $\text{Na}^+$  is prior to be exchanged at lower concentration difference, but  $\text{Ca}^{2+}$  is much more preferable to be exchanged under higher pressure of concentration difference.  $\text{Mg}^{2+}$  is hardly involved in the ion exchange and  $\text{K}^+$  is released from the zeolite by the re-distribution between the liquid and solid phases.

#### ACKNOWLEDGEMENTS

This study is a part of work of the Project, Technology of Non-point Source Pollution Control in the Dianchi Watershed (Approval Number: K99-05-35-02), financially supported by the Chinese Ministry of Science & Technology. The authors thank Dr. Wenqi Li, Dr. Jun Wang, Dr. Weizhong Wu, and Dr. Xi Zhang, who were involved in the project and helped a lot in the laboratory work.

## REFERENCES

1. Barthome, D. and Ha, B.H. (1973) Adsorption of benzene and cyclohexane on faujasite-type zeolites. II. Adsorption site efficiency and zeolite field influence at high coverage. *J. Chem. Soc., Faraday Trans. I*, 69 (12): 2158–2165.
2. Kessaouiouki, S., Cheeseman, C.R., and Perry, R. (1994) Natural zeolite utilization in pollution-control: A review of applications to metals effluents. *J. Chem. Technol. Biot.*, 59 (2): 121–126.
3. Booker, N.A., Cooney, E.L., and Priestly, A.J. (1996) Ammonia removal from sewage using natural Australian zeolite. *Water Sci. Technol.*, 34 (9): 17–24.
4. Englert, A.H. and Rubio, J. (2005) Characterization and environmental application of a Chilean natural zeolite. *Int. J. Miner. Process.*, 75 (1–2): 21–29.
5. Chmielewska-Horvathova, E., Konecny, J., and Bosan, Z. (1992) Ammonia removal from tannery wastewaters by selective ion exchange on slovak clinoptilolite. *Acta Hydroch. Hydrol.*, 20 (5): 269–272.
6. Bergero, D., Boccignone, M., Di Natale, F., Forneris, G., Palmegiano, G.B., Roagna, L., and Sicuro, B. (1994) Ammonia removal capacity of European natural zeolite tuffs: Application to aquaculture wastewater. *Aquacult. Fish. Manage.*, 25 (8): 813–821.
7. Sanchez, E., Milan, Z., Borja, R., Weiland, P., and Rodriguez, X. (1995) Piggery waste treatment by anaerobic digestion and nutrient removal by ionic exchange. *Resour. Conserv. Recy.*, 15 (3–4): 235–244.
8. Cintoli, R., Di Sabatino, B., Galeotti, L., and Bruno, G. (1995) Ammonium uptake by zeolite and treatment in UASB reactor of piggery wastewater. *Water Sci. Technol.*, 32 (12): 73–81.
9. Colella, C. and Pansini, M. (1990) Dynamic data on lead uptake from water by chabazite. *Desalination*, 78 (2): 287–295.
10. Petruzzelli, D., Pagano, M., Tiravanti, G., and Passino, R. (1999) Lead removal and recovery from battery wastewaters by natural zeolite clinoptilolite. *Solvent. Extr. Ion Exch.*, 17 (3): 677–694.
11. Malliou, E., Loizidou, M., and Spyrellis, N. (1994) Uptake of lead and cadmium by clinoptilolite. *Sci. Total Environ.*, 149 (3): 139–144.
12. Yuan, G., Seyama, H., Soma, M., Theng, B.K.G., and Tanaka, A. (1999) Adsorption of some heavy metals by natural zeolites: XPS and batch. *J. Environ. Sci. Heal. A*, 34 (3): 625–648.
13. Loizidou, M., Haralambous, K.J., Loukatos, A., and Dimitrakopoulou, D. (1992) Natural zeolites and their ion exchange behavior towards chromium. *J. Environ. Sci. Heal. A*, 27 (7): 1759–1769.
14. Ouki, S.K. and Kavannagh, M. (1999) Treatment of metals-contaminated wastewaters by use of natural zeolites. *Water Sci. Technol.*, 39 (10): 115–122.
15. Tao, W.P., Gao, X.F., et al. (1994) *Mineralization of Nonmetal Deposit in China*; Press of Geology: Beijing (in Chinese).
16. Tsitsishvili, G.V. and Andronikashvili, T.G. (1992) *Natural Zeolites*; Redwood Press: Oxford.
17. Klieve, J.R. and Semmens, M.J. (1980) An evaluation of pretreated natural zeolites for ammonium removal. *Water Res.*, 14 (2): 161–168.
18. Metropoulos, K., Maliou, E., Loizidou, M., et al. (1993) Comparative studies between synthetic and natural zeolites for ammonium uptake. *J. Environ. Sci. Heal. A*, A28 (7): 1507–1518.
19. Watanabe, Y., Yamada, H., Tanaka, J., Komatsu, Y., and Moriyoshi, Y. (2004) Ammonium ion exchange of synthetic zeolites: The effect of their open-window

sizes, pore structures, and cation exchange capacities. *Sep. Sci. Technol.*, 39 (9): 2091–2104.

- 20. Zhu, B.Y. and Zhao, Z.G. (1996) *Chemical Base of Interface*; Press of Chemical Engineering: Beijing (in Chinese).
- 21. Tao, Z.Y. and Zhao, A.M. (1989) *Equilibrium of Ion Exchange and Dynamics*; Press of Atomic Energy: Beijing (in Chinese).
- 22. Komarowski, S. and Yu, Q. (1997) Ammonium ion removal from wastewater using Australian natural zeolite: Batch equilibrium and kinetic studies. *Environ. Technol.*, 18 (11): 1085–1097.
- 23. Nguyen, M.L. and Tanner, C.C. (1998) Ammonium removal from wastewaters using natural new zealand zeolites. *New Zeal. J. Agr. Res.*, 41 (3): 427–446.
- 24. Rozic, M., Cerjan-Stefanovic, S., et al. (2000) Ammoniacal nitrogen removal from water by treatment with clays and zeolites. *Water Res.*, 34 (14): 3675–3681.
- 25. Njoroge, B.N.K. and Mwamachi, S.G. (2004) Ammonia removal from an aqueous solution by the use of a natural zeolite. *J. Env. Eng. Sci.*, 3 (2): 147–154.
- 26. Bernal, M.P. and Lopez-Real, J.M. (1993) Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. *Bioresource Technol.*, 43 (1): 27–33.
- 27. Liu, C.H. and Lo, K.V. (2001) Ammonia removal from composting leachate using zeolite. I. Characterization of the zeolite. *J. Environ. Sci. Heal. A*, 36 (9): 1671–1688.
- 28. Kithome, M., Paul, J.W., Lavkulich, L.M., and Bomke, A.A. (1998) Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.*, 62 (3): 622–629.
- 29. Kithome, M., Paul, J.W., Lavkulich, L.M., and Bomke, A.A. (1999) Effect of pH on ammonium adsorption by natural zeolite clinoptilolite. *Commun. Soil. Sci. Plan.*, 30 (9–10): 1417–1430.
- 30. Lebedynets, M., Sprynskyy, M., Sakhnyuk, I., Zbytniewski, R., Golembiewski, R., and Buszewski, B. (2004) Adsorption of ammonium ions onto a natural zeolite: Transcarpathian clinoptilolite. *Adsorpt. Sci. Technol.*, 22 (9): 731–741.
- 31. Cai, H.L., et al. (1992) *Exploitation and Application of the Zeolite Ore in Jinyun*; Press of Geology: Beijing (in Chinese).
- 32. Ho, Y.S. (2004) Selection of optimum sorption isotherm. *Carbon*, 42 (10): 2115–2116.