

## Selective Adsorption of $\text{NH}_4^+$ and $\text{Cu}^{2+}$ on Korean Natural Zeolite in Their Dilute Solutions

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Received November 3, 1998

For investigating the effectiveness of Korean natural zeolite for removal of  $\text{NH}_4^+$  in waste waters containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$ , the adsorption of  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  by three Korean natural zeolite samples, which contained mordenite and/or clinoptilolite, was measured by adding solutions containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  or both at a concentration range from 1 to 7 mmol(+)/L of each cation. In the solutions, the zeolite samples adsorbed more amounts of  $\text{NH}_4^+$  than  $\text{Cu}^{2+}$ . By seven successive equilibrations, Korean natural zeolites adsorbed  $\text{NH}_4^+$  corresponding to 23~33% of those cation exchange capacity from the solution containing both  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  at 3 mmol(+)/L of each cation. Whereas, the corresponding adsorption of  $\text{Cu}^{2+}$  was 17-27% of the CEC. Korean natural zeolite exhibited selectivity for  $\text{NH}_4^+$  but not for  $\text{Cu}^{2+}$ . Nevertheless, it using as a soil amendment after removing of  $\text{NH}_4^+$  in waste waters should be carefully controlled on the application rate.

**Key words :** natural zeolite, cation adsorption selectivity, waste water, copper, clinoptilolite, mordenite.

Municipal waste water often contains a considerable amount of  $\text{NH}_4^+$  and creates an environmental problems. Removal of  $\text{NH}_4^+$  from waste water is difficult to solve. Takahashi<sup>1)</sup> reported that activated sludge process including flocculation and active carbon treatment was unable to remove  $\text{NH}_3\text{-N}$  present at concentrations of 25~32 ppm in waste water.

Zeolites are hydrated aluminum-silicate minerals in which the Al and Si tetrahedra are connected by the sharing of O to form a three-dimensional framework structure. This framework structure has interconnecting channels through which cations and water molecules can pass. The cations neutralize the negative charge on the zeolite created by the substitution of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  in tetrahedra. The amount of substitution in the tetrahedra determines CEC of the zeolite.<sup>2)</sup> Korean natural zeolite, which was formed by diagenesis of acidic tuffs in Miocene sediment, is deposited at Youngil Tertiary basin, in Kyung-pook. The amount of the zeolite deposit is estimated to be 14 million tons. The zeolite deposit contains clinoptilolite, mordenite and their mixtures as major minerals. About 120,000 tons are mined every year and most of them is used as a carrier of agricultural chemicals and an additive of organic fertilizers.<sup>3)</sup> The framework structure of clinoptilolite consists of interlinked 4- and 5-tetrahedral rings, creating a layer. Between these layers are open 8- and 10-tetrahedral ring channels. These channel rings have

approximately dimensions of 79 by 35 nm and 44 by 30 nm, respectively. These rings form the ion sieving channels, showing high affinity of adsorption for cation to pass easily through the rings.<sup>2)</sup> Natural zeolite, specifically clinoptilolite and mordenite have a high CEC and an affinity for  $\text{NH}_4^+$ .<sup>4,5)</sup> Therefore, Korean natural zeolites could be used as a good material for removal of  $\text{NH}_4^+$  in waste waters. If the zeolite exhibits high selectivity for  $\text{NH}_4^+$  but not for heavy metals likely to be present in waste water, it can be used for removal of  $\text{NH}_4^+$  and then can be applied to agricultural lands.

In the previous study<sup>6)</sup> on the adsorption of  $\text{NH}_4^+$  and  $\text{Zn}^{2+}$  in their dilute solutions, Korean natural zeolites exhibited a high selectivity for  $\text{NH}_4^+$  but not for  $\text{Zn}^{2+}$ . From the results, It was estimated that the zeolites could be used for removal of  $\text{NH}_4^+$  from municipal waste waters and the resultant  $\text{NH}_4^+$ -zeolites could be applied as a good  $\text{NH}_4$ -fertilizer or a good soil amendment without any excessive accumulation of  $\text{Zn}^{2+}$  in agricultural land. However, wastewaters also contain such heavy metals as Cu, Pb, Cd and Hg. Accordingly, the zeolites applied to agricultural land after waste water treatment should not adsorb heavy metals to dangerous level. There are some reports investigated the adsorption of heavy metals, Cu, Cd and Zn, by Korean natural zeolite.<sup>7,8,9)</sup> Nevertheless, those results could not be available for explaining the competitive adsorption of heavy metals and  $\text{NH}_4^+$  by the zeolite.

The object of this study is to investigate the selective adsorption of  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  by Korean natural zeolite and to evaluate the effectiveness for removal of  $\text{NH}_4^+$  over  $\text{Cu}^{2+}$  from waste waters containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$ .

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**Abbreviation:** CEC, cation exchange capacity.

## Materials and Methods

Hard zeolite samples 1 (light greenish white), 3 (light yellowish white) and 4 (white) used by Kang<sup>6)</sup> were chosen as samples for this study. The samples were numbered identically as being used in the his study for study-continuance. They were collected at Tertiary acidic tuffs<sup>10)</sup> in Woulsung-gun, Kyungpook, South Korea<sup>8)</sup>. All samples were crushed, air-dried and passed through a 0.25-mm sieve.

For identification of mineral species in the samples, <2, 2~20 and 20~250  $\mu\text{m}$  fractions were separated by repeating dispersion at about pH 10 with sonication and sedimentation. X-ray analysis was carried out for the whole and fractionated samples with random and parallel orientations using a Rigaku diffractometer (30 kV, 10 mA, Cu-K $\alpha$  radiation). The parallel-oriented samples were saturated with Mg<sup>2+</sup> or K<sup>+</sup>, and air-dried, glycerol-solvated or heated at 300 and 500°C.

Adsorption of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> was measured by adding a 10-ml portion of solution containing NH<sub>4</sub>Cl, CuCl<sub>2</sub> or both at concentration ranging from 1 to 7 mmol(+)/L of each cation to 0.25 g of the air-dried sample. After overnight shaking at 25°C, the supernatant was obtained by centrifugation and its pH and NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> concentrations were determined. The amounts of adsorbed NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> were calculated as the difference between the amounts of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> added and remained in the supernatant. The adsorption of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> was also measured by six successive equilibrations with a solution containing NH<sub>4</sub>Cl, CuCl<sub>2</sub> or both at a concentration of 3 mmol(+)/L of each cation.

In all the measurements, NH<sub>4</sub><sup>+</sup> was determined by colorimetry using indophenol biue method<sup>11)</sup> and Na, K, Mg, Ca and Cu by atomic absorption spectrophotometry. The amounts of the cations are expressed as mmol(+) per gram of the oven-dry sample, assuming that Cu<sup>2+</sup> is only the form existed in the solution.

## Results and Discussion

**Characterization of zeolite samples.** Two zeolite species, clinoptilolite and mordenite, were identified by X-ray analysis (Table 1). The sum of exchangeable cations and CEC of whole samples (Table 2) were lower than 2.20 mmol(+)/g calculated from the chemical formulas of clinoptilolite Na(AlO<sub>2</sub>)(SiO<sub>2</sub>)<sub>5</sub>·4H<sub>2</sub>O<sup>12)</sup> and mordenite Na(AlO<sub>2</sub>)(SiO<sub>2</sub>)<sub>5</sub>·3H<sub>2</sub>O,<sup>12)</sup> respectively. Vermiculite and/or smectite were present in the finer fractions, particularly the fraction below 2  $\mu\text{m}$  of all samples. Feldspar was present in the 20~250  $\mu\text{m}$  fractions of sample 4 and contributed to the reduction of CEC.

**Adsorption of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> by zeolite samples.** As illustrated for samples 1 in Fig. 1, the adsorption of NH<sub>4</sub><sup>+</sup> was greater than that of Cu<sup>2+</sup> for samples 1 at the solution concentrations from 1 to 7 mmol(+)/L and this difference was greater at the higher concentrations. The adsorption of

**Table 1. Particle-size and mineral analysis of three Korean zeolite samples**

| Sample No. | Fraction content (%) <sup>*</sup> |                    |                      | Minerals in whole sample |                          |
|------------|-----------------------------------|--------------------|----------------------|--------------------------|--------------------------|
|            | <2 $\mu\text{m}$                  | 2~20 $\mu\text{m}$ | 20~250 $\mu\text{m}$ | zeolite <sup>**</sup>    | accessory <sup>***</sup> |
| 1          | 17                                | 5                  | 77                   | C                        | St                       |
| 3          | 23                                | 6                  | 70                   | C>M                      | St                       |
| 4          | 14                                | 4                  | 81                   | M>C                      | Fd, Vt, St, Mc           |

<sup>\*</sup>quoted from Kang<sup>4)</sup>

<sup>\*\*</sup>C=clinoptilolite, M=mordenite

<sup>\*\*\*</sup>Fd=feldspar, Mc=mica, St=smectite, Vt=vermiculate. Based on the analyses of the whole and fractionated samples.

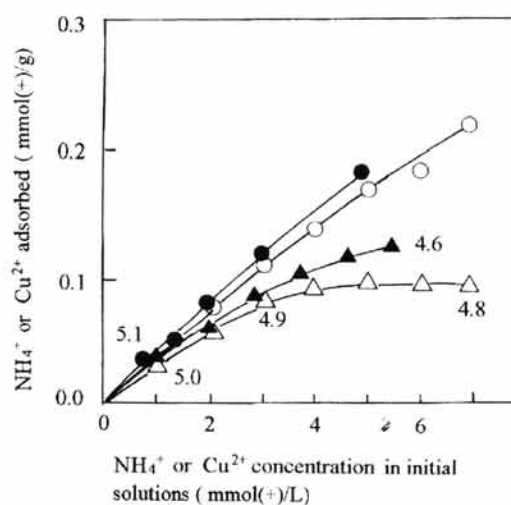
**Table 2. Exchangeable cations and CEC of three Korean zeolite samples<sup>\*</sup>**

| Sample No. | Exchangeable cation [mmol(+)/g] <sup>**</sup> |                |                  |                  |      | CEC <sup>***</sup> [mmol(+)/g] |
|------------|---|----------------|------------------|------------------|------|--------------------------------|
|            | Na <sup>+</sup>                               | K <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | sum  |                                |
| 1          | 0.21  | 0.40           | 0.40             | 1.07             | 2.08 | 1.94                           |
| 3          | 0.41  | 0.28           | 0.43             | 0.69             | 1.81 | 1.72                           |
| 4          | 0.30  | 0.34           | 0.13             | 0.53             | 1.30 | 1.16                           |

<sup>\*</sup>Quoted from Kang<sup>4)</sup>.

<sup>\*\*</sup>Determined by repeating centrifuge washing zeolite sample with 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH=7.0).

<sup>\*\*\*</sup>Determined by extracting NH<sub>4</sub><sup>+</sup>-saturated sample with 1 M KCl (pH=7).



**Fig. 1. Adsorption of NH<sub>4</sub><sup>+</sup> (circles) and Cu<sup>2+</sup> (triangle) by samples 1 from the solutions containing NH<sub>4</sub><sup>+</sup> or Cu<sup>2+</sup> (closed symbols) and those containing both NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> (open symbols). The numbers indicate pH values of equilibrated solutions.**

NH<sub>4</sub><sup>+</sup> increased sharply with increasing concentration of NH<sub>4</sub><sup>+</sup>. The adsorption of Cu<sup>2+</sup> also increased with increasing Cu<sup>2+</sup> concentration, but the increase was smaller. Amounts of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> adsorption among all samples were little different, showing no correlation with the values of their CEC (the results of sample 3 and 4 were not shown). This could be due to using NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> solutions of very low concentration to zeolite samples having very high amounts of exchangeable cations. The concentrations of NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> used in this experiment, 1~7 mmol/L, were not enough to extract the exchangeable cation carried

by samples, especially samples 1 and 3 (Table 2). In the solutions of  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  mixed by the equivalent ratio of 1 to 1, the adsorption of  $\text{NH}_4^+$  was inhibited by the presence of  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$  also by the presence of  $\text{NH}_4^+$ , decreasing the adsorption of each of them. Such inhibition was higher with  $\text{Cu}^{2+}$  than with  $\text{NH}_4^+$ . The ion activity products for  $\text{Cu}(\text{OH})_2$  calculated from the equilibrium pH (5.1–4.5) and  $\text{Cu}^{2+}$  concentration (1–7 mmol(+)/L) were in the range from  $5 \times 10^{-23}$  to  $3.5 \times 10^{-20}$ , indicating that all equilibrium solutions were unsaturated with respect to  $\text{Cu}(\text{OH})_2$  whose solubility product was reported to be  $10^{-19.13}$ .

Fig. 2 shows the difference in the removal of  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  from the solutions containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  at the equivalent ratio of 1 to 1 by the three zeolite samples. The removal percentage of  $\text{NH}_4^+$  decreased with increasing concentration of added  $\text{NH}_4^+$  but was higher than 75% at all the concentration ranging from 1 to 7 mmol(+)/L. There was little difference in the removal percentage of  $\text{NH}_4^+$  among the three samples. On other hand, the removal percentage of  $\text{Cu}^{2+}$  was much lower than that of  $\text{NH}_4^+$  and decreased sharply with increasing  $\text{Cu}^{2+}$  concentration. In the solution of the concentration of 7 mmol(+)/L, the removal percentage of  $\text{Cu}^{2+}$  was in the range from 35 to 40% compared with that of  $\text{NH}_4^+$ . The difference in the  $\text{Cu}^{2+}$  removal between the samples was not great. Kang<sup>6)</sup> reported that same samples in this study removed  $\text{NH}_4^+$  over 85% and  $\text{Zn}^{2+}$  in the range from 22 to 40% at the solution of 7 mmol(+)/L. By comparing with such results, the three samples were estimated to adsorb  $\text{Cu}^{2+}$  more slightly than  $\text{Zn}^{2+}$ . The sequence of ion removal ratio by the three zeolites could be  $\text{NH}_4^+ \gg \text{Cu}^{2+} \geq \text{Zn}^{2+}$ .

For investigating the capacity of successive treatment of

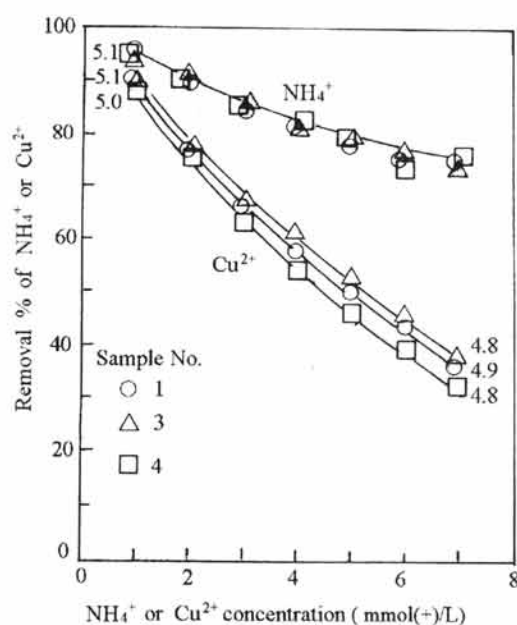


Fig. 2. Removal percentage of  $\text{NH}_4^+$  or  $\text{Cu}^{2+}$  by zeolite samples from the solutions containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$ . The numbers indicate pH values of equilibrated solutions.

solution. The equivalent fractions of exchange cation on zeolite and in solution are defined as followed<sup>12)</sup>:

$$\begin{aligned} \text{NH}_4(\text{R}) \text{ or } \text{Cu}(\text{S}) &= \frac{\text{equivalents of exchanging } \text{NH}_4^+ \text{ or } \text{Cu}^{2+}}{\text{total equivalents of cations on the zeolite}} \\ &= \frac{\text{equivalents of exchanging } \text{NH}_4^+ \text{ or } \text{Cu}^{2+}}{\text{CEC}} \end{aligned} \quad (1-1)$$

$$\begin{aligned} \text{NH}_4(\text{S}) \text{ or } \text{Cu}(\text{S}) &= \frac{\text{equivalents of remaining } \text{NH}_4^+ \text{ or } \text{Cu}^{2+} \text{ in solution}}{\text{equivalents of all cations in solution}} \end{aligned} \quad (1-2)$$

where solution in equation 1–2 is equilibrium solution, all cations in solution are remaining  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  and extracted exchangeable cations after equilibrium. CEC in equation 1-1 can be changed to the mean values of CEC and the sum of exchangeable cations, 2.01, 1.77 and 1.23 mmol(+)/g for samples 1, 3 and 4, respectively (Table 2), for compensating the difference between values of CEC and sum of exchangeable cations.

Fig. 4 shows plots of equivalent fractions calculated from the measurement in Fig. 3. The diagonal line on the plot represents the  $\text{NH}_4(\text{R})\text{-NH}_4(\text{S})$  or  $\text{Cu}(\text{R})\text{-Cu}(\text{S})$  relation that would be expected when all exchange sites have no specific selectivity for all the cations involved. From this figure, the  $\text{NH}_4(\text{R})\text{-NH}_4(\text{S})$  curves above the diagonal line indicate that the samples have selectivity of  $\text{NH}_4^+$ , whereas the  $\text{Cu}(\text{R})\text{-Cu}(\text{S})$  curves plotted below the diagonal line indicate that the samples had no selectivity for  $\text{Cu}^{2+}$ . In this  $\text{NH}_4^+\text{-Cu}^{2+}$  dilute solution system (Fig. 4), the proportion

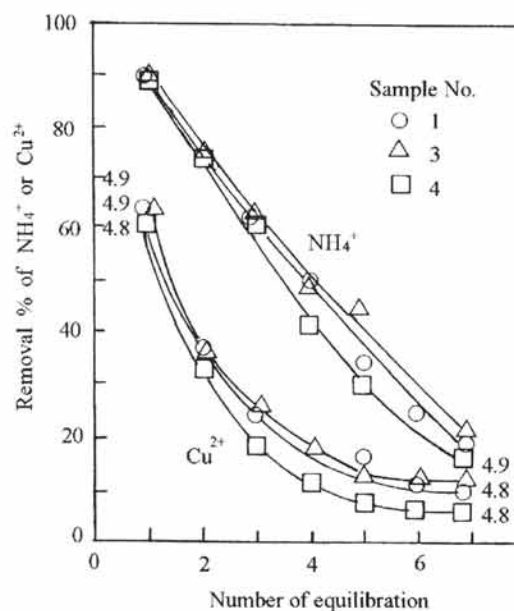


Fig. 3. Removal percentage of  $\text{NH}_4^+$  or  $\text{Cu}^{2+}$  by zeolite samples in seven successive equilibrations with the solution containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  each at a concentration of 3 mmol(+)/L.

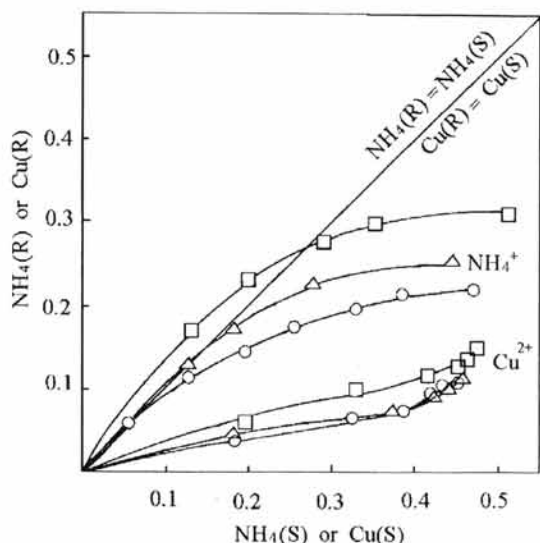


Fig. 4. Adsorption equilibria for  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  by zeolite samples in seven successive equilibrations with the solution containing  $\text{NH}_4^+$  and  $\text{Cu}^{2+}$  each at a concentration of 3 mmol(+)/L. See Fig. 3. for legend.

of  $\text{NH}_4^+$ -selective sites of all exchange sites was shown to be about 27, 13 and 7% for samples 4, 3 and 1, respectively. The proportion is much smaller than the proportion corresponding for same samples 4, 3 and 1, about 45, 32 and 18%, in  $\text{NH}_4^+$ - $\text{Zn}^{2+}$  dilute system by Kang.<sup>6)</sup> Additionally, these proportions related with the major mineral species of samples explain that mordenite has a larger number of  $\text{NH}_4^+$ -selective sites than clinoptilolite.

Conclusively, the three zeolite samples exhibit higher selectivity for  $\text{NH}_4^+$  than for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The sequence of the adsorption of cations by the samples is  $\text{Zn}^{2+} \leq \text{Cu}^{2+} \ll \text{NH}_4^+$ . Retention of  $\text{NH}_4^+$  by mordenite in terms of CEC, is greater than clinoptilolite; retention of  $\text{Cu}^{2+}$  is fairly low with similarity between two minerals. The Korean natural zeolites could be used for removal of  $\text{NH}_4^+$  from municipal waste water and the zeolites used in this way can be applied to agricultural land on the condition of the application rate free from contaminating soil with heavy metals,

which will be adsorbed on zeolite even by small amounts.

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