J. Korean Agric. Chem. Soc.
한국농화학회지 32(4), 386~392(1989)

Characterization of NH_4^+ and Zn^{2+} Adsorption by Korean Natural Zeolites.

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韓國産 天然 제오라이트의 암모늄과 아연이온의 吸着특성

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초 록

4 種類의 韓國産 天然제오라이트를 使用하여 $1\sim7\times10^{-3}$N 濃度의 NH_4^+, Zn^{2+} 및 그것들의 混合溶液內에서 NH_4^+과 Zn^{2+}의 吸着實驗을 하였다. 實驗에 使用된 제오라이트의 主鑛物은 mordenite, clinoptilolite, mordenite를 含有한 clinoptilolite 및 clinoptlolite를 含有한 mordenite였다. 모든 시료에서 Zn^{2+}에 比해 NH_4^+이 많이 吸着되었고 그것들의 吸着量은 高濃度에서 감소하는 경향이었다. 그러나 그 감소의 정도는 NH_4^+은 경미한 반면 Zn^{2+}은 심하였다. Zn^{2+}의 吸着量은 Zn^{2+}의 단일 吸着時에 比해 NH_4^+이 공존할 때 감소하였으나 NH_4^+의 吸着은 Zn^{2+}에 영향을 받지 않았다. 시료간 Zn^{2+}에 대한 NH_4^+의 選擇性은 mordenite>clinoptilolite를 含有한 mordenite>clinoptilolite>mordenite를 含有한 clinoptilolite 순으로 높았다. 3×10^{-3}N의 1 : 1 NH_4Cl-$ZnCl_2$ 溶液으로 연속 6회 세척하였을 때 제오라이트에 의한 NH_4^+ 총 吸着量은 43.7~50.4me/100g이었으며, Zn^{2+}의 총 흡착량은 6.6~17.0me/100g이었다.

이상의 結果로부터 mordenite와 clinoptilolite 특히 mordenite는 도시폐수중에 含有된 NH_4^+의 除去에 효과적일 것으로 사료되며 도시폐수에 처리된 제오라이트는 肥料資源이 될 수 있을 것으로 추정된다.

Introduction

Municipal wastewater in Korea contains a considerable amount of NH_4^+, which should be removed for preventing enviromental pollution[1]. However, the removal of NH_4^+ is difficult even when the most effective activated sludge process is applied[2]. Many scientists also have studied the utilization of municipal wastewater for irrigation, where NH_4^+ in wastewater can be a source of nitrogen for crops[3,4]. However, the continuous irrigation of wastewater containing excess NH_4^+ to agricultural lands could lead to the environmental hazard, because a part of NH_4^+ is transformed into NO_3^- by microorganisms and leached out into the ground water, posing a public health problem[5].

Municipal wastewater can also contain a considerable amount of heavy metals[1,6~8]. Heavy metals such as Zn, Cu, Mo, Mn, and Fe are essential plant nutrients, but their excess causes toxicity to plants[9]. Zeolites such as mordenite and clinoptilolite can be used for removal of NH_4^+ from wastewater owing to their high CEC and selective adsorption for NH_4^+[10~12]. If zeolites adsorb NH_4^+ but not much heavy metals, zeolites treated with wastewater can be used for soil amendment. Some scientists have

Received October 24
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demonstrated that clinoptilolite effectively removes NH_4^+ from wastewater[13~15].

The object of this study is to examine the selective adsorption of NH_4^+ and Zn^{2+} by four Korean zeolite samples and to evaluate their effectiveness for removal of NH_4^+ from wastewater.

Materials and Methods

Zeolite samples

Four Korean zeolite samples, No. 1 to 4 were used in this study. No. 1 and 3 samples were collected from zeolite tuff in Young-il, Kyungpook. No. 2 and 4 samples were provided from Wangpyo Chemical Company and Yangpook Zeolite Company in Kyungpook, respectively. All samples were air-dried, crushed, and passed through a 0.25mm sieve.

For identification of mineral species in the samples, $<2\mu m$, $2\sim20\mu m$, and $20\sim250\mu m$ fractions were separated after H_2O_2-treatment(5g sample/1,000ml water) by repeating dispersion at about pH 10 with sonication and sedimentation. The dispersed $<2\mu m$ and $2\sim20\mu m$ fractions were flocculated by adding a saturated NaCl solution, and the flocculated fraction and the collected $20\sim250\mu m$ fraction were saturated with Mg or K by washing 0.5M-$MgCl_2$ or 1M-KCl. Then, they were selectively washed with water and acetone, dried, and weighed. The whole and fractionated samples were ground and x-rayed. Some of the fractionated samples were x-rayed after parallel orientation. The Mg-saturated samples were air-dried and glycerol-solvated. The K-saturated samples air-dried and heated at 300 and 550°C. All samples were scanned from 3 to 40°2θ using a scan speed of 2°2θ/min on a Rigaku x-ray diffractometer with Cu-target. Identification and approximate quantitative estimation of minerals were made on the basis of the relative intensities of their characteristic x-ray diffraction peaks. The identification results were also ascertained by observation of samples with transmission electron microscopy.

Adsorption experiments

The adsorption of NH_4^+ or Zn^{2+} was measured by adding 10ml portion of the solution containing NH_4Cl or $ZnCl_2$ at a concentration ranging 1×10^{-3}N to 7×10^{-3}N, to 0.25g of the air-dried sample. The adsorption of NH_4^+ and Zn^{2+} was also measured in the solutions in which the equivalent ratio of NH_4^+ and Zn^{2+} was unity(1 : 1 NH_4Cl-$ZnCl_2$ solutions). The sample with the solution was shaken overnight on a reciprocating shaker at 25°C. The supernatant was obtained after centrifugation, and its pH and NH_4^+ and Zn^{2+} concentration were measured. The amounts of NH_4^+ and Zn^{2+} adsorbed were calculated as a difference between their initial concentration and equilibrium concentration. A cumulative adsorption of NH_4^+ and Zn^{2+} was also measured by successive equilibrations with 3×10^{-3}N 1 : 1 NH_4Cl-$ZnCl_2$. The amount of the solution remaining with sample after centrifugation at each equilibration was determined by weighing and was taken into consideration in the calculation of the amounts of adsorbed NH_4^+ and Zn^{2+}.

Exchangeable cations and CEC experiments

Exchangeable cations present in the whole sample were determined by extraction with 1 M-CH_3COONH_4(pH=7). Their CEC determination was performed by extracting NH_4^+ with 1 M-KCl.

In all the measurements NH_4^+ was determined by colorimetry using phenol-sodium hypochlorite[16] and Zn^{2+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+ by atomic absorption spectrophotometry.

All results were expressed on the oven dry basis.

Results and Discussion

Characterization of zeolite samples

Table 1 shows the particle distribution and their mineral compositions in this experiment.

The ratios of particle fractions of <2, 2~20, and 20~250μm in samples were 14 to 23, 4 to 7, and 70 to 81%, respectively. Dominant zeolite species identified in samples No. 1, 2, 3, and 4 were clinoptilolite, mordenite, clinoptilolite with mordenite, and mordenite with clinoptilolite, respectively. All samples contained some smectite and sample No. 2 and 4 contained some feldspar and vermiculite. A trace amount of mineral detected was quartz in samples No. 1 and 3. The CEC of samples No. 1, 2, 3, and 4 were 194, 120, 172, and 116meq./100g (Table 2).

Table 1. The particle distribution and their mineral compositions of Korean natural zeolites used in this experiment

Sample number	<2μm fraction		2~20μm fraction		20~250μm fraction		Whole sample	
	Content (%)	M. S.*	Content (%)	M. S.	Content (%)	M. S.*	Major M. S.*	Minor M.S.*
1	17	C>SM	5	C	77	C⟫Sm	C	Sm⟫Q
2	20	M≫V	7	M≫V	73	M≫F>V	M≫F	Sm>V
3	23	C>M, Sm	6	C>M⟫Sm	70	C>M≫Sm	C>M	Sm⟫Q
4	14	V>Sm>M, C>F	4	M>V>C>F	81	M>C≫F>V	M>C≫F	V>Sm

* Abbreviation of mineral species
C : Clinoptilolite, M : Mordenite, Sm : Smectite, V : Vermiculite, Q : Quartz and F : Feldspar

Table 2. Exchangeable cations and CEC of zeolite samples(me/100g)

Sample number	Exchangeable cation					CEC
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sum	
1	21	40	107	40	208	194
2	33	9	58	10	110	120
3	41	28	69	43	181	172
4	30	34	53	13	130	116

Adsorption of NH_4^+ and Zn^{2+} by zeolite samples

Fig. 1 shows the plots of the amounts of adsorbed NH_4^+ and Zn^{2+} against the initial concentrations of NH_4^+ and Zn^{2+} for four zeolite samples. The adsorption of NH_4^+ was greater than that of Zn^{2+} for all samples at the concentrations of the added solutions ranging from 1 to 7×10^{-3}N and this difference was greater at the higher concentrations. The adsorption of NH_4^+ increased almost linearly with increasing concentration of NH_4^+ and was not affected by Zn^{2+} which was present at the equivalent ratio of 1 to 1 in the added solution. The adsorption of Zn^{2+} also increased with increasing Zn^{2+} concentration, but the increase was smaller at the higher concentrations and the amount of adsorbed Zn^{2+} was decreased by the presence of NH_4^+. The results indicate that NH_4^+ is more selectively adsorbed than Zn^{2+}.

The ion activity product for $Zn(OH)_2$ was calculated from the Zn^{2+} concentration and the pH at each equilibrium. The calculated values ($1.75\times10^{-19.6}$ to $2.55\times10^{-22.8}$) showed that in any equilibrium the solution was unsaturated with respect to $Zn(OH)_2$, whose solubility product was reported to be in the range from 10^{-16} to 10^{-17} [17].

Fig. 2 shows the relation between the adsorption ratio of NH_4^+ and Zn^{2+}(%) and the NH_4^+ and Zn^{2+} concentrations of the added solution. The adsorption percentage of NH_4^+ decreased with increasing concentration of added NH_4^+ but was higher than 85 at all the concentrations ranging from 1 to 7×10^{-3}N. There was not much difference in the adsorption percent-

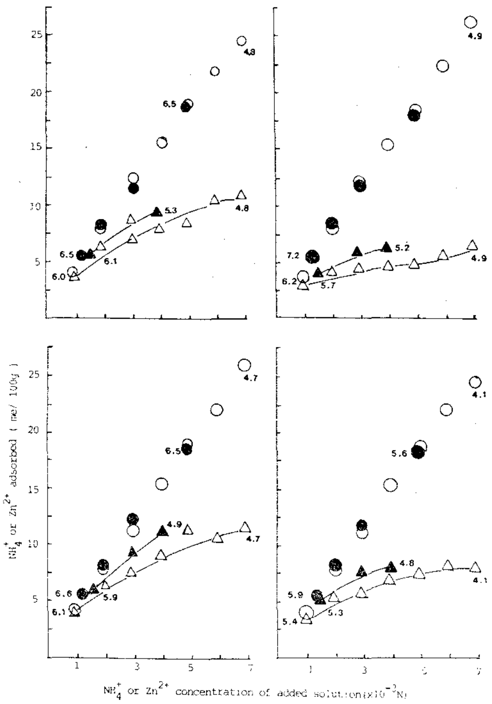

Fig. 1. Adsorption of NH_4^+ (circles) and Zn^{2+} (triangles) by zeolite samples from the solutions containing NH_4Cl or $ZnCl_2$ (closed symbols) and 1 : 1 NH_4Cl-$ZnCl_2$ (open symbols). The numbers indicate the pH values of equilibration solutions.

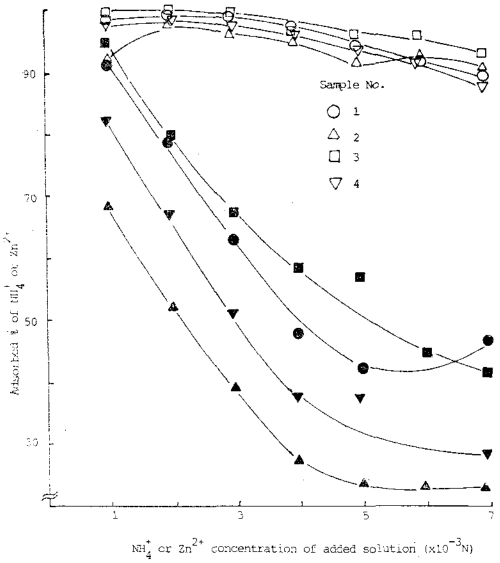

Fig. 2. Adsorbed percentage of NH_4^+ (open symbols) and Zn^{2+} (closed symbols) by zeolite samples from the solution containing 1 : 1 NH_4Cl-$ZnCl_2$

age of NH_4^+ between the four zeolite samples. On the other hand, the adsorption percentage of Zn^{2+} was much lower than that of NH_4^+ and decreased with increasing Zn^{2+} concentration, particularly in the range from 1 to 4×10^{-3}N. The difference in the Zn^{2+} adsorption between the samples was greater than that in the NH_4^+ adsorption and the samples with high mordenite contents exhibit a low Zn^{2+} adsorption.

Fig. 3 shows the equivalent fraction of adsorbed NH_4^+ in adsorbed NH_4^+ plus Zn^{2+} when the sample was equilibrated with different concentrations of 1 : 1 NH_4Cl-$ZnCl_2$. It increased with increasing concentration and its magnitude was highest for sample No. 2(mordenite) followed by sample No. 4 (mordenite> clinoptilolite) and No. 1 (clinoptilolite) and lowest sample for No. 3 (clinoptilolite> mordenite).

The adsorption of NH_4^+ and Zn^{2+} by the whole sample may, however, be affected by the presence of other mineral species such as smectite and vermiculite(Table 1). The 20～250μm fractions separated from the whole sample were found to contain much smaller amounts of vermiculite of smectite. Therefore, the adsorption of NH_4^+ and Zn^{2+} by the whole sample was compared with that of NH_4^+ and Zn^{2+} by the 20～250μm fraction. Table 3 shows that the adsorption of NH_4^+ and Zn^{2+} was very similar between the whole sample and the 20～250μm

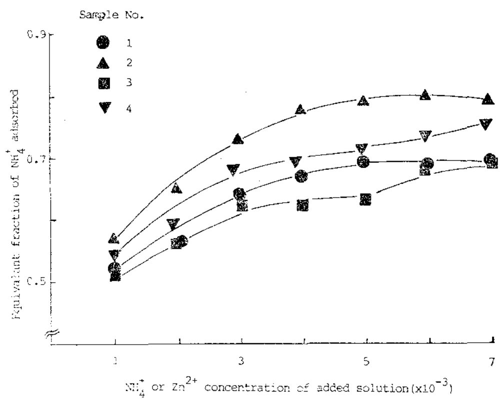

Fig. 3. Equivalent fraction of NH_4^+ and Zn^{2+} adsorbed by zeolite samples from 1 : 1 NH_4Cl-$ZnCl_2$ solutions

Table 3. The amounts of NH_4^+ and Zn^{2+} adsored by the whole samples and the 20～250μm fractions from 1 : 1 NH_4Cl-$ZnCl_2$ of 6×10^{-3}N

Sample number	Whole sample			20～250μm fraction		
	NH_4^+ (me/100g)	Zn^{2+} (me/100g)	Ef NH_4^+*	NH_4^+ (me/100g)	Zn^{2+} (me/100g)	$EfNH_4$
1	22	10	0.69	22	11	0.67
2	22	6	0.79	21	5	0.81
3	23	11	0.68	24	13	0.65
4	22	8	0.73	22	8	0.73

* $EfNH_4$: NH_4^+ adsorbed(me/100g)/NH_4^+ adsorbed(me/100g)+Zn^{2+} adsorbed(me/100g).

fraction. The result indicates that the observed higher selectivity for NH_4^+ over Zn^{2+} is attributed to zeolites and that mordenite has a higher selectivity for NH_4^+ than clinoptilolite.

Fig. 4 shows the relation between the adsorption rations of NH_4^+ and Zn^{2+} and the number of successive equilibrations with 3×10^{-3}N 1 : 1 NH_4Cl-$ZnCl_2$ solutions. The adsorption ratios of Zn^{2+} was lower than that of NH_4^+ and more rapidly decreased with increasing number of equilibration. The adsorption ratio at the 4th equilibration was lower than 15% for Zn^{2+} but was 45 to 65% for NH_4^+. The Zn adsorption by samples No. 1, 2, 3, and 4 after the 6th washing with 3×10^{-3}N 1 : 1NH_4Cl-$ZnCl_2$ amounted to 17.0, 6.6, 16.0, and 11.1 me/100 g, respectively, whereas amounts of NH_4^+ adsorbed by the same samples were 50.4, 43.7, 54.7, and 49.4 me/100g and the values were 3.0, 6.0, 3.4, and 4.5 fold of those of Zn^{2+} adsorbed, respectively(Fig. 5). Zeolites such as clinoptilolite and mordenite have higher selectivities for monovalent cations than divalent

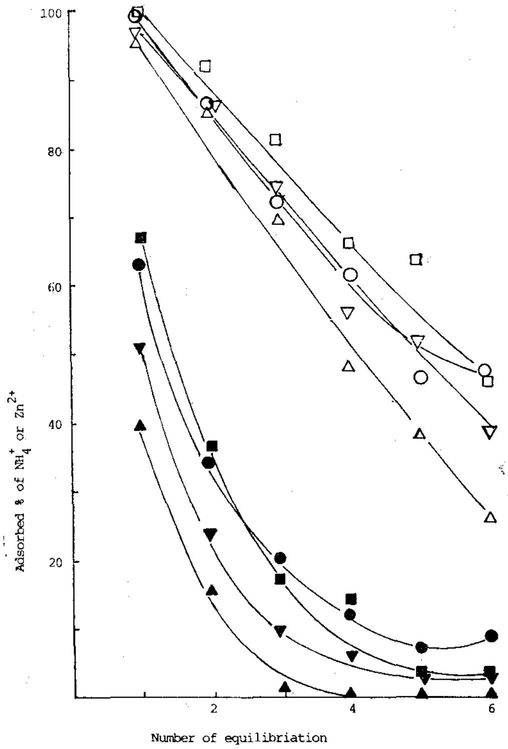

Fig. 4. Adsorbed percentage of NH_4^+ and Zn^{2+} by zeolite samples in six successive equilibrations with 1 : 1 NH_4Cl-$ZnCl_2$ solution of 3×10^{-3}N

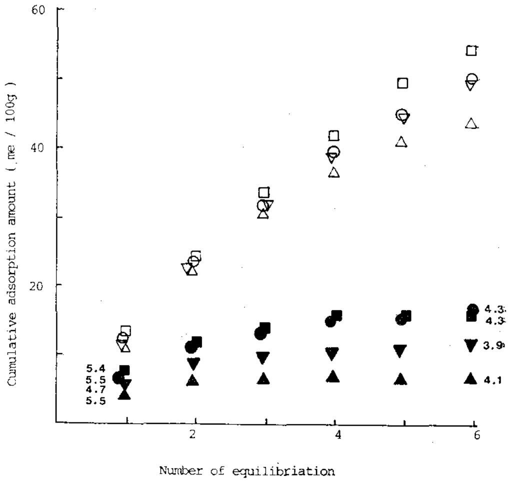

Fig. 5. Cumulative amounts of NH_4^+ and Zn^{2+} adsorbed by zeolite samples in six successive equilibrations with 1 : 1 NH_4Cl-$ZnCl_2$ solution of 3×10^{-3}N. The numbers indicate the pH values of equilibration solutions at each washing time. See Fig. 2 for legend.

cations and cations with smaller hydration radii than those with higher hydration rad.ii[10] The CEC of a zeolite(24.3 me/100g) determined by saturating with Mg^{2+} was much smaller than that(108.3me/100g) determined by saturating with NH_4^+[10].

The above results suggest that zeolites, especially mordenite, can be used for removal of NH_4^+ from wastewater. For example, Lee[1] investigated the extent of pollution of Kemho river and its branches running through Taegu city in Korea from December in 1982 to November in 1983. The river water contained NH_4^+ in the range from 10.2 to 32.2ppm(6×10^{-4}N to 1.8×10^{-3}N) and Zn^{2+} in the range from 1.5 to 3.0ppm(4.6×10^{-5}N to 9.2×10^{-5}N). According to the present results, zeolite can be used for removal of NH_4^+ and Zn^{2+} contained in this river water and the resulting zeolite containing NH_4^+ and Zn^{2+} can be used on agricultural land as a soil amendment, though appropriate methods for the treatment awaits further study.

Abstract

The adsorption of NH_4^+ and Zn^{2+} by four Korean zeolites, the major species of which are clinoptilolite, clinoptilolite with mordenite, mordenite with clinoptilolite, and mordenite was measured in different concentrations of solutions of NH_4^+ and Zn^{2+}, and their mixtures.

The adsorption of NH_4^+ was greater than that Zn^{2+} for all samples at the concentrations of the added solutions from 1 to 7×10^{-3}N and this difference was greater at the higher concentrations. Also, Zn^{2+} adsorption by samples was decreased by the presence of NH_4^+, but that of NH_4^+ by the presence of Zn^{2+} was not. The extent of NH_4^+ selectivity among samples was increased in order of clinoptilolite with mordenite < clinoptilolite < mordenite with clinoplolite < mordenite. Cumulative amounts of NH_4^+ adsorbed by six successive equilibrations with the solution containing both NH_4^+ and Zn^{2+} each at a concentration of 3×10^{-3}N were in range from 43.7 to 50.4 me/100g, whereas those amounts of Zn^{2+} were in the range from 6.6 to 17.0 me/100g.

It was suggested from these results that mordenite and clinoptilolite, particularly the former, can be used for removal of NH_4^+ from municipal wastewater and those zeolites treated with wastewater can be applied to agricultural land.

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