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Ion Exchange Behavior of Natural Zeolites in Distilled Water, Hydrochloric Acid, and Ammonium Chloride Solution

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ABSTRACT

This study presents basic research on the use of natural zeolites for the removal of ammonium ions from aqueous solutions. Three natural zeolites from Shimane, Japan, used in this study are shown to contain varying amounts of clinoptilolite and mordenite. The chemical behavior of these natural zeolites was investigated in distilled water, hydrochloric acid, and ammonium chloride solution. The amount of ammonium ions adsorbed by these zeolites was measured using an electrode specific to ammonium ion. The results were compared with published adsorption

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values for other zeolites. Hydrogen ions displaced the exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) on the natural zeolites in distilled water and hydrochloric acid. With the decrease in equilibrium pH, the amounts of dissolved silica and alumina increased. This behavior indicates that the structures of the zeolites are damaged under this condition. Ammonium ions were preferentially adsorbed on the natural zeolites in ammonium chloride solution. The amount of ammonium ions adsorbed quantitatively corresponded to the theoretically expected amount at high ammonium concentrations. This result indicates that ammonium adsorption occurs by ion exchange of ammonium ions with Na^+, K^+, Mg^{2+}, and Ca^{2+} in cation exchange sites on zeolites. The order of selectivity of ammonium ions for other cations on the zeolites was $Na^+ \gg K^+ > Ca^{2+} > Mg^{2+}$. Ammonium adsorption was the highest in the zeolite containing the highest proportion of clinoptilolite of the three natural zeolites. The maximum adsorption was 1.28 mmol/g.

INTRODUCTION

In recent years, wastewaters are discharged after the primary process of flocculation and the sedimentation, and secondary process of biological treatment. Increasing levels of ammonium and phosphate are the main factors of eutrophication in river or lakes. These levels are now being controlled by legislation on discharge limits in many countries. The increase in ammonium and phosphate levels causes increases in biochemical oxygen demand and chemical oxygen demand in many rivers and lakes. Therefore a process to further reduce the quantity of ammonium and phosphate levels is needed. To achieve better wastewater treatment, the use of activated carbon, which is comparatively expensive, is proposed.

Natural zeolites have been proposed as an alternative to activated carbon, and can also be used as a pretreatment material before biological processing to ensure a constant concentration feed to a biological treatment plant. Clinoptilolite and mordenite are the main minerals of natural zeolites found in abundance in many locations.[1,2] These minerals consist of three-dimensional open-framework structures consisting of AlO_4 and SiO_4 tetrahedra linked together by oxygen sharing and contain channels and cavities in which cations and water molecules can diffuse as well as ion-exchange sites. These are widely used as low-cost ion exchangers.[3,4]

The chemical behavior of natural zeolites in aqueous solutions has been investigated.[5,6] The use of natural zeolites for removal of ammonium in wastewater treatment has also been reviewed by a number of researchers.[7–12]

The method of regeneration of zeolites has also been discussed.[3] Zeolites saturated with ammoniacal nitrogen have been continuously regenerated in biological processes without the use of chemical regenerants such as NaCl.[9] The adsorption behavior of treated zeolites has also been described.[13–16] For example, it has been shown that ammonium ions can be stripped from zeolite using 2 M sodium chloride solution.[17] The ion exchange selectivity of zeolite is related to its ionic charge and ion radius. Zeolites also have the ability to absorb ammonium ions in the low-concentration range that is often observed in rivers or lakes.[18]

In the present study, the chemical behavior of three natural zeolites from Shimane, Japan, was investigated in distilled water and hydrochloric acid. Ammonium adsorption by these zeolites in ammonium chloride solution was also investigated and the results obtained were compared with published adsorption values for other zeolites.

EXPERIMENTAL METHOD

Materials

Three types of natural zeolites mined from Shimane, Japan, were used in this study. Two of the three natural zeolites (CLI1 and CLI2) consisted mainly of clinoptilolite, and the remaining one (MOR3) consisted mainly of mordenite. They were all sieved to below 50 μm particle size before use.

Characterization

Mineral identification was carried out by the powder X-ray diffraction (XRD) with CuKα radiation (RIGAKU RINT 2200). The zeolites were characterized by scanning electron microscopy (SEM) (JEOL S-5500). The chemical compositions of the zeolites were determined by inductively coupled plasma spectroscopy (ICP) (SEIKO HVR 1700).

A photomultiplier tube was used as the detector for ICP. The operating conditions for ICP are given in Table 1. The solutions for ICP were prepared as follows: for Si and Al, 50 mg of sample was mixed with Na_2CO_3 and H_3BO_3 powders. The mixture was dissolved by addition of HCl solution, and pure water was added to the solution to a final volume of 100 mL. For Na, K, Ca, and Mg, 50 mg of sample was dissolved in HF and H_2SO_4 solutions. After the solution was evaporated, the dried residue was dissolved in HCl solution with heating, and pure water was added to the solution to a final volume of

Table 1. Operating conditions for ICP.

Frequency	27.12 MHz
RF power	1.3 kW
Plasma gas	16 L min^{-1}
Auxiliary gas	0.5 L min^{-1}
Carrier gas	1.0 L min^{-1}
Observation height in plasma	18.0 mm
Analytical lines:	
Si: 251.611 nm	Al: 396.152 nm
Na: 588.955 nm	K: 766.490 nm
Ca: 393.366 nm	Mg: 279.553 nm

100 mL. The detection limits of ICP were 0.002 ppm for Na and Si, 0.004 ppm for Al, 0.00004 ppm for Ca and Mg, and 0.030 ppm for K.

Adsorption Experiment

For ammonium adsorption experiments, 30.0 mL of each solution containing different proportions of NH_4Cl (10^{-4}–10^{-1}M) was added to 0.1 g of air-dried zeolite samples in stoppered polyethylene tubes. The tubes were shaken at 25°C for 7 days. The mixture was separated by centrifugation at 15000 rpm for 30 minutes and then filtered with a 0.45 μm membrane filter (Millipore, 0.45 μm HA-type).

The ion concentration of the filtered solution was determined by ICP (SEIKO-SPS4000). pH was determined using a pH meter (Toa Dempa Kogyo HM-60V). Adsorption experiments in distilled water and hydrochloric acid (10^{-5}–10^{-1}M) were also carried out using the same experimental method. The ammonium concentration of the filtered solution was determined using an ammonium ion-specific electrode (Toa Dempa Kogyo IM-20B, ammonia electrode Ae-235). After the adsorption experiments, XRD using CuKα radiation was used to examine the crystal structure.

RESULTS AND DISCUSSION

Identification by XRD

The XRD patterns of the three zeolite powders are shown in Fig. 1. CLI1 and CLI2 consisted mainly of clinoptilolite with traces of quartz, feldspar and

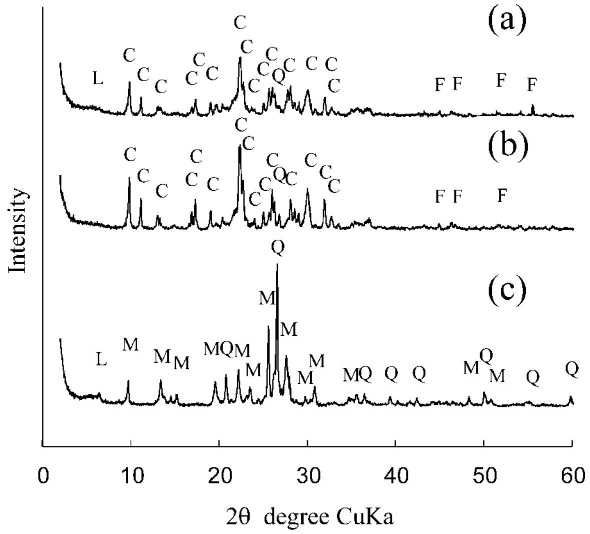

Figure 1. X-ray powder diffraction patterns of natural zeolites. (a) CLI1, (b) CLI2, (c) MOR3. C = clinoptilolite; M = mordenite; Q = quartz; F = feldspar; L = layered silicate.

layered silicate (Fig. 1a and 1b). CLI2 was richer in clinoptilolite than CLI1. MOR3 consisted mainly of mordenite with quartz and layered silicate (Fig. 1c).

SEM

Photographs using SEM showed that the main mineral in CLI1 is clinoptilolite (Fig. 2) and that in MOR3 is mordenite (Fig. 3). Clinoptilolite in CLI1 was crystalline, submicron in size, and assumes a sharp similar to the coffin-shape of heulandite.[19] Mordenite in MOR3 was fibrous and ranged from 0.05 to 0.1 μm in diameter and from 1 to 5 μm in length.

Chemical Composition by ICP

The chemical compositions of the zeolites determined by ICP are shown in Table 2. The Si/Al ratios of the three samples were constant, in the range of

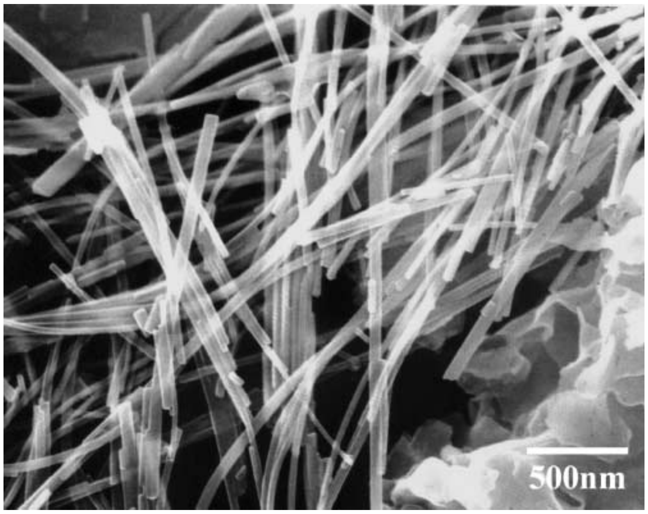

Figure 2. SEM photograph of clinoptilolite in CLI1.

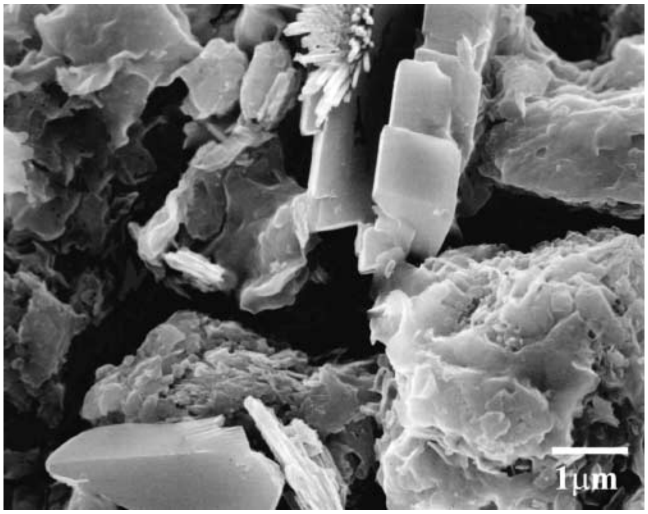

Figure 3. SEM photograph of mordenite in MOR3.

Table 2. Chemical composition of natural zeolites CLI1, CLI2, and MOR3 (wt%).

	CLI1	CLI2	MOR3
Si	29.3	29.3	30.8
Al	5.93	5.93	6.35
Fe	0.76	0.49	0.49
Na	2.57	2.43	1.88
K	1.19	1.42	1.53
Ca	1.40	1.21	0.91
Mg	0.44	0.40	0.40
Si/Al	4.94	4.94	4.85

4.8 to 5.0. The total amount of Na^+, K^+, Mg^{2+}, and Ca^{2+} in ion-exchange sites on the zeolites was about 5 wt%.

Hydrogen Adsorption Behavior

The concentrations of cations, silica, and alumina in solution, initial pH, and equilibrium pH in distilled water are shown in Table 3. The concentrations of all species in the blank solution, that is, distilled water without zeolite, were below the detection limit of ICP. The equilibrium pH increased from the initial pH in distilled water because of exchange of hydrogen ions from the solution

Table 3. The concentration of dissolved cations, silica and, alumina from zeolites in distilled water (mol/L).

	CLI1	CLI2	MOR3
pH_0	5.45	5.45	5.45
pH_{eq}	9.31	6.87	6.59
SiO_2	0.098	0.035	ND
Al_2O_3	0.051	0.035	ND
Na	0.459	0.093	0.056
K	0.019	0.037	0.017
Ca	0.011	0.007	ND
Mg	0.008	0.001	ND

pH_0 = initial pH values; pH_{eq} = equilibrium pH values after reaction; ND = not detected.

with the other cations in the zeolite matrix. The amount of exchanged cations was less than 0.1 wt% in all of the samples. The amount of exchanged cations for MOR3 was the smallest of three samples, and the equilibrium pH was also the smallest in this sample. This may be explained by considering the exchange of cations Na^+, K^+, Mg^{2+}, and Ca^{2+} in ion-exchange sites on zeolites with H^+ ions in distilled water. For each type of zeolite, the exchange of Na^+ in the zeolite structure is the easiest and thus has the largest effect. The results of H^+ ion exchange for MOR3 in hydrochloric acid are shown in Table 4. The increase in the equilibrium pH was due to the increase in cation concentration. This phenomenon was also observed for the other cations—Na^+, K^+, Mg^{2+}, and Ca^{2+}—in ion-exchange sites on zeolites that exchanged with H^+ ions in hydrochloric acid and in distilled water. Sodium was observed to be more easily exchanged than the other cations in the zeolites. By decreasing the equilibrium pH, dissolved silica and alumina concentrations increased. This result indicates that the structures of silica and alumina are destroyed at low pH.

Ammonium Adsorption Behavior

The ammonium adsorption isotherm of the three natural zeolites in ammonium chloride solution is shown in Fig. 4. CLI2 shows the highest ammonium capacity among the three natural zeolites, with a capacity of 1.28 mmol/g. This phenomenon can be explained by the difference in mineral compositions among the three zeolites. CLI2 was shown to be nearly pure

Table 4. The concentration of dissolved cations, silica, and alumina from MOR3 in hydrochloric acid (mmol/L).

pH_0	pH_{eq}	SiO_2	Al_2O_3	Na	K	Ca	Mg
1.33	1.33	0.363	—	1.516	—	—	—
1.78	1.89	0.208	—	1.381	—	—	—
2.17	2.29	0.104	0.104	1.121	0.091	0.242	0.121
2.55	2.87	0.053	0.020	0.800	0.075	0.175	0.122
2.92	3.55	0.034	0.001	0.485	0.031	0.055	0.086
3.34	6.01	0.025	ND	0.290	0.018	0.011	0.013
3.79	6.54	0.021	ND	0.139	0.015	0.004	0.002
4.34	6.69	0.018	ND	0.088	0.013	0.005	0.002

pH_0 = initial pH values; pH_{eq} = equilibrium pH values after reaction; — not determined; ND = not detected.

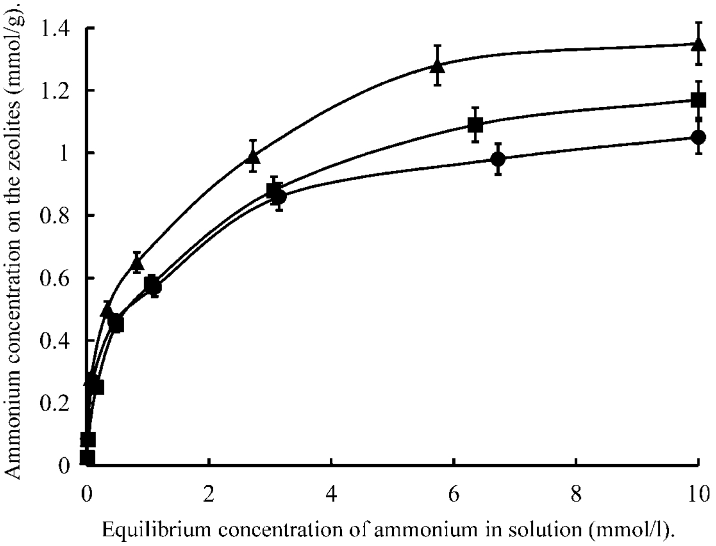

Figure 4. The ammonium adsorption isotherm of three natural zeolites. ■: CLI1, ▲: CLI2, ●: MOR3.

clinoptilolite using XRD m (Fig. 1.) and to have the highest exchange capacity. The ammonium adsorption capacity of the three zeolites was compared with other published data on zeolites in Table 5.[3] The results indicate that the three samples have similar but slightly higher exchange capacities than other previously reported zeolites.

The pH of the solution before and after adsorption, the concentration of silica, alumina and cations in ion-exchange sites on zeolites in solution, and the theoretical and experimental ammonium adsorption levels in $3 \times 10^{-3} \sim 1 \times 10^{-4}$ M ammonium chloride solutions are shown in Table 6. By increasing the initial concentration of ammonium chloride solution, the concentration of silica and alumina decreased. This result indicates that the framework structures of the zeolites are stable in high-ammonium-concentration solution. This was also confirmed by the unchanged crystal structures of the zeolites after ammonium adsorption, as determined by XRD. The order of ammonium ion exchange selectivity for cations on zeolites is $Na^+ \gg K^+ > Ca^{2+} > Mg^{2+}$ (i.e., the exchange of Na^+ on zeolites is the largest). This also indicates that Na^+ exchange on zeolites occurs by

Table 5. Exchange capacities of various zeolites in 1 mmol/L (NH_4^+).

Zeolite origin	Ammonium exchange capacity [meq NH_3 (N)/g]	Ref.
CLI1	0.336	
CLI2	0.359	
MOR3	0.351	
Grant Co., NM	0.288	[7]
Owyhee Co., ID	0.247	[7]
Fremont Co., WY	0.187	[7]
Lander Co., NV	0.255	[7]
Washoe Co., NV	0.140	[7]
Malheur Co., OR	0.377	[7]
Maricopa Co., AZ	0.139	[7]
Hector Clinoptilolite	0.286	[7]

the following ion-exchange reaction (Eq. 1).

$$\text{Na-Ze} + NH_4{}^+ \rightleftharpoons NH_4\text{-Ze} + Na^+ \cdots (\text{Ze : zeolite}) \cdots \tag{1}$$

It is apparent that Na^+ are very weakly bound in the structures of these zeolites. Other ions are strongly held in the structure of all zeolite samples compared with Na^+. The theoretical amounts of various cations exchanged with zeolites are calculated using the formula below (Eq. 2), the assumption that a charge balance on the zeolites with an equivalent number of charged ions are exchanged with ammonium ions (i.e., one Na^+ or K^+ with one $NH_4{}^+$, one-half Ca^{2+} or Mg^{2+} with one $NH_4{}^+$).[20] The concentration of the cations released in distilled water (see Table 3) was deducted from the above concentrations.

$$\left[\text{Total } NH_4{}^+\right] = [Na^+] + [K^+] + 1/2[Mg^{2+}] + 1/2[Ca^{2+}] \cdots \tag{2}$$

The amount of adsorbed ammonium ions determined experimentally is quantitatively in agreement with the amount determined using the above approach at high ammonium concentrations. This result indicates that ammonium adsorption occurs by ion exchange involving Na^+, K^+, Mg^{2+}, and Ca^{2+} in cation exchange sites on zeolites.

Table 6. The concentration of dissolved cations, silica, and alumina from zeolites (mmol/l) and the amount of adsorbed ammonium (mmol/g) in ammonium chloride solution (mmol/L).

	C_0 (NH_4^+)	pH_0	pH_{eq}	SiO_2	Al_2O_3	Na^+	K^+	Ca^{2+}	Mg^{2+}	C_1 (NH_4^+ads)	C_2 (NH_4^+ads)
CLI1	3.0	5.42	8.14	0.072	0.001	1.330	0.187	0.150	0.027	0.544	0.583
	1.0	5.30	8.77	0.086	0.003	0.760	0.065	0.025	0.012	0.252	0.252
	0.3	5.52	9.00	0.116	0.005	0.230	0.026	0.011	0.010	0.072	0.081
	0.1	5.70	9.27	0.114	0.005	0.160	0.020	0.010	0.009	0.048	0.255
CLI2	3.0	5.42	6.34	0.023	ND	1.760	0.140	0.010	0.010	0.631	0.655
	1.0	5.30	6.40	0.022	ND	0.920	0.036	0.006	0.008	0.285	0.279
	0.3	5.52	6.53	0.068	0.006	0.340	0.017	0.007	0.009	0.108	0.086
	0.1	5.70	6.76	0.069	0.007	0.220	0.010	0.006	0.009	0.072	0.026
MOR3	3.0	5.42	5.59	0.017	ND	1.340	0.143	0.086	0.063	0.514	0.568
	1.0	5.30	6.02	0.018	ND	0.700	0.050	0.021	0.022	0.231	0.270
	0.3	5.52	6.17	0.024	0.001	0.210	0.018	0.004	0.002	0.051	0.084
	0.1	5.70	6.43	0.023	0.001	0.130	0.014	0.009	0.003	0.029	0.027

C_0 (NH_4^+) = initial concentration of ammonium chloride solution; pH_0 = initial pH values; pH_{eq} = equilibrium pH values after ammonium removal; C_1 (NH_4^+ads) = calculated values of ammonium adsorption; C_2 (NH_4^+ads) = experimental values of ammonium adsorption; ND = not detected.

CONCLUSION

Three natural zeolites mined from Shimane, Japan, have been shown to have a high ammonium adsorption capacity. Of these three zeolites, CLI2, which is rich in clinoptilolite, was shown to have the highest ammonium adsorption capacity of 1.28 mmol/g. The amount of cation released from this zeolite was less than 0.1 wt% of the initial amount in the sample in distilled water. The lowest ammonium adsorption capacity was observed in MOR3. This indicates that the cations Na^+, K^+, Mg^{2+}, and Ca^{2+} in ion-exchange sites on zeolites exchanged with H^+ ions in distilled water and hydrochloric acid. With decreasing equilibrium pH, silica and alumina concentrations increase. This indicates that the structures of silica and alumina are destroyed under these conditions. Regarding ion exchange of the Na^+ on natural zeolite were used as an alternative to ammonium ion in ammonium chloride solution and H^+ ions in distilled water and hydrochloric acid.

The order of ammonium ion exchange selectivity for cations on zeolite is $Na^+ \gg K^+ > Ca^{2+} > Mg^{2+}$. The amount of ammonium ions adsorbed in this experiment quantitatively corresponded to the theoretically expected amount of adsorbed ions given a mole balance on the zeolite at high ammonium concentrations. This result indicates that ammonium adsorption occurs by ion exchange with Na^+, K^+, Mg^{2+}, and Ca^{2+} in cation-exchange sites on zeolites.

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