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Preparation of a Clinoptilolite-Type Korean Natural Zeolite

Dae Haeng Lee, Seung Jai Kim* and Hee Moon†

Faculty of Applied Chemistry, Chonnam National University, Kwangju 500-757, Korea
*Department of Environmental Engineering, Chonnam National University, Kwangju 500-757, Korea

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Abstract–A clinoptilolite-type natural zeolite was pretreated by HCl, NaOH, and NaCl solutions to improve the ion-exchange capacities for heavy metal ions such as copper, lead, cadmium, and cesium. The pretreated natural zeolite was experimentally investigated based on chemical analyses, X-ray diffraction, and BET experiments etc. From experimental data, it was shown that the pretreatment with NaCl gave the best ion-exchange capacity for all metal ions encountered. The ion-exchange capacity of the NaCl-treated sample is comparable with that of a commercialized natural zeolite, chabazite. On the other hand, the HCl-treated sample has very low ion-exchange capacities for all metal ions even though it has high specific surface area and total pore volume. It was proven by chemical analyses that a strong acid like HCl can damage the structure of the zeolite by extracting aluminum and iron from their skeletal units.

Key words : Pretreatment of Natural Zeolite, Heavy Metal Ions, Ion-Exchange Capacity, Characterization of Zeolites

INTRODUCTION

Recently our environment has been severely contaminated by chemical waste discharges from various industries. In particular, heavy metals such as cadmium, lead, copper, zinc, chromium, and aluminum are major causes for breaking the balance of the ecological environment. These metallic pollutants in lakes and waterways come from various metallurgical processes such as battery, electroplating, extractive metallurgy, and metal treatment/finishing. The presence of heavy metals in the environment is detrimental to a variety of living species. In particular, heavy metals can be accumulated through a typical food chain process and eventually they cause serious health problems to humans.

Therefore, it is very important to devise efficient and economical technologies for removing toxic heavy metals from contaminated surface and ground waters. In the last few decades, many researchers have developed several technologies for heavy metal removal. In general, chemical precipitation is a reliable method for removing heavy metals from industrial wastewater. However, this removal process is a consumptive technique that entails large capital and operating costs and requires retreatment of the sludge. On the other hand, the removal of heavy metals using synthetic and natural zeolites has been known as an improved means to isolate heavy metals. Compared with other chemical methods, this process has the advantage of saving energy and having no secondary pollution. In particular, natural zeolites such as chabazite, clinoptilolite, and modenite are economical media for this purpose since they are cheap, widely distributed all over the world, and have high ion-exchange capacity for toxic metals [Pansini, 1996; Perona, 1993; Pradas et al., 1994]. Natural zeolites would be very attractive ion-exchanging media if one could find a proper method to increase their capacities for heavy metals.

There are several important researches on the use of natural zeolites for removing heavy metal ions from aqueous solutions, including pretreatment methods of natural zeolites [Sun and Kim, 1996]. Recently, Lee [1997] used a commercial natural zeolite to remove radioactive metal ions such as cesium and strontium. Zamzow et al. [1990] also used various natural zeolites to remove copper, zinc, and mercury from mining wastewater. Kim et al. [1996] experimentally studied the effect of acid treatment on the ion-exchange capacity of a clinoptilolite-type natural zeolite.

The objective of this study was to find the pretreatment method of natural zeolites that is more effective, economical, and applicable in industry. Three kinds of treatment with acidic, basic, and neutral solutions were executed to improve the removal efficiency of objective metal ions. Instrument analyses such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) were conducted to check the type of zeolites. Specific surface area, total pore volume, and pore size distribution were measured by a nitrogen adsorption. Other factors such as pretreatment concentration, pH, and particle size influence on the ion-exchange amount were also considered to compare the capacity. The ion-exchange characteristics of heavy metals in aqueous solutions such as lead, cadmium, copper, and cesium were investigated experimentally.

EXPERIMENTAL

In this study, a natural zeolite, which consists of mainly clinoptilolite and heulandite, was used. This natural zeolite is abundant in the Gampo area of Kyung-buk Province, Korea as a natural resource and commercially supplied by Han-Doo Co., Korea. Zeolite particles were classified by sieving with standard sieve trays to collect relatively uniform particles of 16/30 mesh (0.59-1.19 mm). The water content was determined by a thermogravimetric analyzer (TGA) (Shimadzu, Japan). The arithmetic average particle diameter was determined by sieve openings. Prior to

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†To whom correspondence should be addressed.
E-mail : hmoon@chonnam.chonnam.ac.kr

pretreatment, natural zeolite particles were rinsed with distilled water and dried in an oven at 105 °C for 1 day. After about 100 g of the particles was packed in the column, working solutions were passed through the column at 5 ml/min at room temperature. As working solutions for pretreatment, 1 mol/L solutions of NaCl, NaOH, and HCl were used. The concentrations of Na^+ and H^+ were monitored by pH and sodium ion meters (Orion 920 A, USA) in terms of time till the final concentrations became their inlet values. Also, the samples were taken during the pretreatment process and the concentrations of metals eluted from the column were analyzed by an inductively coupled plasma-atomic emission spectrophotometer (IPC-AES) (Varian Liberty 220) in order to check what kinds of cation were exchanged. From experimental results, it was known that the pretreatment process requires a period of about 1 day. Finally, the treated zeolite particles were thoroughly rinsed with distilled water and dried in a vacuum oven at 105 °C for 1 day.

Heavy metals encountered here were lead, cadmium, and copper. Experiments were carried out under ionic concentrations of 0.05-10 mol/m^3 and pH values of 2.0-12.0. For batch kinetic experiments, about 3 mol/m^3 stock solutions were used and the rotation speed in the batch adsorber containing 2 L solution was about 500 rpm, which is enough to neglect the change in the film mass transfer coefficient.

In order to obtain breakthrough curves of metal ions, 1 mol/m^3 stock solutions were passed through a packed bed charged with zeolite particles. The solution pH was kept from 5.0 to 6.0 during experiments and the flow rate was 6 ml/min. The column was made of a glass tube of 1.0 cm diameter and 7.5 cm height. Special cares were needed in maintaining the temperature of the column. The flow rate of the solution through the column was regulated by a precision liquid pump (Model : QSY, FLUID Metering, Inc., USA). The solution was introduced downward into the column and two layers of small glass beads were placed in the top and bottom regions of the bed to prevent channeling and to enhance the distribution across the column. Samples were withdrawn from the effluent line and analyzed by ICP-AES. The ion-exchanged amount of each metal on zeolites was calculated from the mass balance equation after their breakthrough curves were integrated in terms of time.

To determine the adsorption characteristics of zeolites such as total pore volume, specific surface area and pore size distribution, a nitrogen gas adsorption method was used for each pretreated sample. Porosity and densities of sorbents were determined by a methanol pycnometer. XRD analyses were also carried out on raw and pretreated natural zeolites to identify their structure and mineral types using Cu K-alpha/30 kV/40 mA (Model : D/MAS-1200, Rigaku/Japan). SEM (Model : JSM-5400, JEOL/Japan) analyses were conducted to identify the surface characteristics of pretreated natural zeolites.

RESULTS AND DISCUSSION

1. Adsorbent Characterization

Cation Exchange Capacity (CEC) of the original natural zeolite is about 150 meq/100 g, and those values of NaCl-, NaOH-, HCl-treated natural zeolites are 178, 167, and 102 meq/100 g, respectively. When the zeolite was treated with NaCl solution, the CEC was improved over 1.2 times compared with the original natural zeolite. In this work an ammonium acetate (NH_4OAc) saturating method was used to determine the CEC [Sumner, 1979]. These CEC values are comparable with those measured elsewhere [Colella, 1996].

Table 1. Chemical analysis of the natural zeolite used in this study

Component	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	$H_2O(+)$
Content (%)	66.5	14.7	1.68	1.25	1.82	1.90	3.25	0.04	8.04

Chemical components of the natural zeolite are shown in Table 1. The ratio of Si/Al is about 3.87. Its pH, density, and hardness are 7.2, 1.92-1.91 g/cm^3 and 3.5-4.5, respectively. The ratio of Si/Al is an important factor in underst-anding the zeolite structure. When the ratio is over 4.0, the zeolite is a clinoptilolite-type, the structure of which would not be easily broken at high temperatures. If the ratio is less than 4.0, on the contrary, the clinoptilolite-type zeolite would be somewhat shifted to a heulandite-type of which structure would be easily broken over 400 °C.

2. Breakthrough Curves of Metal Ions in Pretreatment Process

Figs. 1-3 show the breakthrough curves of different metal ions in the pretreatment process of the natural zeolite by acidic, basic and neutral solutions. Fig. 1 is the result for 1 mol/L NaCl solution. Sodium ions in the solution were fast exchanged with potassium, calcium and magnesium ions of the zeolite in the initial period, and little exchanged with ferric and aluminum ions which make the main frame of the zeolite. The variations in metal ion concentrations such as Na, K, Ca and Mg are shown in Tables 2-4 in terms of time. The concentration of sodium ions at 0.08 h, when NaCl solution was used in the pretreatment, reached 76 % of the initial concentration as shown in Table 2. It was proven that sodium ion saturation to the natural zeolite had pro-

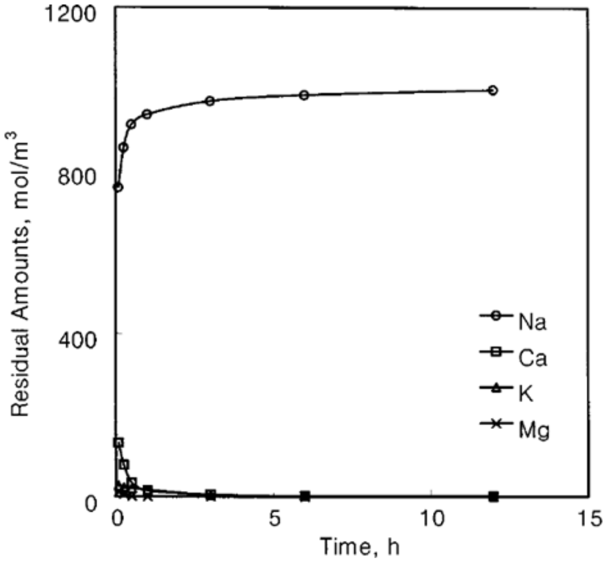


Fig. 1. Breakthrough curves of metal ions during pretreatment process using 1 mol/L NaCl solution.

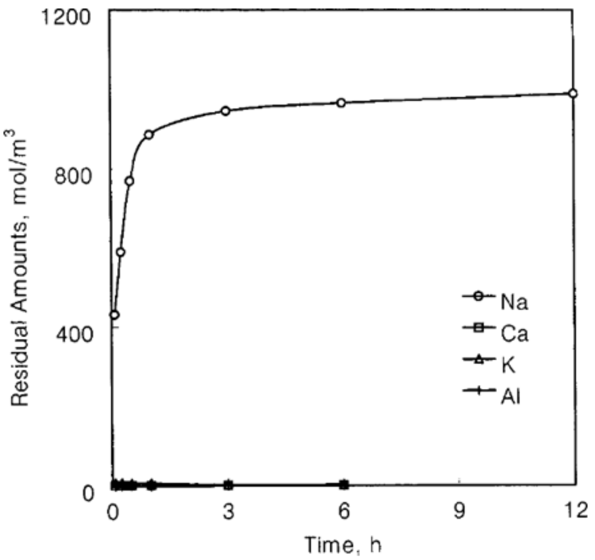


Fig. 2. Breakthrough curves of metal ions during pretreatment process using 1 mol/L NaOH solution.

Table 2. Variation in metal concentrations released during pretreament process by 1 mol/L NaCl solution (unit : mol/m^3)

Time (h)	Na	K	Ca	Mg	Al	Fe
0.08	758	132	27.0	11.3	0.00	0.00
0.50	913	34.4	20.5	2.06	0.00	0.00
1.00	938	15.2	16.5	0.99	0.00	0.00
3.00	971	5.20	4.60	0.40	0.00	0.00
6.00	986	1.30	1.00	0.14	0.00	0.00
12.00	999	0.72	0.00	0.09	0.00	0.00

Table 3. Variation in metal concentration released during pretreatment process by 1 mol/L NaOH solution (unit : mol/m^3)

Time (h)	Na	K	Ca	Al	Mg	Fe
0.08	432	7.60	0.14	0.03	0.00	0.00
0.50	769	10.2	0.09	0.04	0.00	0.00
1.00	886	9.77	0.13	0.04	0.00	0.00
3.00	945	4.00	0.10	0.02	0.00	0.00
6.00	965	2.50	0.07	0.01	0.00	0.00
12.00	949	1.72	0.05	0.17	0.00	0.00

gressed over 99.9 % after 12 h.

The results of pretreatment by 1 mol/L NaOH solution are shown in Fig. 2 and Table 3. The concentration of sodium ions at 0.08 h, when NaOH solution was used in pretreatment, was of about 43 % of the initial concentration as shown in Table 3. The saturation of sodium ions to the natural zeolite had progressed over 94.9 % after 12 h. The amounts of other metals such as calcium, potassium, magnesium etc. released from the zeolite were smaller than those in the case of NaCl-treated sample. Sodium ions were gradually exchanged with other metal ions in the zeolite. A small amount of aluminum ions consisting of the framework of the natural zeolite was released from the zeolite into the solution, of which the Si/Al ratio of the zeolite was changed. If the NaOH-treatment method is used, one must consider that environment can be contaminated by aluminum and iron released from zeolites.

Table 4. Variation in metal concentrations released during pretreatment process by 1 mol/L NaOH solution (unit : mol/m^3)

Time (h)	Na	Ca	K	Mg	Al	Fe
0.08	168	94.8	29.9	11.7	2.15	0.10
0.50	17.5	4.62	13.7	1.60	1.31	0.03
1.00	12.0	7.30	12.4	2.89	1.70	0.06
3.00	4.60	3.30	6.10	1.21	1.00	0.05
6.00	2.00	1.30	3.10	0.90	0.50	0.03
12.00	0.27	0.65	1.35	0.79	0.30	0.05

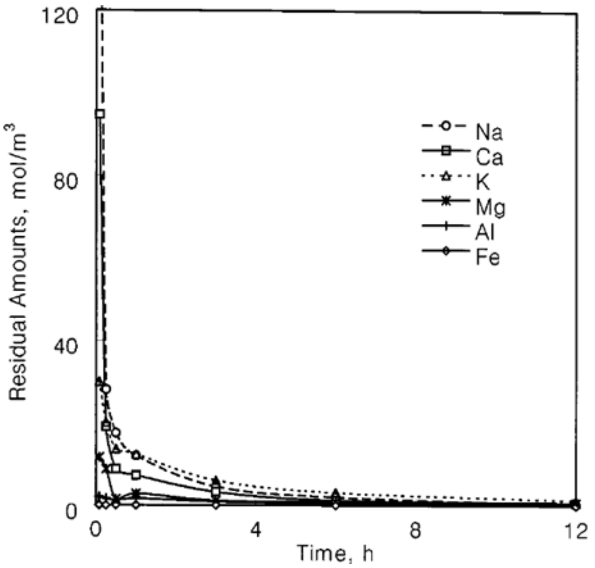


Fig. 3. Breakthrough curves of metal ions during pretreatment process using 1 mol/L HCl solution.

In the case of pretreatment by 1 mol/L HCl solution, 168 and 94.8 mol/m^3 for Na and Ca ions were released at 0.08 h, respectively. All kinds of metal ions that the zeolite contains are found in the effluent as shown in Table 4. This result implies that hydrogen ions in solution are exchanged with alkali and alkaline earth metals in the zeolite. The order of metal amounts released from the zeolite was Na > Ca > K > Mg > Al > Fe as shown in Fig. 3. In this treatment, many aluminum and ferric ions were also released indicating the partial destruction of the zeolite structure.

To check the amounts of metal ions released from the zeolite, metal amounts in solutions after pretreatment in batch systems

Table 5. Metal amounts released from zeolite during pretreatment in batch systems at 30 °C (unit : mol/m^3)

Method	Fe	Al	Na	Ca	K	Mg
NaCl	0.00	0.00	981	2.85	0.97	0.32
NaOH	0.02	0.37	952	0.28	1.93	0.00
HCl	0.55	0.46	2.30	1.95	0.26	1.08

*Solutrion concentration : 1 mol/L
*Shaking : Solution 100 ml+zeolite 1 g for 24 h

Table 6. Physical properties of zeolites accroding to pretreatment solutions

Item	Natural	NaCl-t	NaOH-t	HCl-t	NS-13X
Surface area (m^2/g)	171	225	139	225	684.000
Total pore volume (cc/g)	0.218	0.261	0.248	0.250	0.454

are shown in Table 5 under the conditions that initial concentration was 1 mol/L, adsorbent weight 1 g, volume 100 ml and contact time 24 h at 30 °C. In the NaCl-treated case, aluminum and ferric ions were not released from the zeolite at all. This fact implies that the zeolite structure remains unchanged during the NaCl treatment.

3. Nitrogen Adsorption

Physical properties such as specific surface area, total pore volume and pore size distribution play an important role in adsorption. Internal surface area of microporous materials is often used as one of the measures to describe the degree of development of pores. The concept of nitrogen adsorption isotherm gives the specific surface area by assuming the molecular sectional area of nitrogen to be 16.2 Å^2/molecule. The physical properties were determined by a nitrogen adsorption method as shown in Table 6. When nitrogen adsorption is carried out at liquid nitrogen temperature (77.34 K), nitrogen adsorption on the surface and capillary condensation of nitrogen in the pores take place. The thickness of the adsorbed layer on the surface and the size of the pore where condensation happens depend on the partial pressure of nitrogen. Thus, an adsorption isotherm can be converted to the pore size distribution. The micropore size distributions, measured by HK method [Lowell and Shields, 1984] which should be applied to measurements below $p/p_s = 0.5$, are shown in Fig. 4. The specific surface area of zeolites was followed to the order of molecular sieve-13X > HCl-treated > NaCl-treated > untreated > NaOH-treated zeolites. The total pore volume was in the order of MS-13X, NaCl-treated, HCl-treated, NaOH-treated, and untreated zeolites. The HCl-treated zeolite has the smallest average pore diameter among them except MS-13X because mesopores were formed at aluminum sites by breaking the structure. If the physical adsorption prevails in the adsorption of heavy metals onto zeolites, the adsorption results would be followed to the order of total pore volume and surface area. But the results from equilibrium experiments do not match with this fact because the removal mechanism of heavy metals by zeolites follows the ion-exchange reaction. So, ion-exchange capacities of heavy-metals depend on dielectric strength between metals as well as their affinities to a zeolite. The size of micropores of the natural zeolite is in the range of 3-10 Å. Micropores of the NaCl-treated zeolite were more developed in the range of near about 5 Å than other cases. This implies that the NaCl-treated zeolite could remove selectively metal ions which have a specific size. The size of metal ions is as follows :

Hydrated cations radii : Pb^{2+} : 4.01 Å, Cd^{2+} : 4.26 Å,
Cu^{2+} : 4.19 Å, Cs^{+} : 3.30 Å

When the zeolite was pretreated with HCl, the average pore diameter was lessened while it was enlarged to the largest among all kinds of treatment when treated with NaOH. However the pore diameter was not so much changed as compared to that of the zeolite treated with NaCl.

4. X-ray Diffraction Analysis

X-ray diffraction results and patterns, when the natural zeolite was pretreated with several chemicals such as HCl, NaOH, and NaCl, are shown in Table 7 and Fig. 5. In the cases treated with NaCl and NaOH, it can be seen that the peak intensity at 2-theta values for clinoptilolite and cancrinite types (in which sodium is a main element) become higher than the HCl-treated case. The peak intensity is reduced at the 2-theta value of 11.19, 22.71, and 26.29, when the HCl treatment case is compared with the NaCl and NaOH cases. It can be conjectured that the structure of the zeolite was partially collapsed by a strong acid, HCl.

The natural zeolite used in this study consists of several minerals such as clinoptilolite, heulandite, cancrinite, phillipsite, and α-cristobalite. When the natural zeolite was heated at 400 and 700 °C, X-ray diffraction results are shown in Table 8. Heulandite is weak to the heat treatment and the XRD intensities of the treated

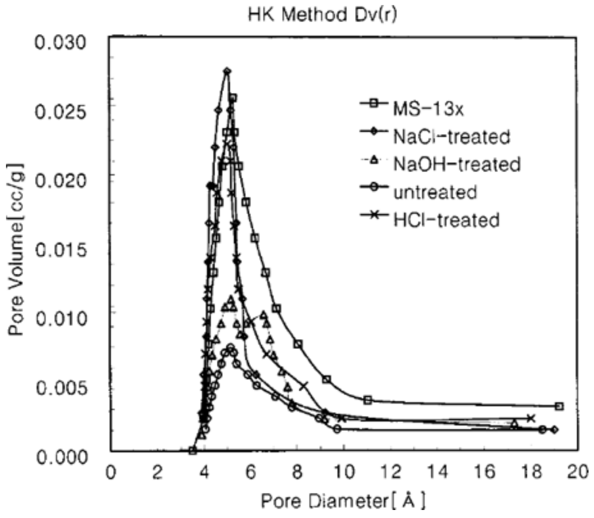


Fig. 4. Micropore size distribution of different zeolites.

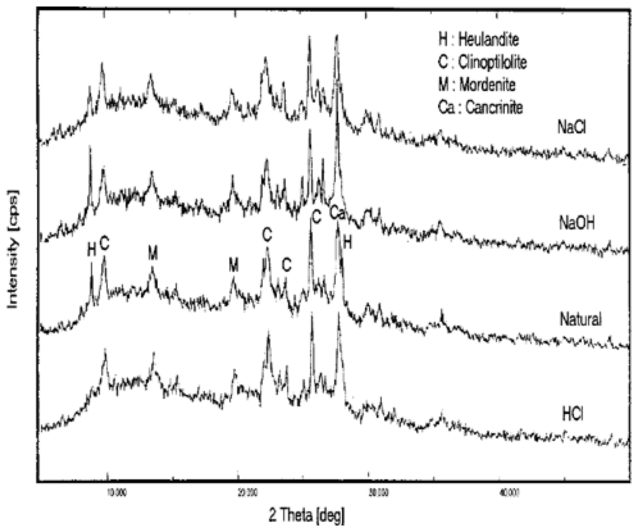


Fig. 5. X-ray diffraction patterns of different zeolites.

Table 7. X-ray diffraction results of natural zeolites pretreated with several chemicals such a HCl, NaOH and NaCl

2-Theta value	Mineral type (cation)	Intensity			
		Natural/Clin	HCl/Clin	NaOH/Clin	NaCl/Clin
8.80	*VIP-7* (Na)	1277	528	1747	-
9.82	*Heulandite* (K, Na, Ba)	1392	-	1301(9.78)	1446(9.81)
9.88	*Clinoptilolite* (Na, K, Mg, Ca)	-	1259(9.86)	1269	1166(9.93)
11.19	*Clinoptilolite* (Na, K, Mg, Ca)	845(11.21)	768(11.24)	972(11.14)	994(11.17)
13.45	*Mordenite* (Na)		1038(13.41)	1154	
13.50	*Bellbergite* (Ca, Sr, K, Na, Ba)	1085	1182(13.54)	1132(13.53)	1127(13.49)
19.63	*Mordenite* (Na)	772(19.71)	683(19.57)	729(19.76)	814(19.63)
22.00	*α-Cristobalite* (Si)	1253(22.04)		1239(21.96)	1246(21.97)
22.21	*Heulandite* (K, Na, Ba)			1236	
22.36	*Clinoptilolite* (Na, K, Mg, Ca)	1432(22.30)	1484(22.31)	1389(22.30)	1517(22.27)
22.71	*Clinoptilolite* (Na, K, Mg, Ca)	700(22.75)	840(22.75)	962(22.71)	1062(22.73)
26.29	*Clinoptilolite* (Na, K, Mg, Ca)	978(26.25)		1042(26.27)	1100(26.28)
27.74	*Cancrinite* (Na, Ca)	1692(27.67)	1327(27.65)	1704(27.64)	1989(27.70)
27.89	*Phillipsite* (K, Ca, Na)	1854(27.77)	2127(27.83)	3355(27.79)	1890(27.83)
28.09	*Heulandite* (K, Na, Ba)	1657(28.05)	1116(28.03)	1205(28.01)	
28.15	*Clinoptilolite* (Na, K, Mg, Ca)	-	1095(28.14)	-	1011(28.11)

Table 8. X-ray diffraction results of zeolites pretreated with heat at 400 and 700 °C

2-Theta value	Mineral type (cation)	Intensity		
		Natural zeolite	Heated at 400 °C	Heated at 700 °C
8.80	*VIP-7* (Na)	1277	1463(8.86)	1800(8.94)
9.82	*Heulandite* (K, Na, Ba)	1392	1339(9.83)	1169(9.78)
11.19	*Clinoptilolite* (Na, K, Mg, Ca)	845(11.21)	979(11.18)	839(11.15)
13.45	*Mordenite* (Na)		971(13.43)	924(13.42)
13.50	*Bellbergite* (Ca, Sr, K, Na, Ba)	1085	-	1057(13.52)
22.00	*α-Cristobalite* (Si)	1253(22.04)	992(21.98)	1178(22.05)
22.36	*Clinoptilolite* (Na, K, Mg, Ca)	1432(22.30)	1058(22.30)	-
22.71	*Clinoptilolite* (Na, K, Mg, Ca)	700(22.75)	-	-
26.29	*Clinoptilolite* (Na, K, Mg, Ca)	978(26.25)	731(26.3)	854(26.33)
27.74	*Cancrinite* (Na, Ca)	1692(27.67)	1919(27.77)	1529(27.76)
27.89	*Phillipsite* (K, Ca, Na)	1854(27.77)	-	2058(27.92)
28.09	*Heulandite* (K, Na, Ba)	1657(28.05)	-	1307(28.12)
28.15	*Clinoptilolite* (Na, K, Mg, Ca)	-	-	939(28.19)

zeolites at 2-theta values of 9.82 and 28.09 are lessened compared to the untreated natural zeolite.

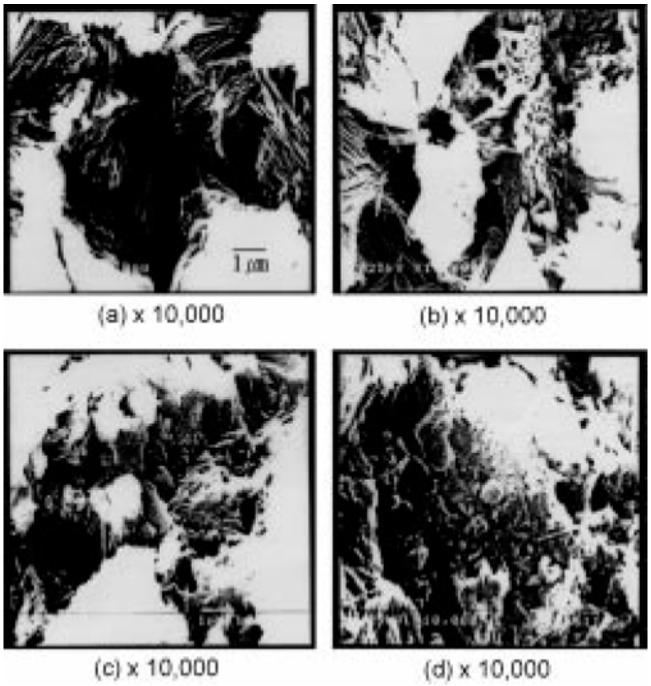
The Si/Al ratio of the natural zeolite used in this study was 3.87, which means clinoptilolite and heulandite types are mixed together. Although the commonly occurring sedimentary mineral, clinoptilolite, is generally considered to be an isostructural variant of heulandite, there is no sufficient evidence for this conclusion. But heulandite has low bond density between the layers, so it can be easily changed structurally during hydration and heating over 230 °C. On the other hand, clinoptilolite is very stable against hydration and thermal treatments, even up to 700 °C in air.

5. SEM Analysis

Scanning electron microscope (SEM) photographs of (a) NaCl-treated (b) NaOH-treated (c) untreated, and (d) HCl-treated zeolites are shown in Fig. 6. When the natural zeolite was treated with HCl, the melted zone irregularly appeared on the surface of zeolite as shown in Fig. 6(d). For the untreated sample, the structure was not well arranged and the pore was not developed on the surface. For the sample treated with NaOH, the surface of the zeolite has some melted zones with some structural change. In treatment with NaCl, the melted zone is not seen at all and the structure is much developed on the surface, which would make ion-exchange reaction easy with metal cations.

6. Ion-exchange Capacities of Different Zeolites for Metal Ions

It is an important aspect of process engineering design to have information on ion-exchange equilibrium. The equilibrium uptake of cadmium on different zeolites is shown in Fig. 7. It is noted that the NaCl-treated zeolite is a bit more favorable than a commercialized natural zeolite, chabazite (Aldrich chem. Co.). For other metal ions such as copper, lead, and cesium, we got similar results. The ion-exchange capacities of different zeolites for all metal ions encountered here are the order of NaCl-treated ≅ chabazite > NaOH-treated > untreated > HCl-treated. According to the



(a) x 10,000 (b) x 10,000

(c) x 10,000 (d) x 10,000

Fig. 6. SEM photographs of (a) NaCl-treated, (b) NaOH-treated, (c) untreated, and (d) HCl-treated zeolites.

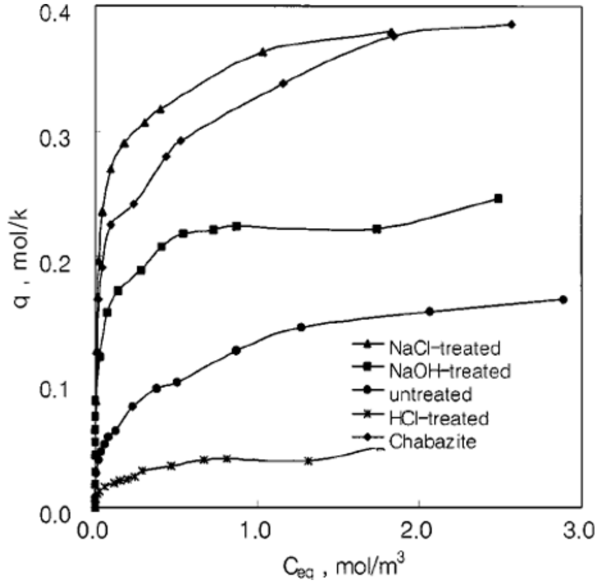


Fig. 7. Ion-exchange amount of cadmium on different zeolite at 30°C.

nitrogen adsorption data, the HCl-treated zeolite has the highest in surface area and pore volume. However the ion-exchange amount was observed as the lowest. It is evident that cationic removal mechanism is not the physical adsorption but ion-exchange phenomenon which depends on the number of cationic sites rather than specific surface area.

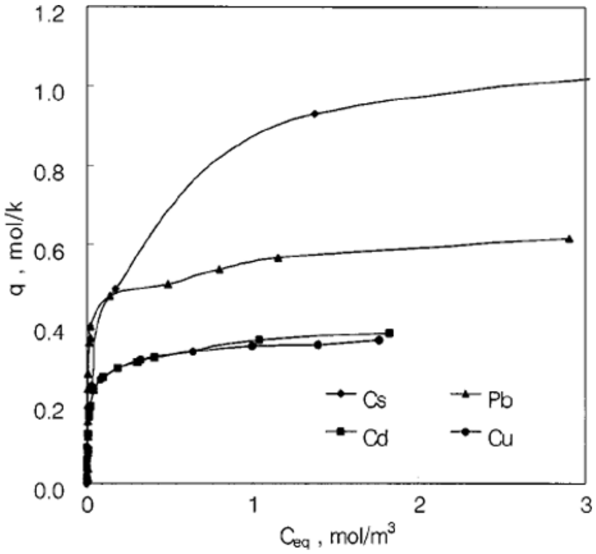


Fig. 8. Ion-exchang uptakes of metal ions on NaCl-treated zeolite.

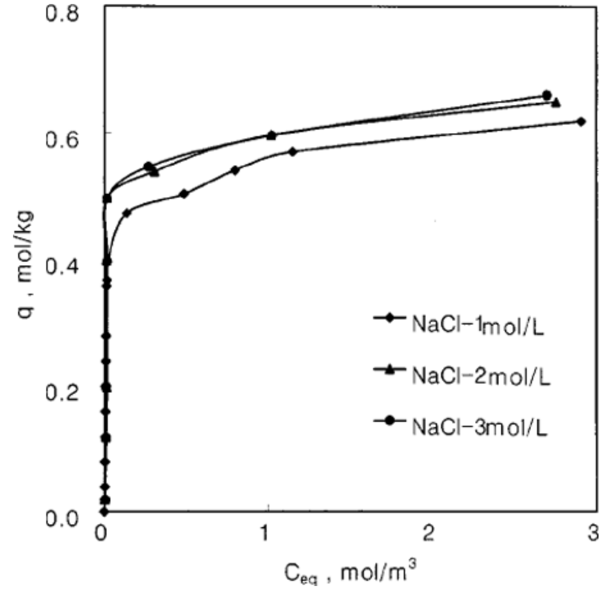


Fig. 9. Effect of NaCl concentration on uptake of Pb^{2+} on NaCl-treated sample at 30 °C.

The selectivity of the NaCl-treated zeolite to heavy metals follows the order of Cs > Pb > Cd > Cu as shown in Fig. 8. The result has a close relationship with the order of hydrated cation radii. Finally, the effect of NaCl concentration in the pretreatment solution on ion-exchange capacity was also experimentally investigated as shown in Fig. 9. However it was found that the solution concentration over 1 mol/L affected ion-exchange capacities for most metal ions marginally.

CONCLUSIONS

When natural zeolites are to be used in the removal process for heavy metals, the efficiency could be changed according to the pretreatment method. The main structure of zeolites was nearly unchanged by 1 mol/L NaCl solution, but changed by NaOH or HCl solution, because aluminum and ferric ions were released from zeolites. When the natural zeolite was treated with HCl solution, the specific surface area was the largest among four different zeolites such as NaCl-treated, NaOH-treated, HCl-treated, and untreated ones. However, the adsorption amounts of heavy metals were the least among them because of the partial destruction of the zeolite structure. According to the pore size distribution obtained by the nitrogen adsorption method of Horvath and Kawazoe, the NaCl-treated zeolite had the largest micropore volume.

X-ray diffraction patterns showed that the peak intensities of the NaCl-treated zeolite at 2-theta values for clinoptilolite and cancrinite types become larger than those in other cases. The 2-theta values of heulandite are 9.82 and 28.09 that of intensities were reduced when it was pretreated with heat. The natural zeolite supplied by Handoo Co. has 3.87 of Si/Al ratio, which implies that it is a mixed mineral of clinoptilolite and heulandite. SEM photographs show that the melted zone has appeared in the HCl-treated case and macropore does not appear in the untreated case.

According to experimental and analytical results, the NaCl-treated natural zeolite showed most favorable aspects among four different zeolites when applied to the removal process of heavy metals.

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