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Removal of Heavy Metals from Model Mine Wastewater by Adsorption Using Mongolian Natural Zeolites

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Mongolian natural zeolites, whose base components were clinoptilolite, mordenite, and chabazite, were characterized in terms of parameters such as their elemental contents, cation exchange capacities, among others. Since the molar ratios of aluminum to silicon for the Mongolian natural zeolites used in this study were lower than those of pure zeolites, it was surmised that the natural zeolite samples contained substantial amounts of impurities. The cation exchange capacities of the natural zeolite samples were dependent on their aluminum content and were greater for the zeolites with higher aluminum contents. Batch equilibrium adsorptions of heavy metals such as copper, zinc, and manganese from model wastewater using the Mongolian natural zeolites were also carried out. The natural zeolites could adsorb and remove the heavy metals from the aqueous model solutions and also helped to adjust pH of the solutions to appropriate levels. The precipitation of the heavy metals in the form of their hydroxides owing to the addition of natural zeolite also aided the removal of the metals. The amounts of the heavy metals adsorbed at saturation as estimated by the Langmuir equation were almost the same for all the metals. In addition, these amounts increased with the pH of the feed solutions as well as with cation exchange capacities of the natural zeolites. Finally, it was found that the adsorption coefficient in the Langmuir equation was correlated with the hydrated ionic radii of the heavy metals being investigated for removal.

Introduction

Large deposits of metals such as gold and copper, among others, were found in Mongolia in 2000 by Ivanhoe Mines Ltd. of Canada. These metal deposits are estimated to as large as 340 tons in the case of gold and 15 million tons for copper and will have a significant impact on the global commodities market. It is expected that these mines, including the copper mine at Oyu Tolgoi, will be developed and be ready to supply the market by around 2013.

However, untreated wastewater from these mines can seriously contaminate the surrounding environment. This mine wastewater, which includes mine drainage and water that has infiltrated the mines, is acidic in nature. Mine drainage is generated when minerals in the crushed ore deposits come in contact with air and water. Water that infiltrates the mines can come in contact with sludges of low-metal-content waste, resulting in it acting as a contaminant. This acidic wastewater is discharged into the environment not only when the mine is

active, but even when the mine is closed. Therefore, when considering the development of these metal mines, the treatment of this wastewater should also be taken into account. Although neutralization is the most widely employed technique for treating such mine wastewater, this method has a number of problems associated with it. These include the facts that it generates sludges in large amounts and requires large-scale facilities.

Mongolia is also abundant in natural zeolites, which are found all over the country and are also expected to be extracted and used in various industrial purposes in the country. The deposit of natural zeolites at Tsagaan Tsav alone is expected to produce about 4.8 million tons of zeolite-containing minerals. Zeolites are well known as microporous materials that are capable of cation exchange and are used to adsorb and remove cations, including metal cations, from aqueous solutions. In addition zeolites are also used to precipitate heavy metals in the form of their hydroxides by raising the pH of the solutions containing these metals.

Motsi *et al.* (2009) investigated the treatment of the wastewater from the Wheal Jane mine by zeolite-based adsorption using natural zeolites from Turkey. They showed that the natural zeolites had the potential to effectively remove heavy metals from relatively dilute mine wastewater. Although others (Bolortamir and Egashira, 2008; Bolortamir *et al.*, 2008a, 2008b) have studied the treatment of chromium-containing tannery wastewater using Mongolian natural zeolites—the natural zeolites, with modification, could remove both hexavalent and trivalent chromium from solutions at the same time—there have been no previous studies on the treatment of mine wastewater using Mongolian natural zeolites.

In this study, we investigated the possibility of using Mongolian natural zeolites to remove heavy metals from the wastewater discharged from a mine also in Mongolia. First, several Mongolian natural zeolites were characterized in terms of parameters such as their base mineral components, elemental contents, cation exchange capacities, among others. Then, the batch equilibrium adsorption of heavy metals from model wastewater that mimicked the wastewater from the Oyu Tolgoi copper mine in Mongolia was carried out using the Mongolian natural zeolites.

1. Experimental

1.1 Characterization of the Mongolian natural zeolites

Table 1 summarizes the sampling conditions used for obtaining the Mongolian natural zeolites as well as the principal characteristics of the zeolites. The base mineral components of the zeolites, which were obtained from the Tsagaan Tsav deposit in the Dornogovi province of Mongolia, had been identified in a previous study (Bolortamir and Egashira, 2008) and had been found to be clinoptilolite (CLP), mordenite (MOR), and chabazite (CHA). The zeolite samples were crushed (Wonder Blender, WB-1, Osaka Chemical Co., Ltd.), sieved using a testing sieve (sieve aperture 150×10^{-6} m, wire diameter 100×10^{-6} m; Tokyo Screen Co., Ltd.), and placed in a desiccator with a saturated aqueous solution of ammonium chloride under room temperature prior to the characterization and adsorption runs.

The zeolite samples were analyzed using X-ray diffraction (XRD) analysis, performed with a diffractometer (MultiFlex, Rigaku Corp.), and energy-dispersive X-ray spectroscopy (EDX) (EAGLE μ -Probe, EDAX Inc.). The surface areas of the particles in the samples were measured from their nitrogen-gas-adsorption isotherms obtained at 77 K (SA 3100, Beckman Coulter, Inc.) and the Brunauer-Emmett-Teller (BET) method. The cation exchange

Table 1 Sampling conditions and principal characteristics of the Mongolian natural zeolites obtained from the Tsagaan Tsav deposit (the results in parentheses are from a previous study (Bolortamir and Egashira, 2008))

	Clinoptilolite (CLP) ^{a)}	Mordenite (MOR) ^{b)}	Chabazite (CHA) ^{c)}	Pure mordenite ^{d)}	Beta type zeolite ^{e)}
Sampling date	09/2004	09/2004	12/2005	-	-
Sampling depth [m]	60	60	150	-	-
Sample color	Grey	Light yellow	Light grey	-	-
Surface area [$\text{m}^2 \cdot \text{g}^{-1}$] (by BET)	32 (31)	8 (26)	164 (159)	358	400–600

a) “NZ-4” in Bolortamir and Egashira, 2008

b) “NZ-1” in Bolortamir and Egashira, 2008

c) “NZ-9” in Bolortamir and Egashira, 2008

d) de Oliveira *et al.*, 2007

e) Tosoh Corp.

Table 2 Principal experimental conditions for the batch equilibrium adsorption processes

Feed solution	aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$
Volume of feed solution, L_0 [m^3]	20×10^{-6}
Molar concentration of metal in feed solution, C_0 [$\text{kmol} \cdot \text{m}^{-3}$]	0–0.018
pH of feed solution, pH_0	2.5–5 (adjusted by H_2SO_4 solution)
Adsorbent	Mongolian natural zeolite: CLP, MOR, CHA (see Tables 1, 3, and 4 in detail)
Adsorbent particle diameter [m]	smaller than 150×10^{-6}
Ratio of adsorbent mass to feed solution volume, S/L_0 [$\text{kg} \cdot \text{m}^{-3}$]	50
Contacting time [h]	0–240
Contacting temperature [K]	300

Fig. 1 Estimated solubility curves of the heavy metal hydroxides and the relation between the solution pH values and the concentrations of the metals as determined from the adsorption runs

capacities (CEC) of the samples were measured using Method 9081 of the US Environmental Protection Agency (EPA) (Chapman, 1965). Using this method, all the cations present in the original zeolite samples were exchanged with sodium cations using sodium acetate. These sodium cations were again exchanged using ammonium acetate, and the amounts of the sodium cations thus released were determined. The aqueous solutions of the samples used in these characterizations were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (SPS 7800 Series, Seiko Instruments Inc.) in order to determine the concentrations of the metals present in them. Undiluted and diluted versions of commercially available standard solutions of the metals (Wako Pure Chemical Ind., Ltd.) were used to calibrate the spectrometer.

1.2 Batch equilibrium adsorption of heavy metals by the Mongolian natural zeolites

The principal experimental conditions for the batch equilibrium adsorption process are tabulated in **Table 2**. An aqueous solution of analytical grade copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) or manganese sulfate ($\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$) (Wako Pure Chemical Ind., Ltd.) was used as the feed solution, i.e., as the model wastewater, for the adsorption runs. As mentioned previously, the model wastewater mimicked the wastewater from the Oyu Tolgoi copper mine in Mongolia. The mine wastewater also contains copper, zinc, and manganese in the form of sulfates. **Figure 1** shows the approximate solubility curves of the electrically neutral hydroxides $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, and $\text{Mn}(\text{OH})_2$ in an aqueous solution as estimated from the solubility products of these hydroxides and the ion product of water. Depending on the pH of the feed solution, the cations of Cu, Zn, and Mn bond with the hydroxide ion and precipitate out when the pH is suitably high. This is because the solubilities of the hydroxides of these metals are quite low. Among the

three metals, Cu precipitates at the lowest pH, and is followed by Zn and then Mn. In order to further study the effect of the pH on the adsorption of these metals, the pH of the feed solution, pH_0 , was varied. This was done by adding aqueous sulfuric acid (H_2SO_4) solution.

The feed solution and the adsorbent were placed in a $100 \times 10^{-6} \text{ m}^3$ Erlenmeyer flask that had a screw cap and were shaken in a constant-temperature bath (either Thomastat T-2S or T-N22S, Thomas Kagaku Co., Ltd.). After being shaken, the solution and the adsorbent were separated via simple gravitational filtration using commercially available filter paper (No.3, Toyo Roshi Kaisha, Ltd.).

In addition, some of the shaken adsorbent-containing solution was also filtered using commercially available hydrophilic membrane filter ($0.20 \times 10^{-6} \text{ m}$; DISMIC-25AS, Toyo Roshi Kaisha, Ltd.). Both this solution and the original feed solution were then analyzed by ICP-AES and tested with a pH meter (HM-26S with a GST-5311C electrode, DKK-TOA Corp.) in order to determine the elemental concentrations of the metals in the solutions and the pH of the solutions, respectively.

2. Results and Discussion

2.1 Characterization of the Mongolian Natural Zeolites

On the basis of the results of the XRD analyses, it was confirmed that the zeolite samples used in this study comprised CLP, MOR, and CHA. This was in keeping with the results of a previously reported study (Bolortamir and Egashira, 2008). The surface areas of the particles of the zeolite samples measured in this study are compared with their previously reported values in Table 1. Except for mordenite, the surface areas determined in this study using the BET method were almost the same as those previously reported. The surface area of the mordenite particles as determined in this study was smaller than that reported earlier. Although the exact cause of this discrepancy is not known, it might, among other things, be due to inhomogeneities in the two mordenite samples arising from the presence of impurities. Nevertheless, it was clear that the surface areas increased in the following order: mordenite, followed clinoptilolite, and then chabazite. The surface areas of the mordenite particles both as determined in this study as well as by Bolortamir and Egashira (2008) were much smaller than that for pure mordenite. This was further proof of the presence of impurities. **Table 3** shows the ratios of concentrations of the various elements on the surfaces of the zeolite samples to that of aluminum (X_i , with i denoting the various elements), as

Table 3 Molar ratios of element i to aluminum in the natural zeolite samples (X_i), those of silicon to aluminum in pure zeolites (X_{Si}^p), and ratios of X_{Si} to X_{Si}^p

	Clinoptilolite (CLP)	Mordenite (MOR)	Chabazite (CHA)
X_{Al} [-]	1	1	1
X_{Si} [-]	7.88	9.28	8.87
X_S [-]	0.206	0.245	0.390
X_K [-]	1.41	2.24	1.28
X_{Ca} [-]	0.495	3.98	0.749
X_{Ti} [-]	0.114	0.120	0.0183
X_{Mn} [-]	0	0	0.0583
X_{Fe} [-]	0.831	0.409	0.465
X_{Si}^p [-]	5.0	5.0	1.4–4.0
X_{Si}/X_{Si}^p [-]	1.6	1.9	2.2–6.3

Table 4 Cation exchange capacities of the natural zeolite samples (CEC), those of pure zeolites (CEC^p) (Baerlocher and McCusker, 2012), and their ratios (CEC/CEC^p)

	Clinoptilolite (CLP)	Mordenite (MOR)	Chabazite (CHA)
Natural zeolite sample, CEC [kmol·kg-Zeo ⁻¹]	62×10^{-5} – 76×10^{-5}	48×10^{-5} – 69×10^{-5}	31×10^{-5} – 43×10^{-5}
Pure zeolite, CEC ^p [kmol·kg-Zeo ⁻¹]	177×10^{-5}	226×10^{-5}	262×10^{-5} – 444×10^{-5}
Ratios, CEC/CEC ^p [-]	0.35–0.43	0.21–0.31	0.07–0.16

determined by EDX. The molar ratios of Si to aluminum (X_{Si}^p) on the surfaces of pure zeolites samples as well as the ratio of X_{Si} to X_{Si}^p are also given in the table. For every zeolite, the X_{Si} value was greater than the X_{Si}^p value. Therefore, on the basis of these results, it could be surmised the zeolite samples contained substantial amounts of impurities such as quartz, sanidine, and muscovite.

The cation exchange capacities (CEC) of the natural zeolites as determined in this study and those of pure zeolites (CEC^p) (Baerlocher and McCusker, 2012) are given in **Table 4**. The cation exchange capacities of the natural zeolites were lower than those of their pure counterparts. This was true for all the natural zeolites and was because X_{Si} was greater than unity for all the natural zeolites. That is to say, in all the natural zeolites, the molar concentration of aluminum was lower than that of silicon, as shown in Table 2. Table 2 and Table 3 also show the ratios of X_{Si} to X_{Si}^p and those of CEC to CEC^p, respectively. The CEC/CEC^p ratio increased with a decrease in the X_{Si}/X_{Si}^p ratio. This observation could qualitatively explain the fact that higher the aluminum content in a zeolite, the higher was its cation exchange capacity.

2.2 Batch Equilibrium Adsorption of Heavy Metals by Mongolian Natural Zeolite

Since the change in the volume of the feed solution after adsorption was negligible, the material balance relationship for the metals could be written as follows:

$$L_0 \cdot C_{i,0} = L_0 \cdot C_i + S \cdot q_i \quad (1)$$

and the fraction of metal i , that was removed, Y_i , was defined by the following equation:

$$Y_i = (C_{i,0} - C_i) / C_{i,0} \quad (2)$$

where L_0 denotes the volume of the feed solution, S is the mass of the adsorbent (the natural zeolite being investigated), $C_{i,0}$ and C_i are the molar concentrations of the metal i in the feed solution and that in the solution after adsorption, respectively, and q_i represents the number of moles of the metal adsorbed per unit mass of the zeolite. The factor $S \cdot q_i$ in Eq. (1) included the amount of heavy metal i that precipitated in the form of its hydroxide. The amount of metal i adsorbed, q_i , was obtained by substituting the volume of the feed solution, L_0 , the mass of the zeolite, S , and the concentrations of the metal in the solutions, $C_{i,0}$ and C_i , in Eq. (1).

The isotherm representing the adsorption of metal i on a zeolite was represented by the Langmuir equation as follows:

$$q_i = q_i^* \cdot K_{L,i} \cdot C_i / (1 + K_{L,i} \cdot C_i) \quad (3)$$

The Langmuir equation was considered as this equation is widely used and is easy to apply, although it should be noted that some of the heavy metals precipitated in the form of their hydroxides during some of the runs.

It took a relatively long time, up to 240 h, to attain equilibrium between the solution and the adsorbent. This was especially true in the cases where the concentration of the heavy metals was high. Therefore, keeping this fact in mind, all later adsorption runs were carried out for 240 h.

The pH values of the equilibrium solutions after adsorption (represented by pH) are plotted against those of the feed solutions (pH₀) in **Figure 2**. The pH values of the equilibrium solutions, which were

initially in the acidic range, increased after the addition of the natural zeolites to the solutions. This was the case even there were no metal cations in the feed solution and was owing to the adsorption of the hydrogen ions by the zeolites. Thus, it was found that the natural zeolites could help adjust the pH of the wastewater from the mines to appropriate levels. The pH values of the equilibrium solutions increased in the following order: clinoptilolite, followed by chabazite, and then mordenite. In addition, the pH values decreased with an increase in the concentrations of metal cations in the feed solution ($C_{i,0}$). The pH was also independent of the metal cation present in the solution.

The isotherms of the various heavy metal-zeolite combinations investigated in this study are shown in **Figure 5**, and the Langmuir parameters for these adsorption isotherms are summarized in **Table 5**. The metal that was adsorbed the most was copper and the adsorbent that adsorbed the most amount of metal, as

estimated by Eq. (1), was mordenite. The amount of copper adsorbed at saturation, q_{Cu}^* , was higher than those of the other metals. In particular, in the case of the removal of copper with mordenite, the Langmuir parameters could not be calculated, since the copper in the solution was removed completely. This was mainly due to the removal of Cu by the precipitation of its hydroxide. **Figure 6** shows the relation between cation exchange capacity of a sample zeolite and the amount of the metal i adsorbed at saturation, q_i^* , in the cases where precipitation did not take place. The value of q_i^* was larger at higher value of pH; it increased with an increase in the CEC of the zeolites; and, finally, it was independent of the metal present in the solution. It is possible that zinc and manganese are adsorbed on the same adsorption sites and may be exchanged with the cations of the elements present in original zeolite samples, such as those detected by EDX analysis and listed in Table 3. The adsorption coefficient in the Langmuir equation represented the affinity between the adsorbate and the adsorption sites, and the adsorption coefficient for zinc, $K_{L,Zn}$, was larger than that for manganese, $K_{L,Mn}$, as can be seen from Table 5. This was mainly attributable to the difference in the respective hydrated ionic radii of the metals: the hydrated ionic radii of zinc and manganese were 4.3×10^{-10} m and 4.38×10^{-10} m, respectively (Nightingale, 1959). In general, the $K_{L,i}$ value of the metal with the larger hydrated ionic radius was greater.

Conclusion

Since the molar ratios of aluminum to silicon for the Mongolian natural zeolites used in this study were lower than those of pure zeolites, it could be surmised that the natural zeolite samples contained substantial amounts of impurities. The cation exchange capacities of the natural zeolite samples increased with an increase in the aluminum content in the zeolite sample. That is to say, the samples with higher concentrations of aluminum exhibited higher

Fig. 5 Comparisons of the adsorption isotherms for various heavy metal-zeolite combinations

Fig. 6 Relation between cation exchange capacity (CEC) and the amount adsorbed at saturation (q_i^*) in cases where precipitation did not take place (The CEC values in this figure are the averages of the highest and lowest values given in Table 4)

cation exchange capacities. The natural zeolites could adsorb and remove copper, zinc, and manganese from aqueous solutions modeled on mine wastewater, and could also adjust the pH levels of these solutions. The precipitation of heavy metals in the form of their respective hydroxides due to the addition of the

Table 5 Langmuir parameters for the various adsorption isotherms

Metal, i	pH ₀	Langmuir parameter	Clinoptilolite (CLP)	Mordenite (MOR)	Chabazite (CHA)
Copper, Cu	2.5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00016	-	0.00013
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	23000	-	71000
	3 ~ 5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00020	-	0.00018
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	32000	-	10000
Zinc, Zn	2.5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00014	0.00083	0.00007
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	1700	980	2500
	3 ~ 5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00015	0.00084	0.00011
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	5600	2000	8500
Manganese, Mn	2.5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00013	0.00017	0.00011
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	1900	50	430
	3 ~ 5	q_i^* [kmol·kg-Zeo ⁻¹]	0.00015	0.00017	0.00012
		$K_{L,i}$ [m ³ ·kmol ⁻¹]	2100	110	320

natural zeolites also aided the removal of the metals. The amounts of the heavy metals adsorbed at saturation as estimated by the Langmuir equation were almost the same for all the metals. In addition, these amounts increased with the pH of the feed solution as well as with the cation exchange capacities of the natural zeolites. Finally, it was also found that the adsorption coefficient in the Langmuir equation was correlated with the hydrated ionic radii of the heavy metals being investigated for removal.

Nomenclature

C_i	=	molar concentration of metal i in aqueous solution	$[\text{kmol}\cdot\text{m}^{-3}]$
CEC	=	cation exchange capacity of a zeolite	$[\text{kmol}\cdot\text{kg-Zeo}^{-1}]$
$K_{L,i}$	=	adsorption coefficient of metal i in the Langmuir equation	$[\text{m}^3\cdot\text{kmol}^{-1}]$
L	=	volume of the aqueous solution	$[\text{m}^3]$
pH	=	pH of the aqueous solution	
q_i	=	number of moles of metal i adsorbed per unit mass of adsorbent	$[\text{kmol}\cdot\text{kg-Zeo}^{-1}]$
q_i^*	=	number of moles of metal i adsorbed at saturation per unit mass of the adsorbent in the Langmuir equation	$[\text{kmol}\cdot\text{kg-Zeo}^{-1}]$
S	=	mass of the adsorbent	$[\text{kg}]$
X_i	=	molar ratio of element i to Al on the surface of a zeolite sample as determined by EDX	$[-]$
Y_i	=	fraction of metal i removed	$[-]$
<Subscript>			
0	=	feed solution	
Al	=	aluminum	
Ca	=	calcium	
Cu	=	copper	
Fe	=	iron	
i	=	element or metal i	
K	=	potassium	
Mn	=	manganese	
S	=	sulfur	
Si	=	silicon	
Ti	=	titanium	
Zn	=	zinc	
<Superscript>			
p	=	pure zeolite	

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