Adsorption Properties of Heavy Metals from Aqueous Solution by Mongolian Natural Minerals

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Abstract

The adsorption properties of heavy metals, such as copper(II), zinc(II), lead(II) and cadmium(II), and also arsenic(V) from aqueous solution were investigated using natural zeolite and clay mineral produced from Mongolia. The chemical structure of the zeolite is clinoptilolite zeolite, which is $(Ca_{1.8}Mg_{1.6}Na_{4.24}K_{28})Al_{6.59}Si_{29.41}O_{72}H_2O_{28.64}$, and the clay mineral was albite, which is $Na(AlSi_3O_8)_6$. The natural clinoptilolite zeolite (MNZ) and albite (ALB) were adsorbed all heavy metals. The adsorption order of heavy metals with on MNZ and ALB was almost same as $Pb^{2+} >> Cu^{2+} > Cd^{2+} = Zn^{2+}$. The adsorption amount of heavy metals with MNZ was higher than that with ALB. The natural ALB has high ability to adsorb arsenic from aqueous solution compared with MNZ. By the modification of magnesium oxide, the adsorption amount of arsenic with MNZ successfully increased, however ALB was not affected.

Keywords: Adsorption, Heavy metals, Natural zeolite, Albite

1. INTRODUCTION

Nowadays, heavy metal pollution is increasing dramatically in water sources which mostly depends on anthropogenic activity. The most common methods for the removal of heavy metals are ion exchange and chemical precipitation (Ali and El-Bishtawi 1996). The development of adsorbent originated from low-cost raw materials with high removal efficiency is important to facilitate the application of adsorption process for heavy metal removal.

Recently natural zeolites have been intensively studied because of their applicability of removing trace heavy metal ions from aqueous solutions by ion exchange phenomenon (Peric et al. 2004). Thus, the abundance of natural zeolites in many countries provides low-cost adsorbent materials by ion exchange process.

Mongolia has plenty of natural zeolite source. However, adsorption properties and studies of Mongolian natural zeolite are not so many reported. Egashira et al. reported that study about the removal of heavy metals from mine wastewater by using Mongolian natural zeolites (Egashira et al. 2013).

In this study, we investigated adsorption properties of Mongolian natural zeolite and clay mineral for heavy metal removal.

2. EXPERIMENTAL

2.1 Materials

The natural zeolite and clay mineral samples used in this study are from Mongolia (Dornogovi province, Tushleg deposit). All samples were used in unmodified natural state and modified state described below section. Prior to modification, Mongolian natural zeolite and clay minerals were washed with distilled water of pH 6.02 by several times, and dried at 110°C

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for 4 h.

The heavy metal standard solution of 1000 mg/l (ICP multi-element standard solution IV, Merck, Germany) and arsenate standard solutions of 100 mg/l (Arsenate (V) from NMIJ, National metrology institute of Japan, AIST) were used as initial stock solutions diluted by distilled water at each desired concentration.

2.2 Modification methods

Mongolian natural zeolite and clay mineral samples were modified with supersaturated magnesium oxide according to Mejia et al. (2009). The modified samples were obtained by mixture of 30 ml 2N HNO_3, 3 g of magnesium oxide powder and washed sample was stirred with magnet stirrer for 20h at room temperature. The solid and aqueous phase was separated by filter paper (125 mm, 5C). Afterwards, modified MNZ (M-MNZ) and ALB (M-ALB) samples were washed with distilled water of pH 6.13 and dried at 110°C for 2 h.

2.3 Analysis of minerals with X-ray diffraction

The mineral samples identification was determined by XRD analysis via 2 theta degree (X'Pert PRO X-ray diffractometer). The measurements were performed by applying 40 mA current and 45 kV voltages.

2.4 Batch sorption studies

The experimental condition of the batch sorption studies was shown in Table 1. The pH value was adjusted by 1M NaOH and 1M HCl solutions. Before and after adsorption pH value is both measured via Horiba pH meter F-21. Initial and final concentrations were determined by Shimadzu, ICPS-8100. All results measured twice and the arithmetic average of the two analyses results was reported in this study.

Table 1 Experimental conditions of zeolite sample's adsorption study

Stock solutions	Multi-element standard and As (V) solutions
Concentration of feed solution, [mg/L]	1-20
pH of stock solution, pH_0	3, 4, 6, 7, 9
Ratio of adsorbent mass and stock solution volume [kg/m^3]	0.0033
Contacting time, [h]	24 h
Temperature, K	303

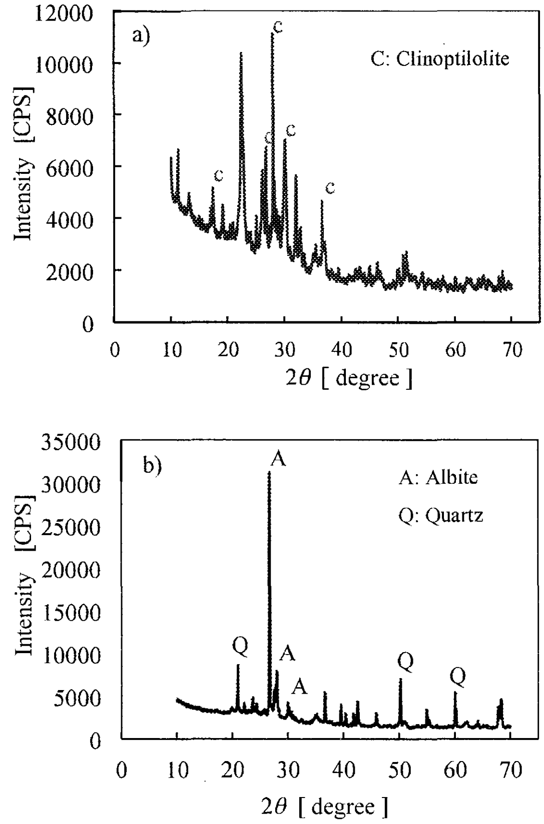

Fig. 1 XRD analysis of the Mongolian minerals a) MNZ, b) ALB

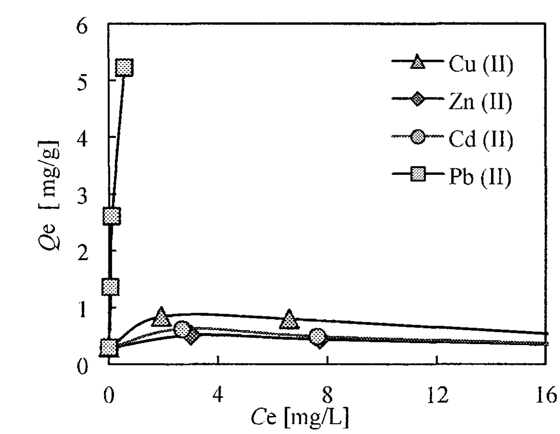

Fig. 2 Adsorption isotherm of heavy metals on MNZ

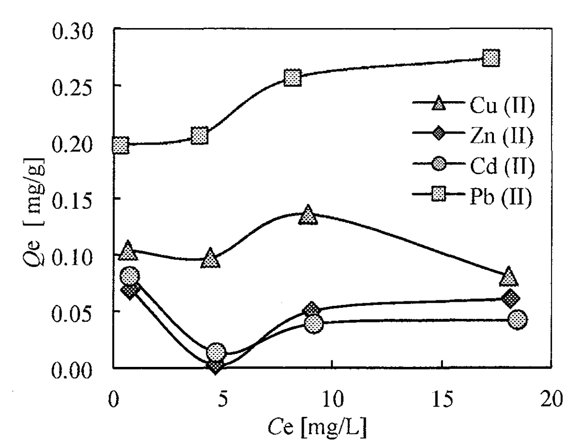

Fig. 3 Adsorption isotherm of heavy metals on ALB

Adsorption capacity and arsenic uptake were calculated following expressions:

$$\text{Adsorption percentage} = (C_i - C_f) \cdot 100/ C_i \, [\%] \quad (1)$$

$$Q_e = (C_i - C_f) \cdot V/m \, [\text{mg/g}] \quad (2)$$

Where Q_e is the adsorption amount which adsorbed milligram per gram of the adsorbent, C_i and C_f are initial and final concentrations of metals (mg/L) in the solution, V is volume of the feed solution and m is the adsorbent weight added into the solution.

3. Results and Discussions

3.1 Characterization analysis the minerals

The mineral samples were identified by XRD analysis. The natural zeolite confirmed as clinoptilolite type zeolite and its empirical formula was $(Ca_{1.8}Mg_{1.6}Na_{4.24}K_{28})Al_{6.59}Si_{29.41}O_{72}H_2O_{28.64}$ The clay was identified as albite low, sodium tecto-alumotrisilicate, and its empirical formula with $Na(AlSi_3O_8)$. It also contains quartz and potassium sodium rubidium tecto-alumosilicate.

3.2 Adsorption of heavy metals on MNZ and ALB

The adsorption of heavy metals (Cu, Zn, Cd and Pb) with the unmodified samples, MNZ and ALB, was carried out at initial concentrations 1, 5, 10, 20 mg/L, respectively. Figure 2 and 3 shows heavy metals uptake of MNZ, ALB samples. The adsorption order of heavy metals with on MNZ and ALB in unit of mg/g was: $Pb^{2+} > Cu^{2+} > Cd^{2+} = Zn^{2+}$. Same result was observed by Qiu et al., (2009), who used cancrinite-type of zeolite. This result shows that both natural samples tend to adsorb lead and copper ions more to comparing from zinc and cadmium. Egashira et al. (2013) studied removal of heavy metal (Cu, Zn and Mn) by using Mongolian natural zeolite. The natural zeolite used in this study shows lower adsorption capacity than that of the reported result (Egashira et al. 2013) that comparing between adsorption amounts. In the further study, various modifications would be needed to increase the adsorption capacity of MNZ.

3.3 Adsorption of arsenate ion on M-MNZ and M-ALB

The adsorption experiments of arsenate ion with the modified and unmodified samples were carried out by taking 0.05-0.3g adsorbent and 15-30 ml of the arsenate stock solution under agitation. The results are summarized in Table 2. The unmodified ALB showed higher adsorption amount than that of MNZ. Though the modified MNZ (M-MNZ) increased the adsorption amount, the modified ALB (M-ALB) was not changed and almost same with the unmodified one. For determining arsenate adsorption capacity, which increased the stock solution volume and decreased the adsorbent mass, the arsenate adsorption amount with M-MNZ still increased from 0.041 to 0.569 mg/g. This suggests the modification with magnesium oxide is effective to only MNZ.

Table 2 Result of arsenate adsorption on M-MNZ and M-ALB

	Sample	Ratio of sample mass to volume, [kg/m³]	Arsenate adsorption [mg/g]	Adsorption percentage [%]
MNZ	Unmodified	0.02	0.018	36.0
	Modified	0.02	0.041	90.8
		0.001	0.569	97.3
ALB	Unmodified	0. 02	0.047	96
	Modified	0.02	0.048	97.4
		0.001	0.404	69.1

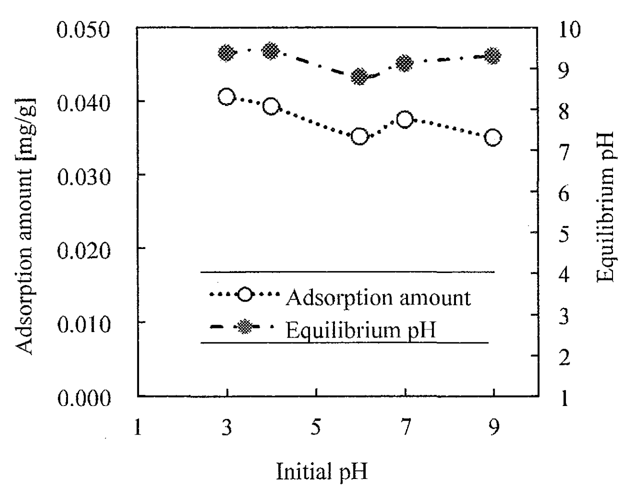

Fig 4. Effect of solution pH on arsenic adsorption by M-MNZ

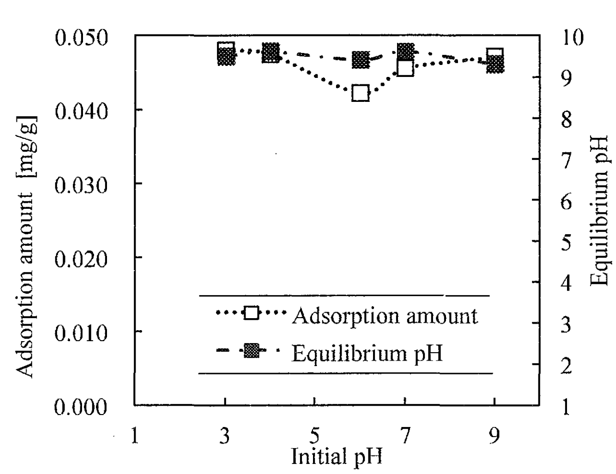

Fig 5. Effect of solution pH on arsenic adsorption by M-ALB

3.4 The effect of pH on the arsenic adsorption

The effect of pH on the arsenic adsorption was carried out to evaluate the removal efficiency of M-MNZ and M-ALB at the pH range around 3-9. Fig 4 and 5 shows the effect of initial pH on arsenic adsorption amount and the equilibrium pH. After adsorption process, all equilibrium pH values in the solution were shifted to 9.3 - 9.7 in M-ALB and 8.7 - 9.5 in M-MNZ. The higher equilibrium pH gave the higher adsorption performance in both samples.

4. Conclusions

The adsorption properties of Mongolian natural zeolite and clay minerals for removal of heavy metals (copper, zinc, lead and cadmium) and arsenic were evaluated. The samples were characterized by XRD as to be clinoptilolite and albite, respectively.

MNZ and ALB samples were adsorbed heavy metals from aqueous solution without modification. It confirms that natural zeolite and albite has the ability of heavy adsorption. In both MNZ and ALB, heavy metals adsorbing selectivity order was $Pb^{2+} >> Cu^{2+} > Cd^{2+} = Zn^{2+}$.

ALB shows higher adsorption amount of arsenic than that of MNZ. After modification of MNZ with supersaturated magnesium oxide, the adsorption amount of arsenic was increased to from 0.018 to 0.569 mg/g while the adsorption efficiency was 97.3 %. The modification of MNZ was quite effective for the arsenic adsorption.

After arsenic adsorption with M-MNZ and M-ALB, equilibrium pH increased at around 9. In this pH range, the arsenate ion was effectively adsorbed by M-MNZ and M-ALB.

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