Adsorption of Trivalent Chromium in Aqueous Solution Using Natural Zeolite

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1. Introduction

In developing countries, water resource pollution by heavy metals such as chromium from industrial wastewater is serious problem. In Mongolia, tannery effluent including chromium causes water pollution. Since leather industry is important industrials in Mongolia economical water quality improvement technique is needed.

Nowadays, in general, trivalent chromium (Cr (III)) is used for chromium tanning process. However, some small tanneries in Mongolia illegally use old method in which hexavalent chromium (Cr (VI)) is used. Cr (VI) is high toxic and causes diseases. Many researches to remove Cr (VI) have been conducted and in some cases zeolite is used as adsorbent. Since natural zeolite occurs in Mongolia, it is supposed that using Mongolian natural zeolite as adsorbent is economical. Natural zeolite can not remove Cr (VI) anion since it posses a net negative charge resulting from isomorphic substitution of cations in the crystal lattice. Therefore natural zeolite is modified with surfactant such as HDTMA[1] and BaCl2[2] and zeolite with modification can adsorb Cr(VI).

Although Cr (III) is slightly less toxic than Cr (VI), it is also should be removed. Japanese tannery use only Cr (III) for chromium tanning and there are regulations about amount of Cr atom remained in wastewater. In Japanese large tannery, the precipitation of Cr (III) by changing pH and so on was used to remove Cr (III).

Since Cr (III) exists in aqueous solution as a cation, this can be adsorbed by natural zeolite without modification[3]. On the other hand, when Cr (III) should be removed together with Cr (VI), Cr (III) is necessary to be adsorbed by natural zeolite with any modification which can adsorb Cr (VI).

This study tried to remove Cr (III) from aqueous solution by adsorption using Mongolian natural zeolite. The adsorption performances were discussed in terms of the effects of modification, pH of the solution, zeolite samples, and so forth.

2. Experimental

Table 1 shows the Mongolian natural zeolite samples used here. After appropriate pretreatments, these samples were used without modification or with modification by BaCl2 aqueous solution[4],[5]. The principal conditions for adsorption runs are shown in **Table 2**. Cr (NO3)3×9H2O was dissolved into ion-exchanged water to prepare the initial solution for batch adsorption run. The pH of the initial solution was adjusted by 0.1 N HCl or NaOH. Thus prepared solution and the adsorbent were brought into contact in a Erlenmeyer flask with screw cap and were shaken in a constant temperature bath for 72 hours which was long enough for equilibration[2]. After contacting, the solution and adsorbent were separated into each other by simple filtration. The initial solution and that after adsorption were analyzed by ICP spectrophotometer (SPS-7800 Plasma Spectrometer, SII - Seiko Instruments Inc.) and pH meter (NM-26S, TOA Electronics Ltd.) to determine the concentration of chromium atom and the pH of solution, respectively.

Table 2   Principal conditions for adsorption run

Initial solution	aq. solution of $Cr(NO_3)_3 \times 9H_2O$
Mass of initial solution, L [g]	50
Mass fraction of Cr atom in initial solution, $x_{Cr,0} \times 10^6$ [−]	10~100
pH of initial solution, pH_0	2~ 5.5
Adsorbent	Mongolian natural zeolite (see Table 1) with and w/o modification by $BaCl_2$
Mass ratio of adsorbent to initial solution, S/L [−]	0.01
Contacting time [h]	72
Contacting temperature [K]	303

3. Results and Discussion

The material balance relationship of Cr atom can be written as,
$$L \cdot x_{Cr,0} = L \cdot x_{Cr} + S \cdot q_{Cr} \qquad (1)$$
where x_{Cr} is the mass fraction of Cr atom, q_{Cr} is the mass of Cr atom adsorbed per unit mass of zeolite after adsorption, S is the mass of adsorbent and L is the mass of solution. From this relationship with S, L, x_{Cr0}, and x_{Cr}, q_{Cr} was obtained.

3.1 pH of aqueous solution of Cr (III)
Figure 1 shows the pH of initial solutions before adjusting pH. The pH of the solutions were from 3 to 4 in the range of $10^{-5} \sim 10^{-4}$ of $x_{Cr,0}$.

3.2 Effect of modification on adsorption performance
The adsorption isotherms are shown in **Figure 2**. Adsorption capacity increased in the order of NZ-4, 2, 3, and 1. NZ-1 showed highest adsorption capacity, about 100% Cr atom was removed except the cases of highest initial concentration which pH_0 was 2 (**Figure 2 (a)**).

Surface modification did not affect the adsorption performance of natural zeolite. **Figure 2** shows that modified
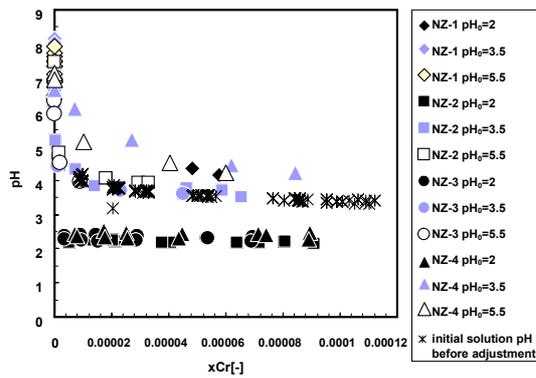
Table 1   Principal information about studied Mongolian natural zeolites[2],[6]

Sample	Deposit	Depth [m]	Sampling Date	Color	Base component (by XRD)	BET surf. area [$m^2 \cdot g^{-1}$]	BET pore volume $\times 10^6$ [$m^3 \cdot g^{-1}$]
NZ-1	Tsagaan Tsav	60	09/2004	green grey	mordenite etc.	26	0.041
NZ-2	Tsagaan Tsav	60	09/2004	grey	quartz etc.	36	0.065
NZ-3	Urgon	150	10/2006	light grey	clinoptilolite etc.	43	0.096
NZ-4	Tsagaan Tsav	150	12/2005	light grey	chabazite etc.	160	0.082

Fig.1 The change of pH before and after adsorption.

zeolite could absorb Cr atom similarly to no modified zeolite. The BaCl$_2$ modified zeolite could remove Cr (III) and Cr (VI) together at the same time.

3.3 Effect of pH on adsorption performance

Figure 1 shows the pH of initial solutions before and after adjustment and pH of equilibrium. In the case of pH$_0$ adjusted to 3.5 and 5.5, equilibrium pH returned to pH before adjustment. However, equilibrium pH of several samples that pH$_0$ adjusted 2 did not change expect the case of NZ-1.
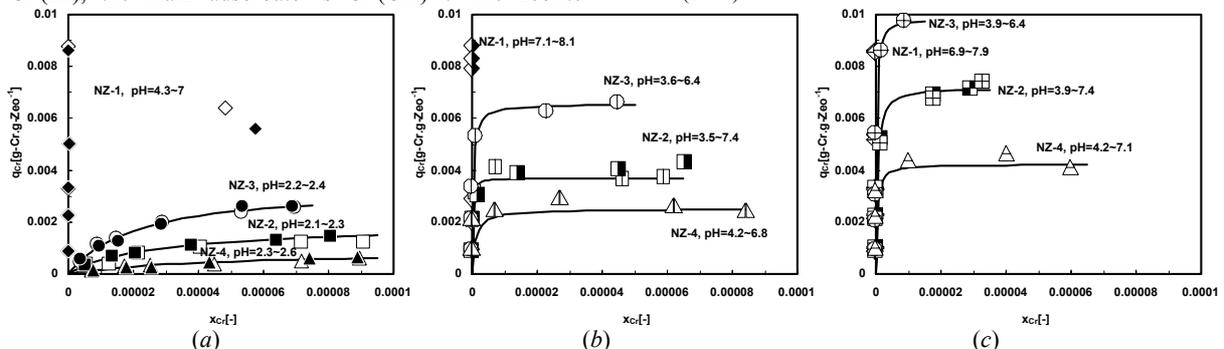
In the case of NZ-2, 3, and 4, the adsorption capacity became higher according to increase of initial solution pH. Equilibrium pH slightly increased to range 2.1-2.5 when pH$_0$ was adjusted to 2. In other cases, pH increased to range 6.9-7.5 at lowest initial solution concentration, range 3.5-4.2 at highest. In the case of NZ-1, expect highest initial solution concentration that pH$_0$ was adjusted 2, about 100% Cr atom was adsorbed. Equilibrium pH increased to range 6.5-8.1, only the case of highest initial solution concentration that pH$_0$ was adjusted 2 increased approximately 4. The adsorption performance was higher at higher pH range, especially around 6. According to this result and the hydrolysis of Cr (III)[7], the main adsorbate was Cr (OH)$^{2+}$.

3.4 Comparison of adsorption by Langmuir equation

The adsorption isotherm, in case of NZ-2, 3, and 4, could be described by Langmuir equation as shown by solid curves in **Figure 2**. K_L and q_{Cr}* was calculated by Langmuir equation as shown in **Table 3**. The relations between q_{Cr}* and equilibrium pH at highest Cr concentration are shown in **Figure 3**. Saturated adsorption capacity became higher according to increase of equilibrium pH.

4. Conclusion

The effect of pH on the adsorption isotherm of Cr (III) in case of unmodified zeolite could adsorb Cr (III) and the hydrolysis of Cr (III), the main adsorbate is Cr (OH)$^{2+}$. The zeolite

Table 3 Langmuir constant and saturated adsorption capacity of the experimental data

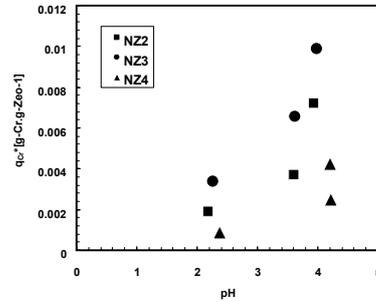| Sample	pH$_0$	q_{Cr}* [g-Cr·g-Zeo^{-1}]	K_L [-]
NZ-2	2	1.9×10^{-3}	2.6×10^{-5}
	3.5	3.7×10^{-3}	1.1×10^{-7}
	5.5	7.2×10^{-3}	4.3×10^{-7}
NZ-3	2	3.4×10^{-3}	2.1×10^{-5}
	3.5	6.6×10^{-3}	3.3×10^{-7}
	5.5	9.9×10^{-3}	2.0×10^{-7}
NZ-4	2	8.8×10^{-4}	4.2×10^{-5}
	3.5	2.5×10^{-3}	1.0×10^{-6}
	5.5	4.2×10^{-3}	3.4×10^{-7}

Fig.3 The relation between q_{Cr}* and equilibrium pH

modified with BaCl$_2$ could also adsorb Cr (III), that is, the modified zeolite would remove Cr (III) together with Cr (VI) from wastewater at the same time. The modification of zeolite did not affect the adsorption isotherm. The adsorption capacity increased in the order of NZ-4, 2, 3, and 1.

Nomenclature

K_L	=	Langmuir constant	[-]
L	=	mass of solution	[g]
q_{Cr}	=	mass of Cr atom adsorbed per unit mass of zeolite	[g-Cr·g-Zeo^{-1}]
q_{Cr}*	=	saturated adsorption capacity	[g-Cr·g-Zeo^{-1}]
S	=	mass of adsorbent	[g]
x_{Cr}	=	mass fraction of Cr atom	[-]

Literature Cited

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Fig.2 Adsorption isotherm of Cr(III) on Mongolian natural zeolite: (*a*) pH$_0$=2; (*b*) pH$_0$=3.5; (*c*) pH$_0$=5.5