EFFECT OF MODIFICATION OF MONGOLIAN NATURAL ZEOLITES ON ADSORPTION OF CHROMIUM FROM AQUEOUS SOLUTION

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Abstract

Removal of chromium (Cr (III)) as well as hexavalent chromium (Cr (VI)) from tannery wastewater at same time by adsorption using Mongolian natural zeolite was studied in terms of the characteristics, modification, and chromium adsorption performance of the zeolite.

The cation exchange capacity of the zeolite ranged from 37×10^{-3} to 144×10^{-3} eq·g^{-1}. From the results of phase identification and elemental analysis of the zeolite after modification run, the zeolite was not decomposed and was modified successfully. The zeolites modified by Ba^{2+}, Cu^{2+}, and HDTMA-Br could adsorb Cr (III) as well as the unmodified one could. The higher pH gave the higher adsorption ability, similarly to the adsorption of Cr (VI). Consequently, this adsorption method with Mongolian natural zeolite was proposed to remove Cr (III) together with Cr (VI) from tannery wastewater at same time.

Keywords: Chromium, Adsorption, Mongolian Natural Zeolite, Zeolite Modification, Tannery Wastewater

1. Introduction

Chromium is one of the regulated toxic heavy metals in the environment. Chromium compounds are widely used in industries such as leather tanning, electroplating, manufacturing of dye, paint and paper. Chromium exists in the aqueous solution mainly in two states Cr (III) and Cr (VI). Cr (III) is extensively used in the tanning agent. Although Cr (III) is considerably less toxic than Cr (VI), its disposal as a dissolved species in natural waters or as sludge in soils may pose serious health risks because it can be oxidized to Cr (VI) in the environment [1].

In Ulan Bator, water resource pollution by hexavalent and trivalent chromiums (Cr (VI), Cr (III)) in wastewater from tannery, which is one of the most important industries in Mongolia, becomes serious. In the fact, in Mongolia, there are plenty of natural zeolite deposits, although these resources are not sufficiently exploited and studied yet. The most common, stable and abundant forms are hexavalent (Cr (VI)) and trivalent (Cr (III)) chromiums. There has been various works studying the removal of chromium (Cr) from aqueous solution by adsorption using natural zeolite. The zeolite modified by Ba^{2+} could adsorb and favorably remove Cr (VI), which exists as chromate anion in aqueous solution, whereas the unmodified one could not [1], due to the zeolite surface is charged negatively. On the contrary, Cr (III) forms cation in aqueous solution.

In this study, removal of Cr (III) as well as Cr (VI) from tannery wastewater at same time by adsorption using Mongolian natural zeolite was studied in terms of the characteristics, modification, and chromium adsorption performance of zeolite.

2. Experimental

The natural zeolite samples obtained from Tsagaan Tsav and Urgon deposit in Mongolia. In previous study reported that five kinds of natural zeolite used for modification and adsorption run. These samples have different base components in their content and different porous properties. The detailed information of Mongolian natural zeolites is shown in **Table 1** [1]

The principal conditions of zeolite modification are shown in **Table 2.** The zeolite samples and the aqueous solution of Ba^{2+}[1,2], Cu^{2+}[2], or HDTMA-Br [3] were brought into contact with each other to modify the samples. The modified samples were washed twice and dried. Thus obtained samples with and without modification were kept in a desiccator before in characterization and adsorption. The element composition on the zeolite surface was determined by energy dispersive X-ray fluorescence spectrometry (EDX) and the modification of zeolite samples with Ba^{2+} was characterized by XRD to know that after modification zeolite samples based component. The cation exchange capacities (CEC) of the zeolites were measured by the method of US-EPA Method 9081[4].

The principal conditions of batch adsorption run are summarized in **Table 3**. $Cr(NO_3)_3 \times 9H_2O$ was used as a source of Cr (III). The respective aqueous solutions were analyzed by pH meter and ICP spectrometer.

Table 1 Principal characteristics of Mongolian natural zeolites

Sample	Deposit [1]	Base component (by XRD)[1]	Surface area $[m^2 \cdot g^{-1}]$[1]	Pore volume $[m^3 \cdot g^{-1}]$[1]	Cation exch.cap. (C.E.C.) $[eq \cdot g^{-1}]$
NZ-1	Tsagaan Tsav	mordenite etc.	26	0.041×10^{-6}	74×10^{-3}
NZ-2	Tsagaan Tsav	gismondine etc.	36	0.065×10^{-6}	54×10^{-3}
NZ-3	Tsagaan Tsav	clinoptilolite etc	15	0.027×10^{-6}	100×10^{-3}
NZ-4	Tsagaan Tsav	chabazite etc.	159	0.082×10^{-6}	37×10^{-3}
NZ-5	Urgon	clinoptilolite etc.	43	0.096×10^{-6}	144×10^{-3}

Table 2 Principal conditions of zeolite modification by Ba^{2+}, Cu^{2+}, and HDTMA-Br

Zeolite	Mongolian natural zeolite (see Table 1)
Mass of zeolite [g]	20; 50
Modification solution	aqueous solution of metal cation (Ba^{2+}, Cu^{2+}); surfactant (HDTMA-Br)
Concentration of modifier in modification solution [$mol \cdot m^{-3}$]	0.05×10^3; 0.13×10^3
Volume of modification solution to mass of zeolite [$m^3 \cdot g^{-1}$]	3×10^{-6}; 10×10^{-6}
Temperature [K]	333; 298
Time [h]	168; 24

Table 3 Principal experimental conditions of adsorption run

Feed solution	Aqueous solution of $Cr(NO_3)_3$ x $9H_2O$
Mass of feed solution, L_0 [g]	50
Mass fraction of chromium atom in feed solution, $x_0\times10^6$ [–]	10–100
pH of feed solution, pH_0	2,3.5, 5.5 (Adjusted by HCl and NaOH)
Adsorbent	NZ-1, 2, 3, 4, 5 (without or with mod Ba^{2+}, Cu^{2+}, HDTMA-Br)
Mass ratio of adsorbent to feed solution, S/L_0 [–]	0.01
Contacting time, t [h]	72
Contacting temperature [K]	303

3. Results and Discussion

Table 1 shows the cation exchange capacity (C.E.C) together with the previous results of base component, surface area, and pore volume of the zeolite[1]. The C.E.C ranged from 43×10^{-3} to 144×10^{-3} $eq \cdot g^{-1}$.

Figure 1 shows the comparison between the element compositions on the surface of zeolite with and without modification by Ba^{2+}. The content of Ba^{2+} in the modified zeolite was much higher than that in the unmodified one, similarly to the previous results[1], and the successful zeolite modification could be reconfirmed.

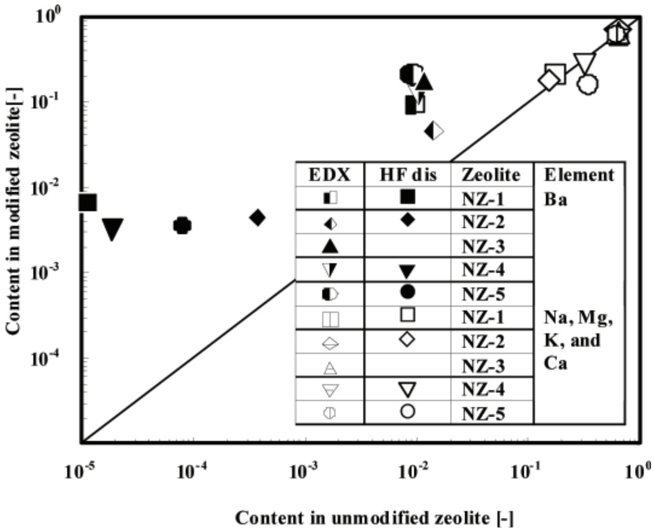

Figure 1 Comparison of element contents between surface of zeolite without and with modification by Ba^{2+}

The result of XRD spectra of natural zeolite samples were before and after modification shown in **Figure 2.** The before and after zeolite modification with Ba^{2+}, the spectra did not changed almost same as unmodified one. The zeolite were not decomposed with the modification solution.

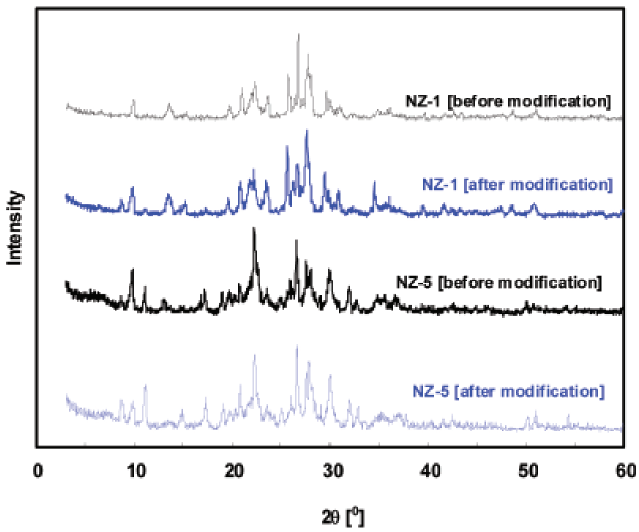

Figure 2 XRD spectra before and after modification of natural zeolite

The adsorbed amount of Cr on zeolite, q, was calculated by the material balance relationship.

Figure 3 shows the effects of modifications on the adsorption isotherms of Cr (III) on the zeolite. The unmodified zeolite could adsorb Cr (III) as expected. Zeolites modified by Ba^{2+}, Cu^{2+}, and HDTMA-Br could also adsorb Cr (III), namely, Cr (III) would be removed by the modified zeolite as well as Cr (VI)[1] at same time. While the modifications with Ba^{2+} and Cu^{2+} did not affect the adsorption performances, the performance of the zeolite modified by HDTMA-Br was lower.

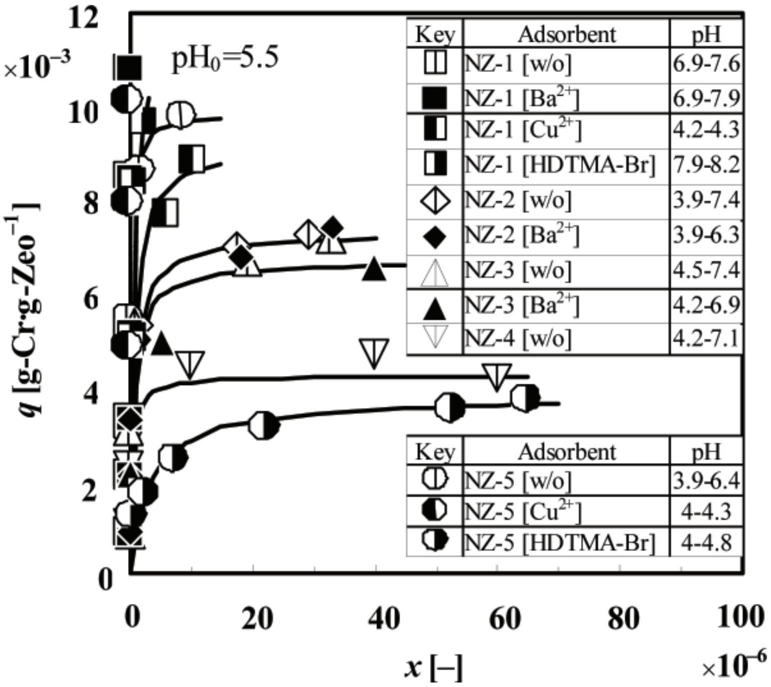

Figure 3 Effect of modification on adsorption isotherm of Cr (III) on Mongolian natural zeolite

In the solution of higher pH in this study, $Cr(OH)^{2+}$ is dominant[5]. The adsorption isotherms were described by Langmuir equation. **Figure 4** shows the saturated adsorption amount, q^*, and the adsorption coefficient, K_L, are plotted the average of equilibrium pH. The q^* and K_L values increased with increasing pH.

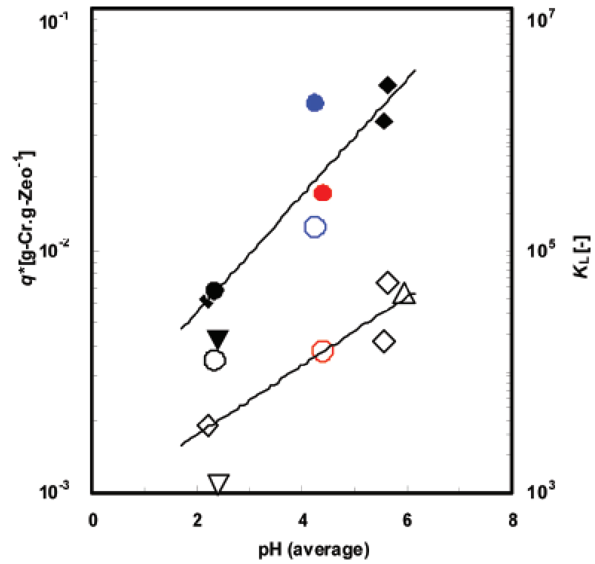

Figure 4 Effect of the pH of equilibrium solution on the saturated adsorption amount, q^*, and adsorption coefficient, K_L, in Langmuir equation

Figure 5 shows the relation between Cr (VI) and Cr (III) adsorption parameters with pH. The K_L adsorption parameters of Cr (III) much higher than that of K_L of Cr (VI)[1]. The q^* parameter were adsorption performances almost same as each other.

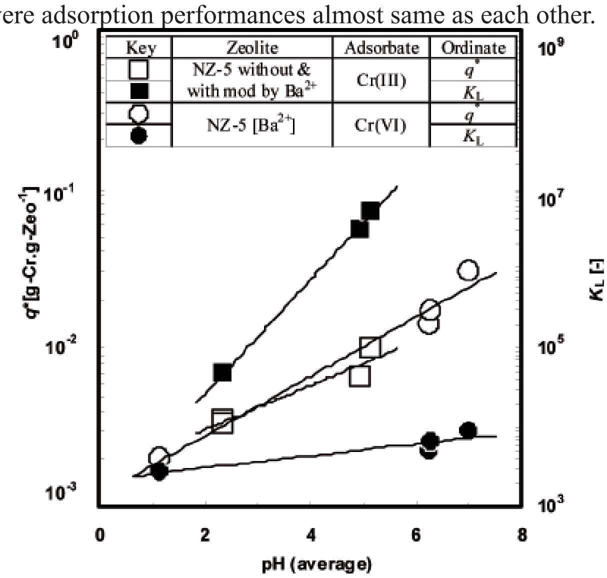

Figure 5 The relations between Cr (VI) and Cr (III) adsorption parameters with pH

4. Conclusions

The cation exchange capacity of the zeolite ranged from 43×10^{-3} to 144×10^{-3} $eq\cdot g^{-1}$. The zeolites modified by Ba^{2+}, Cu^{2+}, and HDTMA-Br could adsorb Cr (III) as well as the unmodified one could. The higher pH gave the higher adsorption ability. The K_L adsorption parameters of Cr (III) are much higher than that of K_L of Cr (VI). The $q*$ parameters adsorption performances almost same as each other.
Consequently, the adsorption using Mongolian natural zeolite was proposed to remove Cr (III) together with Cr (VI) from tannery wastewater at same time.

Nomenclature

K_L = adsorption coefficient in Langmuir equation [–]
L_0 = mass of solution [g]
pH = pH in solution
q = adsorption mass of chromium atom per unit mass of adsorbent [g-Cr·g-Zeo^{-1}]
q^* = saturated adsorption mass of chromium atom per unit mass of adsorbent in Langmuir equation [g-Cr·g-Zeo^{-1}]
S = mass of adsorbent [g]
x = mass fraction of chromium atom in solution [–]

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