Pb AND Cr(VI) REMOVAL USING Fe-LOADED ZEOLITE

Seunghak Lee, Kwanghun Lee, and Junboum Park[†]

School of Civil, Urban & Geosystem Engineering, Seoul National University, Seoul 151-742, Korea

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Abstract : Current research focuses on Pb and Cr(VI) removal in water by a newly developed material having both abilities of sorption and reduction. The material was derived from zeolite modified by ferrous chloride followed by reduction with sodium borohydride. XRF analysis has shown that Fe content in Fe-loaded zeolite ("ZanF") increased by 1.8 times than that of pure zeolite. For the removal of Pb with initial concentration of 2-15 mM, Fe-loaded zeolite showed over 90% removal efficiency, which was similar with that of pure zeolite. During Pb removal desorption of Fe developed in Fe-loaded zeolite was not significantly detected, which indicated that Fe in Fe-loaded zeolite was stable against the cation exchange reaction. For Cr(VI) removal, 0.5 mM of Cr(VI) was rapidly reduced by Fe-loaded zeolite below detection limit within 5 hrs. However, Cr(VI) in pure zeolite maintained constant, which indicated that Fe developed in Fe-loaded zeolite is responsible for Cr(VI) removal observed. From the test results, Fe-loaded zeolite was proven to have high Pb sorption capacity and rapid Cr(VI) reduction ability in a single medium. And Fe-loaded zeolite could possibly find its use in the field applications as permeable reactive barrier for treating the contaminated water simultaneously with cationic and anionic heavy metals.

Key Words : Fe-loaded zeolite, Pb, Cr(VI), Permeable Reactive Barriers(PRBs)

INTRODUCTION

Both natural and synthesized zeolites find uses in industry as sorbents, soil amendments, ion exchangers, and molecular sieves.[1] Especially, natural zeolites exhibited high sorption capacity for inorganic cations including heavy metals,[2,3] and ammonium.[4] Moreover, they were proven to be effective for environmental applications such as permeable barriers for controlling the spread of cation-contaminated groundwater.[5] However zeolites have little or no affinity for anionic species like Cr(VI)(e.g. CrO_4^{2-}), as they possess a net negative structural charge.

To achieve the simultaneous sorption for anionic contaminants with cationic species,

organo-clay or surfactant-modified zeolite (SMZ) has been developed as a novel materials.[1,6,7] SMZ has been reported to sorb inorganic cations and oxy-anions as well as organic compounds from water.[8,9] For these materials, the conformation and quantity of surfactant on the surface are potentially responsible for the ability of materials to retain oxyanions.[10] The admicelles which present the anion exchange site, are formed only when the surfactant concentration in solution exceeds its critical micelle concentration (CMC).

Besides the sorption removal, another effective strategy to treat the anionic species, especially redox-active anionic heavy metals like chromate, is the electrochemical reduction using iron metal (Fe^0).[11,12] Cr(VI) (e.g. CrO_4^{2-}) reduction has been previously studied.[11,13] Those studies reported that Cr(VI) was completely removed at

[†] Corresponding author
E-mail: junbpark@snu.ac.kr
Tel: +82-2-880-8356, Fax: +82-2-875-6933

fairly rapid rate under appropriate conditions and the reaction rate was lowered at high pH value.

In this study, a new material having both abilities of sorption and reduction was developed as a possible alternative to organo-clays or SMZ. The material was derived from zeolite modified by ferrous chloride followed by reduction with sodium borohydride. The potential applicability of Fe-loaded material was verified by performing a series of batch experiments with cationic and anionic heavy metals. Lead was chosen as a cationic heavy metal, and chromate as an anionic heavy metal due to their importance as environmental contaminants. We report here on the removal of two heavy metals with different ionic forms in aqueous solution using a single medium, Fe-loaded zeolite. We suggest the possible field application of Fe-loaded zeolite as an alternative to SMZ.

MATERIAL AND METHODS

Fe-Loaded Zeolite Production Processes

Natural zeolites were obtained from Wangpyo Co. in Pohang, one of the largest zeolite deposits in Korea. Fifty grams of zeolite were stirred with 500 mL of 350 mM Fe(II) solution for 24 hrs at ambient temperature to cause Fe(II) to be introduced into zeolite matrix. Fe(II) solutions were prepared by dissolving the ferrous chloride ($FeCl_2$, extra pure reagent, Yakuri Pure Chemicals Co. Ltd., Japan) in deionized water (18.2 MΩ, milli-Q water, milli pore, USA). Concentration of Fe(II) solution was preliminarily determined by ion-exchange experiments, which can cause the maximum loading of Fe(II) in zeolite. Then, the Fe(II)-sorbed zeolites were washed several times with deionized water, and stirred in 500 mL of 20 mM sodium borohydride ($NaBH_4$, 98%, Sigma, USA) solution for 30 min. The concentration of $NaBH_4$ was calculated based on the following reactions (Eq. 1) to fully reduce the sorbed amount of Fe(II) in zeolite to Fe(0).

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \quad (1)$$
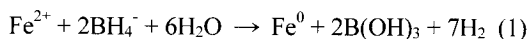
The obtained Fe-loaded zeolite was washed several times with deionized water, and dried in the vacuum dry oven at 90°C for 1hr, and stored in anaerobic condition.

Material Characterization of Fe-loaded zeolite

Chemical composition of Fe-loaded zeolite was investigated with sequential X-ray fluorescence spectrometer (Shimadzu XRF-1700, Japan). Analytical conditions for XRF were 40 KV and 30 mA for electrical potential and current, respectively. Specific surface area of Fe-loaded zeolite was estimated by N_2-BET method.

Lead Removal Experiment

Unit gram of ZanF and 30 ml lead solution were placed in 37 mL-amber tube. Pb solution was prepared by dissolving $Pb(NO_3)_2$ in deionized water, and its initial concentration was ranged from 2 mM to 15 mM. The tubes were shaken at 50 rpm on a vertical rotary shaker for 24 hrs. Parallel experiments were performed with no material (blank), Fe(II)-sorbed zeolite and pure zeolite. After shaking, supernatant was separated from solid by filtering with 0.45 μm-membrane. And the solution was analyzed for pH and residual concentrations of Pb, Fe, and Na.

Chromate Removal Experiment

Three grams of Fe-loaded zeolite and 30 mL of 0.5 mM (equivalent to 26 ppm as Cr(VI)) Cr(VI) solution were placed in 37 mL-amber tube. Cr(VI) solution was prepared by dissolving the potassium chromate (K_2CrO_4) in deionized water. The tubes were shaken on a rotary shaker at 50 rpm for 50 hrs, and each tube was taken at pre-determined time intervals. Duplicates were prepared at each time interval in Fe-loaded zeolite containing system. Supernatants were then separated from solid phase by filtering through 0.45 μm membrane, and residual Cr(VI) concentration and pH of solution were measured.

Chemical Analysis

Pb and Fe concentrations were measured with AAS Vario 6 (analytik jena). Sodium was analyzed by IC (Waters 432) using IC-Pak Cation M/D (3.9 mm × 150 mm). The mobile phase was 0.1 mM EDTA/3.0 mM HNO_3, and flow rate was 1 ml/min. The retention time of sodium was 3.75 min. Cr(VI) concentration was measured with an HPLC (Waters 515). Analysis was conducted at a wavelength of 365 nm and with a flow rate of 0.6 mL/min, a mobile phase of water with 20% acetonitrile (Fisher, optima grade), and a 3.9 mm × 300 mm μ-bondapak C_{18} reverse phase column (Waters). Retention time of chromate was 2.5 minutes, and the linear response was 0.5-240 mg/L based on peak area.

RESULTS AND DISCUSSION

Material Characterization of Fe-loaded Zeolite

X-ray diffraction analysis showed that the zeolites were about 60% clinoptilolite, and the remainder consisted of feldspar, quartz, calcite and illite. Zeolite used has a BET surface area of 27 m^2/g.

To estimate the change in chemical composition of materials by material production process, X-ray fluorescence (XRF) analysis was performed for the materials found in each process. Table 1 shows the XRF results. In Fe-loaded zeolite and Fe(II)-sorbed zeolite, Fe amount increased to 2.77 wt% from 1.50 wt% of pure zeolite. But the difference in Fe amount of Fe-loaded zeolite and Fe(II)-sorbed zeolite was not significant because changing the charge valence of Fe does not change the weight. For the sodium element which is one of the most exchangeable ions in zeolite, Fe-loaded zeolite showed similar contents with pure zeolite as around 3.0 wt%. However, sodium in Fe(II)-sorbed zeolite was lower than that of Fe-loaded zeolite or pure zeolite as 2.24 wt%.

The surface area of zeolite was 27.00 m^2/g, and that of Fe-loaded zeolite was 25.26 m^2/g. Fe-loaded zeolite maintained the high surface area of raw material (zeolite), which indicated that pore channel for ion exchange was not damaged or blocked by Fe developed in material production processes.

To evaluate the removal capacity of Fe-loaded zeolite for cationic heavy metal, Pb removal experiments were performed by varying the initial concentration of Pb. Figure 1 presents the removal efficiency of each material at different initial concentration of lead, which was calculated as follows (Eq. 2).

$$\text{Removal efficiency} = (C_0 - C_{residual}) / C_0 \qquad (2)$$

where, C_0 represents the initial concentration of lead, and $C_{residual}$ for residual concentration of Pb in aqueous solution.
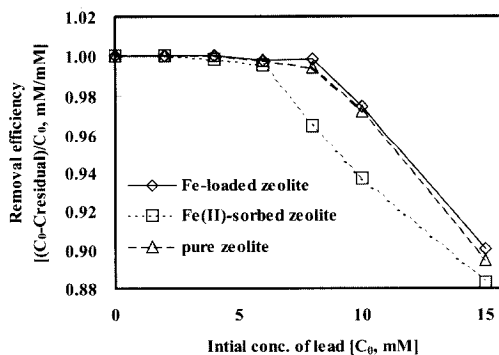

Figure 1. Removal efficiency at different initial concentration of lead through 24 hr reaction.

Table 1. Chemical composition of each material found in Fe-loaded zeolite production process(%)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	LOI	total
Pure	66.51	12.93	.25	1.50	0.68	1.75	2.93	2.55	0.04	0.05	11.27	100.46
Fe(II)-Z	66.22	12.90	0.24	2.76	0.60	1.74	2.24	2.53	0.04	0.06	10.92	100.25
Fe-Z	66.07	12.85	0.23	2.77	0.59	1.60	3.01	2.39	0.06	0.05	11.11	100.72

* Pure : Pure zeolite, Fe(II)-sorbed zeolite, Fe-loaded zeolite * LOI : Loss on ignition Pb Removal

At initial concentration of 0-6 mM, all of the materials showed complete removal for Pb, that is, removal efficiency was around 1. However, at higher concentration above 6 mM, removal efficiency was slightly decreased. It was because Pb concentration in solution exceeded Pb-exchange capacity of materials, and more severe became the competition of Pb ion for the limited exchanging site. In Fe(II)-sorbed zeolite, the extent of decrease in removal efficiency was most significant, which implied that Fe(II)-sorbed zeolite had less lead removal capacity than Fe-loaded zeolite or pure zeolite. It is probably due to the loss of exchangeable ion like sodium during Fe(II) sorption process (see Table 1). However, Fe-loaded zeolite showed the similar removal efficiency with pure zeolite, which indicated that Fe-loaded zeolite recovered removal capacity through the reduction process possibly by sodium treatment (20 mM NaBH4 treatment). To support this speculation, residual Na concentration in the residual solution was measured after reaction as shown in Figure 2. The sodium concentration in Fe-loaded zeolite system was similar with that in pure zeolite system. However sodium concentration in Fe(II)-sorbed zeolite system was less than Fe-loaded zeolite or pure zeolite.

To evaluate the possibility of Fe desorption during lead removal, Fe concentration in the residual solution after reaction was measured for the samples with initial Pb-concentrations of 10
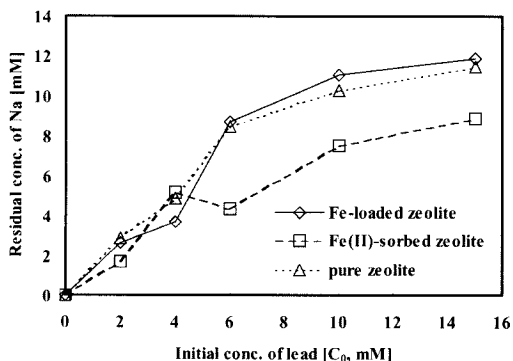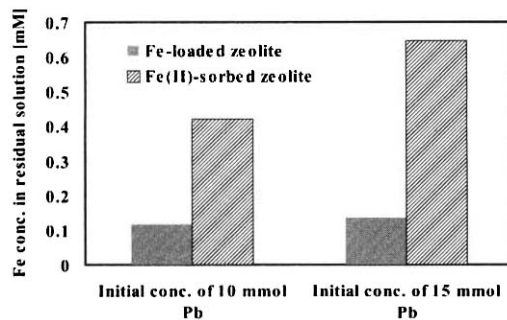

Figure 3. Fe concentration in Fe-loaded zeolite and Fe(II)-sorbed zeolite system after reaction at different Pb initial concentration.

mM and 15 mM. These samples were chosen because most amount of Pb-exchange might be occurred among the tested samples, and so most clearly the desorption phenomenon could be observed. In Figure 3, the solid column shows Fe-concentration in Fe-loaded zeolite system, and the dashed column for Fe(II)-sorbed zeolite system. Fe concentrations from Fe(II)-sorbed zeolite were 4-6 times higher than that from Fe-loaded zeolite. As initial concentration increase, Fe concentration in Fe(II)-sorbed zeolite system increased distinctly from 0.4 mM to 0.6 mM. However in Fe-loaded zeolite system, the variation of Fe-concentration was negligible as around 0.1 mM. This can be explained with the oxidation state of Fe in zeolite. Fe in Fe-loaded zeolite is not available in ion exchange while Fe in Fe(II)-sorbed zeolite can be exchanged with lead. Therefore Fe element existing in Fe-loaded zeolite could be considered stable during the reaction.

Cr(VI) Removal

To evaluate the removal ability of Fe-loaded zeolite for anionic heavy metals, Cr(VI) removal experiments were performed. Figure 4 shows the test results, in which each symbol represents average value of duplicates.

Residual Cr(VI) concentration in Fe-loaded zeolite and Fe(II)-sorbed zeolite rapidly decreased below the detection limit within 5 hrs. However Cr(VI) concentration in pure zeolite

Figure 2. Residual Na-concentration in each system at different initial concentration of lead after 24 hr reaction.
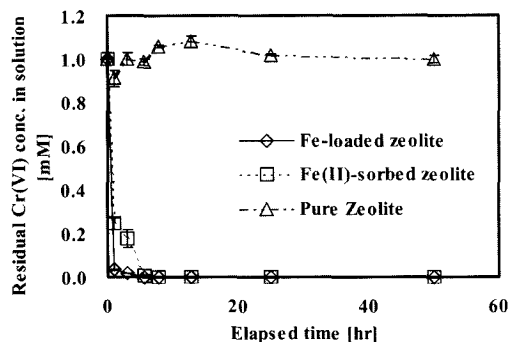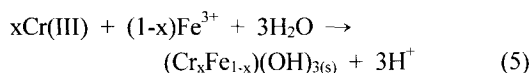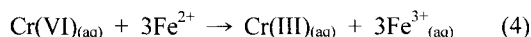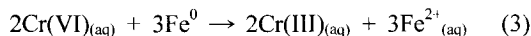
Figure 4. Relative concentration of Cr(VI) in the solution containing each material during 50 hr reaction.

maintained constant during the reaction, which indicated that Cr(VI) sorption on zeolite structure was not significant. Considering the change of chemical compositions of each material, it is apparent that Fe developed in Fe-loaded zeolite and Fe(II)-sorbed zeolite is responsible for Cr(VI) removal observed. Previous researches have reported that the Cr(VI) reduction rate by Fe^0 appeared to be fairly rapid (half-lives<5 hr).[14~16], and the primary removal pathway was reduction of Cr(VI) to Cr(III) and subsequent precipitation of chromium(III)/iron (III) oxyhydroxides.[11,13,17] These reactions can be described as follows (Eq. 3 ~ Eq. 5). However, Fe in pure zeolite was not available for Cr(VI) reduction probably because it was the structural mineral which could not be easily oxidized.

$$2Cr(VI)_{(aq)} + 3Fe^0 \rightarrow 2Cr(III)_{(aq)} + 3Fe^{2+}_{(aq)} \quad (3)$$

$$Cr(VI)_{(aq)} + 3Fe^{2+} \rightarrow Cr(III)_{(aq)} + 3Fe^{3+}_{(aq)} \quad (4)$$

$$xCr(III) + (1-x)Fe^{3+} + 3H_2O \rightarrow$$
$$(Cr_xFe_{1-x})(OH)_{3(s)} + 3H^+ \quad (5)$$

Although Fe contents in Fe-loaded zeolite and Fe(II)-sorbed zeolite were almost same as 2.77 %, Fe-loaded zeolite showed higher removal rate than Fe(II)-sorbed zeolite. This might be explained with the oxidation state of Fe in the materials that might be zero valent iron in Fe-loaded zeolite and ferrous iron (Fe^{2+}) in Fe(II)-sorbed zeolite. This could be supported by Blowes et al. (1997)[11] who reported Cr(VI) reduction rate with Fe^0 is higher than pyrite which contains Fe as the form of Fe^{2+}.

Table 2 presents pH variation in each system during the reaction. Initial pH of Cr(VI) solution was 6.20, however, pH was increased in all systems as the reaction proceeded. This could be possibly explained with the buffering effect of zeolite providing the body structure of each materials. In buffering reaction, H^+ might be exchanged with exchangeable ions in zeolite like Na. The pH in Fe-loaded zeolite and Fe(II)-sorbed zeolite systems were always lower than in pure zeolite system at every time intervals observed. This might be responsible for the reducing reaction occurred in Fe-loaded zeolite and Fe(II)-sorbed zeolite systems, which produce H^+ as shown in Eq. 5. Higher pH in Fe-loaded zeolite than in Fe(II)-sorbed zeolite might be explained with higher contents of exchangeable ion in Fe-loaded zeolite. pH buffering capacity of Fe(II)-sorbed zeolite was decreased possibly by loss of exchangeable ion during Fe-exchange process whereas that of Fe-loaded zeolite was recovered during borohydride-reduction process by Na dissolved from NaBH₄.

CONCLUSION

In summary, Fe-loaded zeolite showed high

Table 2. pH variation in each system during the reaction

	Elapsed time [hr]					
	2	**5**	**10**	**15**	**24**	**50**
Pure	7.37	7.95	7.91	8.06	8.30	8.40
Fe(II)-Z	5.78	5.73	5.91	5.62	6.30	6.58
Fe-Z	7.08	7.28	7.33	7.18	7.31	7.53

* Pure : Pure zeolite, Fe(II)-Z : Fe(II)-sorbed zeolite, Fe-Z : Fe-loaded zeolite
* Initial pH of Cr(VI) solution : 6.20

exchange capacity for Pb more than 49.68 mg-Pb/g, and also complete reduction of Cr(VI) less than 5 hr. Fe-loaded zeolite showed electrochemical reduction ability, which was not observed in natural zeoltie, while maintained original high cation exchange capacity of natural zeolite. These results indicated that ZanF has the potential applicability in treating the contaminated water with both cationic and anionic heavy metals instead of organo-clay or surfactant modified zeolite. Especially with its high hydraulic conductivity, Fe-loaded zeolite could find its use in permeable reactive barriers (PRBs) as a reactive material. The Fe-loaded zeolite is expected to reduce the cost and construction complexity in installing the PRBs for the contaminated groundwater with both cationic and anionic heavy metals. However, for the field application additional issues should be addressed such as the reactivity of Fe-loaded zeolite for the co-existing heavy metals under dynamic flowing conditions.

REFERENCES

1. Haggerty, G. M. and Bowman, R. S., "Sorption of chromate and other inorganic anions by organo-zeolite," *Environ. Sci. Technol.*, **28**(3), 452-458 (1994).

2. Curkovic, L., Cerjan-stefanovic, S., and Filipan, T., "Metal ion exchange by natural and modified zeolites," *Water Res.*, **31**(6), 1379-1382 (1997).

3. Mier, M. V., Callejas, R. L., Gehr, R., Cisneros, B. E. J., and Alvarez, P. J. J., "Heavy metal removal with Mexican clinoptilolite multi-component ionic exchange," *Water Res.*, **35**(2), 373-378 (2001).

4. Semmens, M. J. and Goodrich, R. R., Jr. "Biological regeneration of ammonium-saturated clinoptilolite I. Initial observations," *Environ. Sci. Technol.*, **11**(3), 255-259 (1977).

5. Park, J. B., Lee, S. H., Lee, J. W., and Lee, C. Y., "Lab scale experiments for permeable reactive barriers against contaminated groundwater with ammonium and heavy metals using clinoptilolite (01-29B)," *J. Hazard Mater*, **95**(1-2), 65-79 (2002).

6. Li, Z., Jones, H. K., Bowman, R. S., and Helferich, R., "Enhanced reduction of chromate and PCE by palletized surfactant-modified zeolite/zero valent iron," *Environ. Sci. Technol.*, **33**(23), 4326-4330 (1999).

7. Lee, J. J., Choi, J. Y., and Park, J. W., "Simultaneous sorption of lead and chlorobenzene by organobentonite," *Chemosphere*, **49**(10), 1309-1315 (2002).

8. Li, Z. and Bowman R. M., "Sorption of perchloroethylene by surfactant-modified zeolite as controlled by surfactant loading," *Environ. Sci. Technol.*, **32**(15), 2278-2282 (1998).

9. Sullivan, E. J., Hunter, D. B., and Bowman, R. S., "Fourier transformation raman spectroscopy of sorbed HDTMA and the mechanism of chromate sorption to surfactant-modified clinoptilolte," *Environ. Sci. Technol.*, **32**(13), 1948-1955 (1998).

10. Bowman, R. S., Haggerty, G. M., Huddlestone, R. G., Neel, D., and Flynn, M. M., *In surfactant-enhanced subsurface remediation* Sabatinim, D. A., Knox, R. C., Hardwell, J. H., Eds.; ACS symposium series 594; American chemical society: Washington, DC, 54-64 (1995).

11. Blowes, D. W., Ptacek, C. J., and Jambor, J. L., "In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: laboratory studies," *Environ. Sci. Technol.*, **31**(12), 3348-3357 (1997).

12. Su, C. and Puls, R. W., "Arsenate and arsenite removal by zero valent iron: kinetics, redox transformation, and implication for in situ groundwater remediation," *Environ. Sci. Technol.*, **35**(7), 1487-1492 (2001).

13. Alowitz, M. J. and Scherer, M. M., "Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal," *Environ. Sci. Technol.*, **36**(3), 299-306 (2002).

14. Gould, J. P., "The kinetics of hexavalent chromium reduction by metallic iron," *Water*

Res., **16**, 817-877 (1982).

15. Cantrell, K. J., Kaplan, D. I., and Wietsma, T. W., "Zero valent iron for in situ remediation of selected metals in groundwater," *J. of Hazard Mater*, **42**(2), 201-212 (1995).

16. Powell, R. M., Puls, R. W., Hightower, S. K., and Sabatini, D. A., "Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation," *Environ. Sci. Technol.*, **29**(8), 1913-1922 (1995).

17. Eary, L. E. and Rai, D., "Chromate removal from aqueous wastes by reduction with ferrous ion," *Environ. Sci. Technol.*, **22**(8), 972-977 (1988).