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Application of iron-coated zeolites (ICZ) for mine drainage treatment

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Abstract−To evaluate iron-coated zeolite (ICZ) for the treatment of mine drainage contaminated arsenic (As), cadmium (Cd) and lead (Pb), a full scale treatment system was installed and operated for nine months. Because it is well known that ICZ can remove As from the water stream, the removal characteristics of cationic metal ions (Cd(II), Cu(II), and Pb(II)) using ICZ were investigated by batch and column experiments before the field test. In the batch test, over 99% of the heavy metal ions were removed by the ICZ within 30 min. The results for the adsorption kinetics and adsorption isotherms were fitted well by a pseudo-second-order model and the Langmuir equation, respectively. An affinity analysis showed that the adsorption of heavy metal ions onto ICZ was favorable. In the column experiments, the cadmium breakthrough point was about 50 bed volumes, while the copper breakthrough occurred immediately in the zeolite column. The lead was not detected in any of the columns in the experiments. In the field experiment, the removal efficiency of arsenic onto ICZ was approximately 99% and the removal of heavy metals onto ICZ field-scale experiments was quite lower compared to the results of laboratory experiments. The value of pH in influent and effluent was about 7.0. Based on the results, ICZ is a suitable material to treat the mine drainage or wastewater bearing As(V) and slightly higher concentration of heavy metals simultaneously.

Key words: Adsorption, Heavy Metal Ions, Iron-coated Zeolite, Arsenic Field Aapplication

INTRODUCTION

In Korea, abandoned mines have been serious problems because of mine tailings and acidic mine drainage containing cadmium, copper, lead, and arsenic. Arsenic and heavy metals are leached by the oxidation of sulfide minerals and contaminate groundwater and surface water. They are not biodegradable, can be accumulated in tissues, and cause various diseases such as skin cancer and brain damage [1]. Arsenic exists in anion form while heavy metal ions, such as Cd(II), Cu(II), and Pb(II), exist in cation form in an aqueous system. Generally, hydroxide precipitation, in the form of a metal hydroxide, has conventionally been accomplished by pH control [2,3]. However, the precipitation method produces a large amount of sludge, and is not effective for removing arsenic and chromate, in spite of pH control to a neutral range. As an alternative to precipitation, adsorption techniques have mainly been used for the removal of arsenic and heavy metals, because they are cost effective, simple, and have high removal efficiency [4]. It is well known that zeolite has a high adsorption capacity for cationic metals [5]. The removal process for cationic metals is based on ion exchange, such as through the use of sodium and potassium [6,7], or on the precipitation of metal hydroxides over the external surfaces of the zeolite [8,9]. The ion exchange process in zeolite is affected by the pH value and the concentrations of cations and anions.

Most abandoned mines are contaminated with both arsenic and heavy metal ions [10]. Therefore, a new adsorbent is necessary to remove the arsenic and cationic metals simultaneously. In a previous study, we suggested the use of iron-coated zeolite as an adsorbent of arsenic and found that it was very effective at removing arsenic, and arsenic was removed by iron oxyhyroxide on the surface of zeolite [11]. In this study, we evaluated the adsorption characteristics of ICZ for Cd, Cu and Pb through batch and column experiments, and compared the results with raw zeolite. Then, ICZ was applied to treat mine drainage contaminated As, Cd and Pb in a real abandoned gold mine.

MATERIALS AND METHODS

1. Preparation of Iron-coated Zeolite

The zeolite was obtained from Handoo Co. Ltd., Republic of Korea. The chemical composition of the zeolite was analyzed by X-ray fluorescence (XRF, PW2400, Philips, Netherlands) and it is summarized in Table 1.

To prepare the ICZ, the raw zeolite was cleaned using deionized water to remove the impurities before the experiment. $FeCl_3$ solution (10 wt%) was prepared by dissolving ferric chloride (Junsei,

Table 1. Chemical composition of the raw zeolite

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2
wt%	11.24	70.63	2.32	1.61	1.24	2.16	0.84	0.12	0.25

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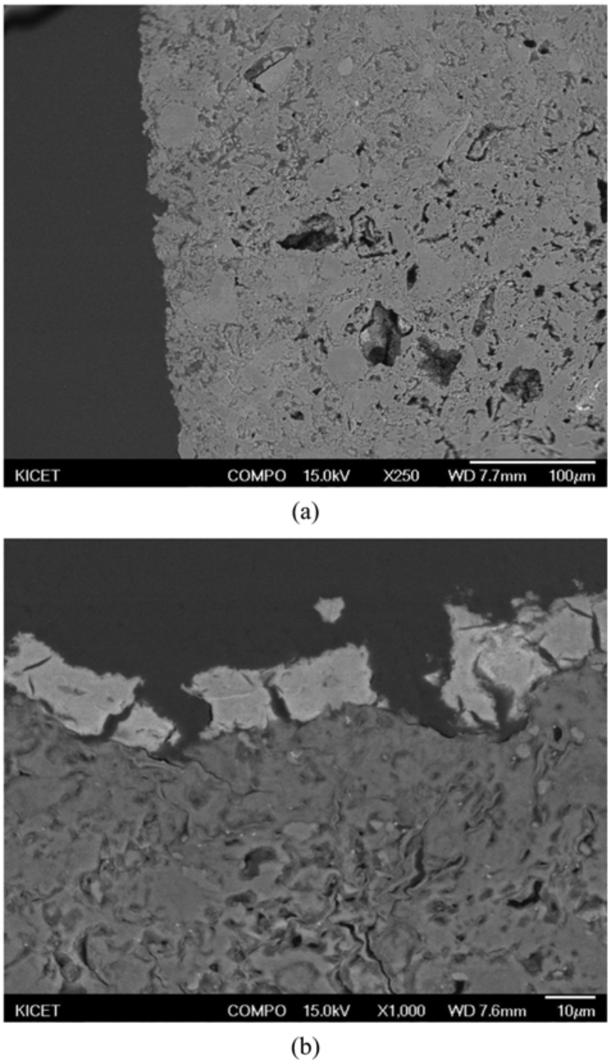


Fig. 1. SEM image of (a) raw zeolite and (b) ICZ.

Japan). One liter of this $FeCl_3$ solution and 100 g of raw zeolite were mixed, and the solution pH was adjusted to 10.0 using 6 N NaOH. The slurry containing zeolite was mixed in a rotary evaporator for 24 hours at 90 °C, after which the mixture was filtered using 5B filter paper (Advantec, Japan). The filtered mixture was then calcinated in a furnace for 4 hours at 250 °C.

Fig. 1 shows an SEM image (SEM-EDX, S-3400N, Hitachi, Japan) of the zeolite and ICZ. As shown in Fig. 1, the ICZ was formed by coating the surface of the zeolite with iron. The other physic-chemical properties were shown in our previous work [11].

2. Adsorption Characteristics of Heavy Metal Ions onto Zeolite and ICZ

Batch experiments were conducted to investigate the adsorption characteristics of heavy metal ions onto zeolite and ICZ. Stock solutions of cadmium, lead, and copper were prepared by dissolving $CdCl_2$, $PbCl_2$, and $CuCl_2$ (Sigma, USA). In the adsorption kinetic study, the initial concentrations of cadmium, lead, and copper ions were about 80 mg/L and the pH of the stock solution was adjusted to 3.0 using 0.1 N HCl to prevent the formation of metal hydroxides. For each of the metal ion solutions, 3 g of zeolite or ICZ was mixed with 30 mL of the metal ion solution in a polyethylene tube and continuously mixed by an overhead shaker at 20 °C for 24 hours. Samples were taken at regular intervals and centrifuged for 10 min

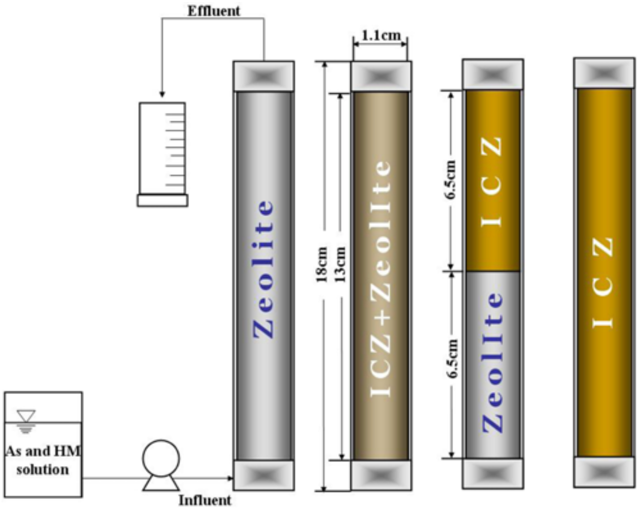


Fig. 2. A schematic diagram of column reactors. Initial concentration of Cd(II), Pb(II), and Cu(II) was 10 mg/L, flow rate was 30 mL/h, and 1 BV of reactor was 13 cm³.

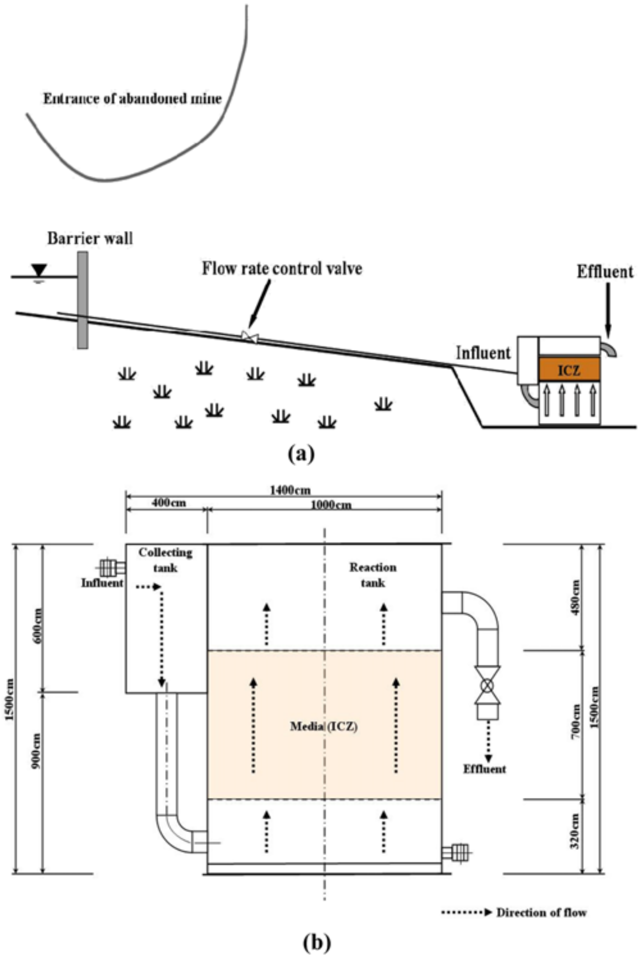


Fig. 3. A schematic of field scale experiment (a) and front view of equipment (b).

at 3,000 rpm. In the adsorption isotherm experiment, 3 g of zeolite or ICZ was shaken with 30 mL of the heavy metal ion solution at various concentrations. After 24 hours, the samples were taken, centrifuged, and the metal ion concentration in a supernatant was analyzed using atomic absorption spectroscopy (AA-6300, Shimadzu, Japan).

3. Column Experiments

Fig. 2 shows a conceptual diagram of the columns used in this study. The column was packed with zeolite and/or ICZ and the bed volume was about 13 cm^3. A peristaltic pump (Masterflex L/S, Cole-Parmer 7524-45, USA) was used to supply 10 mg/L of the metal ion solution adjusted by pH 3.0. The solution was supplied from the bottom to the top of the column. The empty bed contact time was 0.45 hour.

4. Field Application

To apply ICZ system to the field, a field-scale experiment was performed at an abandoned mine site contaminated with As, Cd, and Pb. Average concentration of As, Cd and Pb was about 200, 50 and 250 μg/L, respectively, and the pH of mine drainage was about 7.0. A schematic of field scale and front view of equipment are shown in Fig. 3(a) and 3(b). The adsorption bed was 1 m×1 m and 0.9 m in height, and approximately 900 Kg of ICZ was packed in the tank. Mine drainage was introduced into the equipment packed with ICZ by hydraulic gradient and flow rate was 4.5 m^3/day, and the average residence time in the tank was 2.4 hours. A field-scale experiment lasted for nine months, and influent and effluent were sampled and measured for arsenic concentration, heavy metal concentration and pH, periodically.

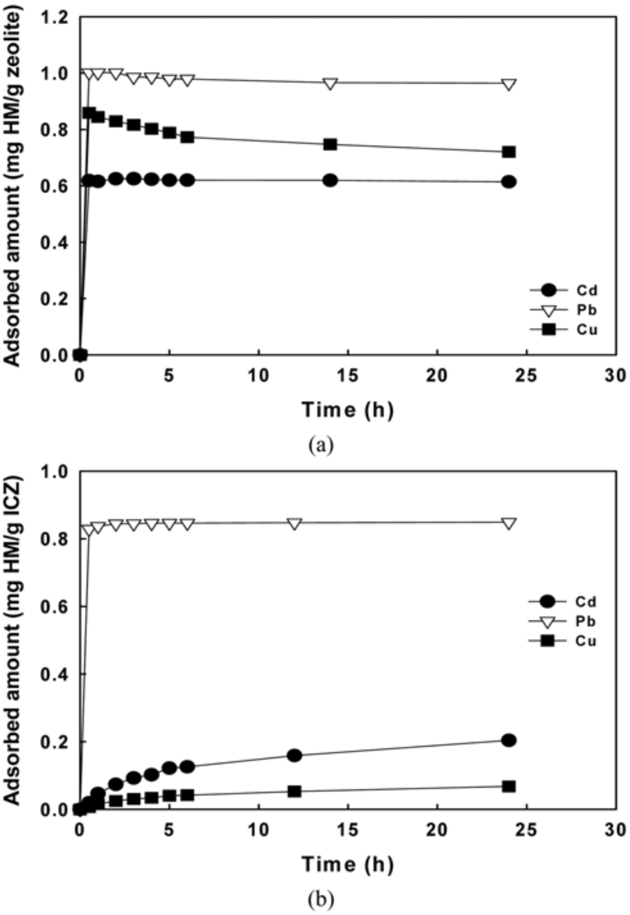


Fig. 4. Effect of contact time on the adsorption of heavy metal ions by (a) zeolite and (b) ICZ. Initial concentration of Cd(II), Pb(II), and Cu(II) was 78, 86, and 100 mg/L, respectively, initial pH was 3.0, dose of zeolite and ICZ was 100 g/L. Equilibrium pH was 3-5.

RESULTS AND DISCUSSION

1. Adsorption Kinetics of Heavy Metal Ions onto Zeolite and ICZ

Fig. 4 shows the adsorption kinetics of the heavy metals onto the zeolite and ICZ. In the case of the zeolite, the heavy metals were immediately adsorbed by the zeolite, and the adsorption reached equilibrium, while the adsorption onto the ICZ occurred slowly, compared with the raw zeolite.

To investigate the adsorption characteristics of the heavy metals, the experimental results were fitted with pseudo-first order and second-order kinetic models (Fig. 5). The two kinetic models are expressed as follows [12]:

$$\text{Pseudo-first-order model: } \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (1)$$

$$\text{Pseudo-second-order model: } \frac{t}{q_t} = \frac{1}{K_1 q_e^2} + \frac{1}{q_e}t \qquad (2)$$

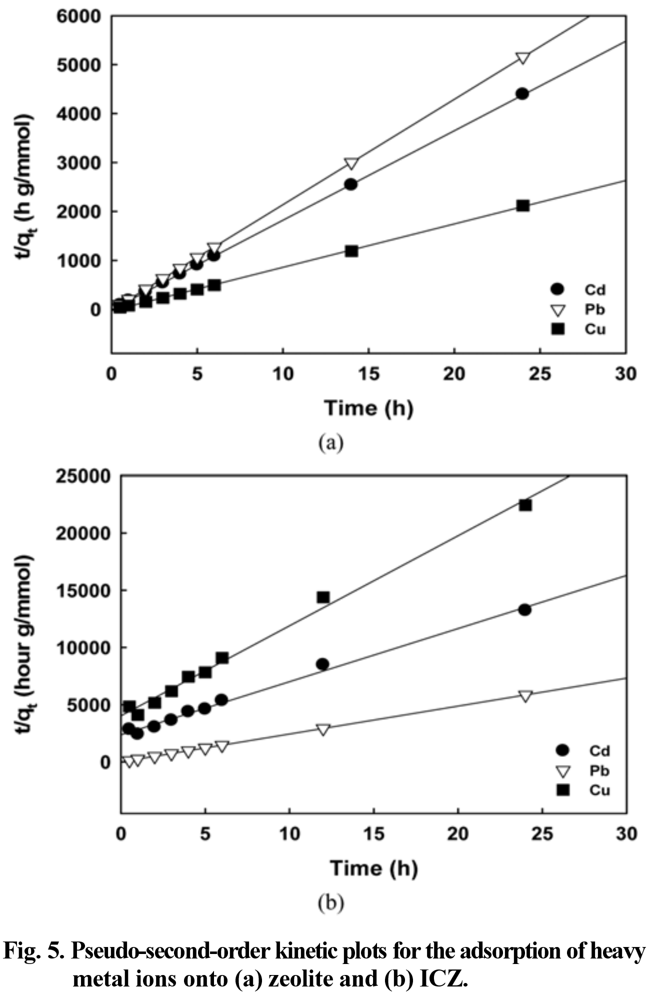


Fig. 5. Pseudo-second-order kinetic plots for the adsorption of heavy metal ions onto (a) zeolite and (b) ICZ.

Table 2. Kinetic parameters for the adsorption of heavy metals onto zeolite and ICZ

Zeolite							
Pseudo-first-order				Pseudo-second-order			
Metal ions	q_e (mg g^{-1})	K_1 (h^{-1})	R^2	Metal ions	q_e (mg g^{-1})	K_2	R^2
Cd(II)	0.52	0.04×10^{-2}	0.28	Cd(II)	0.61	4.85×10^{3}	0.99
Pb(II)	1.21	0.17×10^{-2}	0.75	Pb(II)	0.96	3.11×10^{3}	0.99
Cu(II)	0.82	0.69×10^{-2}	0.85	Cu(II)	0.73	3.26×10^{2}	0.99
ICZ							
Pseudo-first-order				Pseudo-second-order			
Metal ions	q_e (mg g^{-1})	K_1 (h^{-1})	R^2	Metal ions	q_e (mg g^{-1})	K_2	R^2
Cd(II)	0.15	0.07	0.51	Cd(II)	0.07	9.1×10	0.99
Pb(II)	1.18	5.98	0.33	Pb(II)	0.83	1.55×10^{4}	0.99
Cu(II)	0.34	0.07	0.51	Cu(II)	0.22	1.54×10^{2}	0.99

*q_e Values was calculated based on the model equation

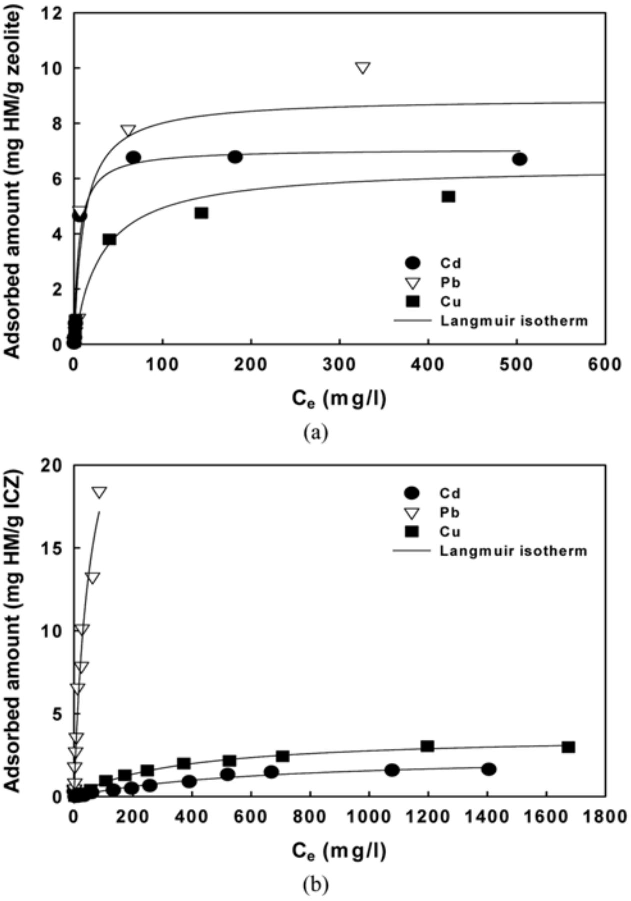
where q_e and q_t (mmol/g) are the amounts of adsorbed heavy metal ions at equilibrium and at time t, respectively. K_1 and K_2 are the first-order rate constant (h^{-1}) and second-order rate constant (h g/mmol), respectively.

The coefficient of determination and model parameters are shown in Table 2. Because the pseudo-second-order kinetic model is suitable to describe ion exchange reactions, the pseudo-second order kinetic model explained the adsorption kinetics of the heavy metals onto the zeolite and ICZ well, compared with the pseudo-first order kinetic model. Except for the Pb, the adsorption rate constants for the zeolite were much higher than those for the ICZ. This means that the adsorption of the copper and cadmium onto the zeolite was faster than that onto the ICZ because the adsorption of the cadmium and copper was due to an ion exchange reaction. The iron coating blocked the surface of zeolite to be ion-exchanged, and the metals were diffused into the zeolite through only the crack of iron on the surface of zeolite. Zeolite is well known as a natural adsorbent for heavy metals because it has a net negative surface charge. Coating with iron hydroxide decreased this surface charge [13]. However, lead might form a surface complexation with the ferrihydrite on the surface of ICZ [14]. Trivedi et al. reported that lead ions predominantly sorbed onto ferrihydrite via inner sphere complexation [15]. Probably, lead formed mondentate and bidentate sorption complexes on the surface of ICZ.

2. Adsorption Isotherms of Heavy Metal Ions onto Zeolite and ICZ

Fig. 6 shows the adsorption isotherms of the heavy metal ions onto the zeolite and ICZ. The coated iron decreased the adsorption of the cadmium and copper onto the zeolite. However, the adsorption of lead onto the ICZ was much higher than that for zeolite. To determine the maximum adsorption capacity of the heavy metal ions onto the zeolite and ICZ, and to explain the adsorption characteristics of the metal ions, the Langmuir adsorption isotherm model was applied as follows [16-22]:

$$q_e=\frac{q_{max}bC_e}{1+bC_e} \tag{3}$$



(a)

(b)

Fig. 6. The adsorption isotherm of heavy metal ions onto (a) zeolite and (b) ICZ. Dose of zeolite and ICZ was 100 g/L, initial pH was 3.0, and equilibrium pH was 3-5.

where C_e (mg/L) is the equilibrium concentration of heavy metals. q_{max} (mg/g) and b (L/mg) are the maximum adsorbed amount and Langmuir isotherm constant, respectively. Table 3 shows the parameters of the Langmuir adsorption isotherm model for the zeolite and ICZ. On the basis of the determination of coefficient, the adsorption of the heavy metal ions onto the zeolite and ICZ followed the Langmuir type of isotherm, which means the adsorption of the heavy metal ions onto the zeolite and ICZ was a monolayer and site-specific

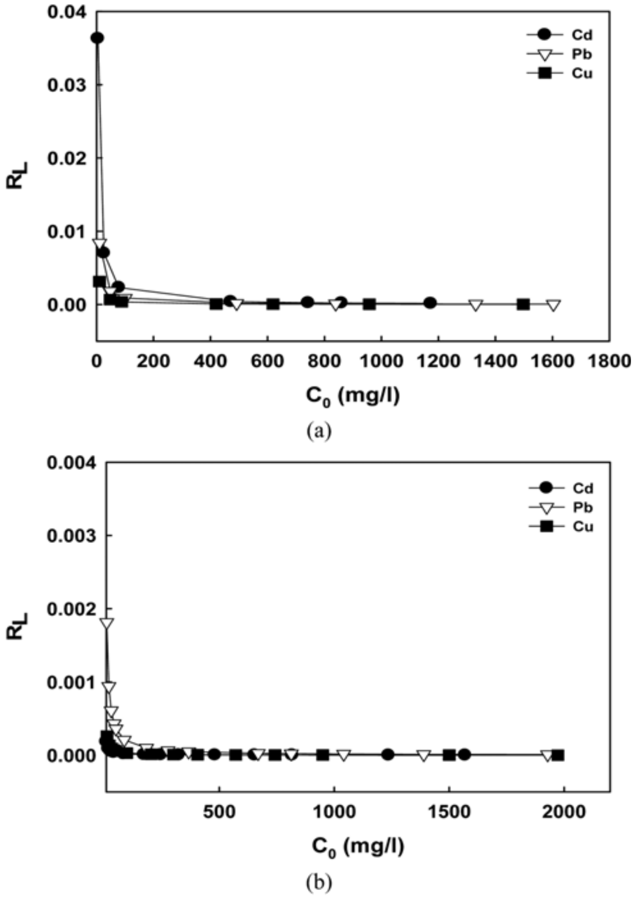
Table 3. Parameters for Langmuir isotherm models

	Metal ions	q_{max} (mg/g)	b	R^2
Zeolite	Cd	7.07	5.49	0.99
	Pb	8.91	8.91	0.96
	Cu	6.45	6.45	0.92
ICZ	Cd	2.55	638	0.99
	Pb	28.3	55.4	0.99
	Cu	3.72	350	0.99

adsorption. For the cadmium, lead, and copper, the maximum adsorption capacity of the zeolite was 7.07, 8.92, and 6.45 mg/g, while that of the ICZ was 2.55, 28.3, and 3.72 mg/g, respectively. The maximum adsorption capacity of the ICZ for lead was higher than that of the zeolite because lead easily forms a complex with iron oxide. The affinity between the heavy metal ions and adsorbent can be predicted using the Langmuir isotherm parameter b from the factor R_L [23,24].

$$R_L = \frac{1}{1 + bC_e} \tag{4}$$

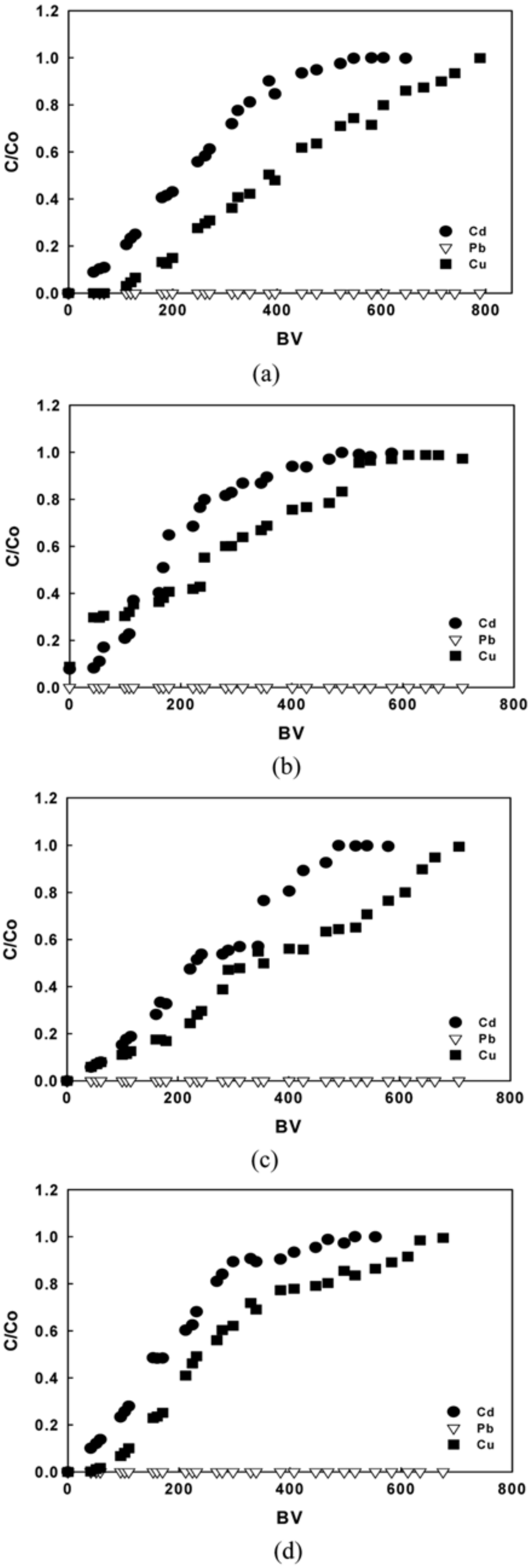
where C_0 is the initial concentration of the heavy metal ions (mg/L). A value of $R_L<1$ represents favorable adsorption, while a value of $R_L>1$ means unfavorable adsorption. The values of R_L for the adsorption of the heavy metals onto the zeolite and ICZ are shown



(a)

(b)

Fig. 7. The value of R_L for adsorption of heavy metal ions onto (a) zeolite and (b) ICZ.



(a)

(b)

(c)

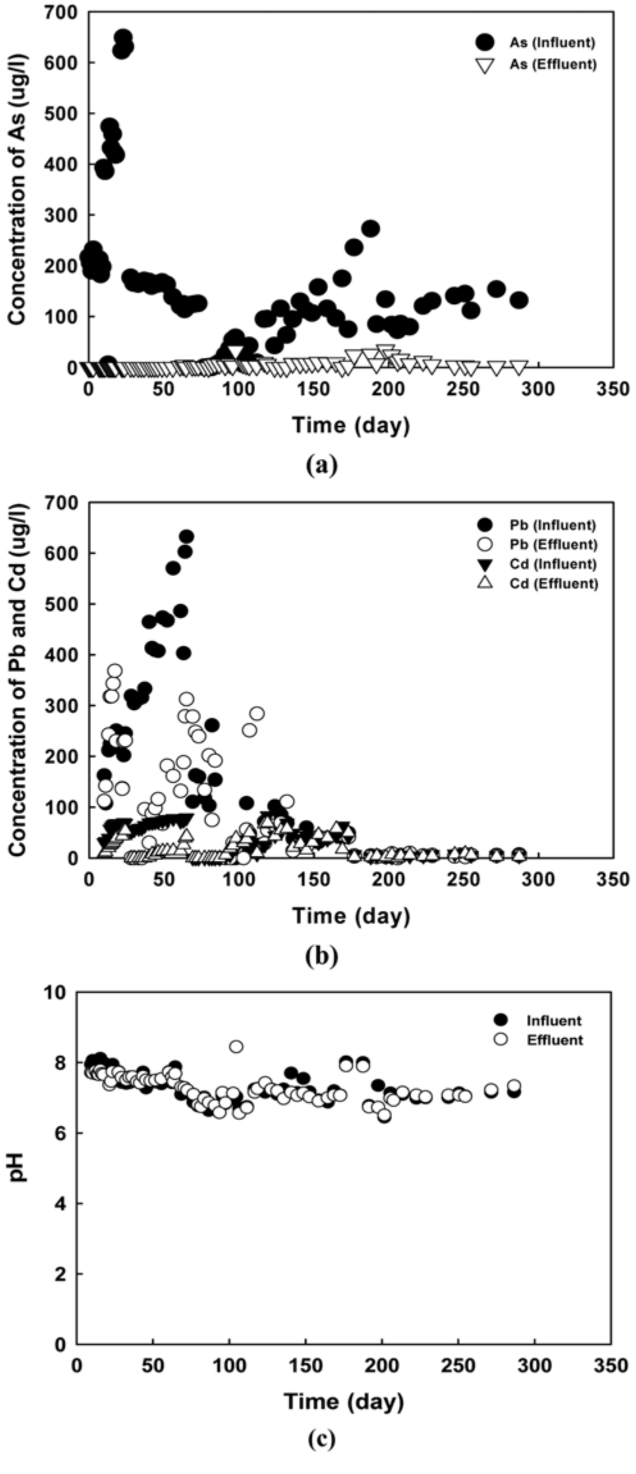
(d)

Fig. 8. The breakthrough curves of heavy metal ions in four different columns. (a) Only-raw zeolite, (b) Mixed-zeolite and ICZ, (c) Layer-zeolite and ICZ, and (d) Only-ICZ, Initial concentration of Cd(II), Pb(II) and Cu(II) was 10 mg/L and initial pH was 3.0.

in Fig. 7. The R_L values were lower than 1.0, representing a favorable adsorption of the heavy metals onto the zeolite and ICZ.

3. Column Experiments

A column experiment for the heavy metal ions was performed to determine the breakthrough points. A heavy metal solution of 10 mg/L was continuously supplied from the bottom of the column. Fig. 8 shows the breakthrough curves of the heavy metal ions from the four different column systems. The adsorption amount of Cd and Cu in the columns containing zeolite was higher than that in the only ICZ column. In the only-zeolite column, the effluent concentrations of cadmium and copper reached the influent concentration at 600 bed volumes (BV) and 800 BV, respectively (Fig. 8(a)). The breakthrough points for the cadmium and copper in the mixed zeolite-ICZ and layered zeolite-ICZ columns were similar (Fig. 8(b) and (c)). In the only-ICZ column, the breakthrough points of the cadmium and copper occurred immediately and the effluent concentrations of the cadmium and copper reached the influent concentrations at 500 BV and 600 BV, respectively (Fig. 8(d)). During the entire experiment, no lead was detected in any of the columns because of huge adsorption capacity of ICZ for lead.



(a)

(b)

(c)

Fig. 9. The concentrations of As(a), Cd(b), Pb(b), and pH(c) in influent and effluent of field system. Average initial concentration of As, Cd and Pb was 200, 50 and 250 μg/L, and flow rate was 4.5 m^3/day.

4. Field Application

The concentration of arsenic, heavy metals and pH in the influent and effluent during the experiment is shown in Fig. 9(a)-(c). The influent concentration of arsenic and heavy metals depends on rainfall, after 100 days, concentration of that slightly decreased. In case of As, maximum inlet concentration is 650 μg/L (average 200 μg/L); more than 99% of As was removed (Fig. 9(a)), and most effluent was lower than 10 μg/L, the guideline value of WHO. The high removal of arsenic was similar to the result of batch and column in the laboratory [11]. The removal efficiency of the Cd and Pb was very low in the field-scale experiments compared to batch experiments (Fig. 9(b)). Probably, the low removal of Cd and Pb comes from the low initial concentration compared to batch and column experiment in the laboratory. Because the pH value in influent and effluent was maintained at approximately 7, another explanation on lower removal of Cd and Pb might be complexation of Cd and Pb with other anions existing in groundwater such as bicarbonate, chloride, and hydroxide. For example, Pb can exist as a dissolved $PbCO_3$ or colloidal hydroxide form in aqueous stream at neutral pH. Also, dissolved organic matter (DOM) in groundwater can complex with cationic Cd and Pb and the DOM-heavy metal complexes decreased the adsorption of metals onto ICZ.

CONCLUSIONS

This study investigated the adsorption characteristics of Cd(II), Cu(II), and Pb(II) with zeolite and ICZ in batch and column tests. In an adsorption kinetic study, heavy metal ions were rapidly removed by the zeolite within 30 min, while the adsorption of copper and cadmium by ICZ was slower than that by zeolite. The adsorption kinetic results were fitted well by the pseudo-second-order model. The adsorption of Cd(II), Pb(II), and Cu(II) onto ICZ was monolayer, site-specific, and favorable. The breakthrough points of cadmium and copper were about 500 BV, and the lead was not detected during the experiment. Even though the adsorption capacity of the ICZ for cadmium and copper decreased, the capacity for lead increased dramatically compared to the raw zeolite. The field study showed that ICZ was very effective to remove As from mine drainage, but it was ineffective to remove low concentration of cationic metals at neutral pH. Therefore, to enhance the removal efficiencies of As and heavy metals simultaneously in real site, we suggest the combinational use of ICZ, which is for removal of As, and zeolite, which is for removal of heavy metals.

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