



Evaluation of factors affecting performance of a zeolitic rock barrier to remove zinc from water

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ABSTRACT

This study examined the factors affecting the performance of zeolitic rocks as reactive media in a permeable reactive barrier (PRB) used to remediate groundwater contaminated with Zn. Serial batch kinetic and sorption tests were conducted on zeolitic rock samples under a variety of conditions (i.e., reaction time, pH, initial Zn concentration, and particle size) using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions. Serial column tests were also conducted on zeolitic rock samples at various flow rates. The removal of Zn increased approximately from 20–60 to 70–100% with increasing pH from 2 to 4 and decreasing initial Zn concentration from 434 to 5 mg/L. Zn removal was not affected by the particle size, regardless of the zeolitic rock samples used in this study. The Zn removal increased approximately from 20–70 to 60–100% with increasing the cation exchange capacity (CEC) from 124.9 to 178.5 meq/100 g and increasing zeolite (i.e., clinoptilolite and mordenite) and montmorillonite contents from 53.7 to 73.2%. The results from the column and batch tests were comparable. Increasing the flow rate caused the earlier breakthrough of Zn (sorbing cation) and a rapid decrease in the concentration of Na, Ca, and Mg (desorbing cations). The hydraulic conductivities of the samples were unaffected by the particle size and mineral components.

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1. Introduction

Natural zeolites have been used as reactive media in a permeable reactive barrier (PRB) to remediate groundwater contaminated with heavy metals on account of their high cation exchange capacity (CEC) and low-cost [1–5]. The PRB is a passive in situ reactive barrier placed in the subsurface to intercept contaminants or convert toxic chemicals into non-toxic chemicals [6–8]. A suitable reactive medium in the PRB requires strong reactivity, high hydraulic conductivity as well as long-term physical and chemical stability [7–9].

Zeolites are hydrated alumino-silicates with infinite three-dimensional lattices of silica tetrahedrons (SiO_4) [10]. Zeolites have a net negative charge on their surface due to the isomorphous substitution of Al^{3+} ions for Si^{4+} ions in the three dimensional lattices of the silica tetrahedron. The negative charges on the surface are balanced by exchangeable cations (e.g., Ca^{2+} and Na^+), which are easily exchanged by other cations (e.g., Pb^{2+} and Zn^{2+}) [11].

Several studies have evaluated natural zeolites as reactive media to remove heavy metals from wastewater or contaminated groundwater [12–27]. These studies have shown that natural zeolites can remove heavy metals from water through a cation exchange pro-

cess and the removal efficiency can be affected by a variety of factors (e.g., particle size of natural zeolites, initial concentration, and influent pH). Most of these studies focused on how these factors affect the reactivity of zeolites. However, these factors (e.g., particle sizes and mineral components) may affect the hydraulic conductivity of the barrier, which is one of important parameters affecting the PRB performance. For example, the mineral components of natural zeolites can vary according to their origin, particularly the montmorillonite contents, which can affect the hydraulic conductivity of the zeolite barriers.

Therefore, in order to evaluate the performance of a PRB using natural zeolites as reactive media, there is a strong need to examine both the hydraulic conductivity and reactivity of natural zeolites with various mineral components at different particle sizes. This study examined the influence of the influent pH, particle size, mineral components and exchangeable cations of natural zeolitic rocks, and flow rate on the performance of the zeolitic rock barrier (i.e., reactivity and hydraulic conductivity) to remove zinc from groundwater. Three zeolitic rocks samples obtained from different zeolite mines located in Gyeongsang province of Korea were used. Batch and column tests were conducted on zeolitic rock samples with various mineral components and exchangeable cations to evaluate the removal efficiency of Zn in aqueous solutions under various conditions (e.g., reaction time, influent pH, initial Zn concentration, and flow rate). Hydraulic conductivity tests were also conducted on zeolitic rock samples with various particle sizes to determine the

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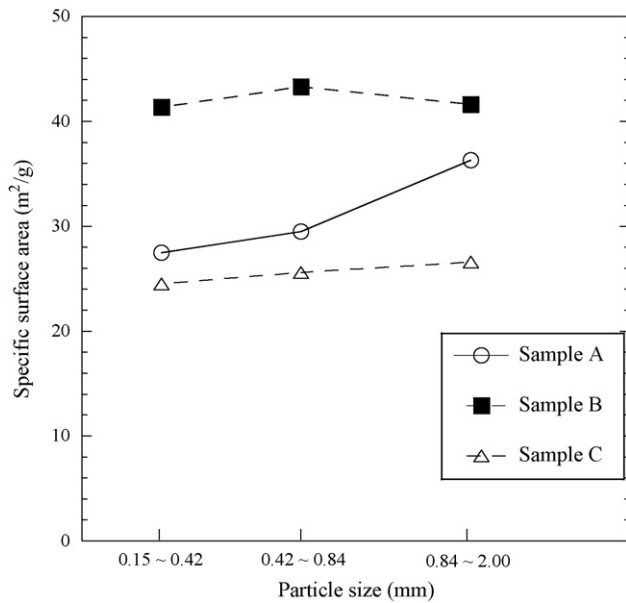


Fig. 1. Specific surface areas of the samples as a function of the particle size.

effect of the particle size and mineral components on the hydraulic conductivity.

2. Materials and methods

2.1. Zeolitic rocks

Three zeolitic rock samples (A, B, and C) were obtained from three different zeolite mines located in the Kyungju and Pohang areas of Korea. Each zeolitic rock sample was crushed and sorted into three groups with different particle sizes. Groups 1, 2, and 3 for each zeolitic rock sample had particle sizes ranging from 0.15 to 0.42, 0.42 to 0.84, and 0.84 to 2.00 mm, respectively. Table 1 summarizes the physical and chemical properties of the samples. The specific gravity of the samples was measured according to the ASTM C 618 [28] and ranged from 2.19 and 2.29. The paste pHs of the samples were measured on pastes prepared using de-ionized (DI) water [29]. Sample A had a relatively higher paste pH than the other samples. X-ray diffraction showed that the samples contained primarily clinoptilolite, mordenite, plagioclase, and quartz. The clinoptilolite content in samples A, B, and C were 39.4, 66.6, and 29.5%, respectively. Sample C only contained montmorillonite (12.1%). The CECs of the samples were determined using the ammonium acetate method [30]. The exchangeable cations were determined to be the difference between the soluble salts extracted with DI water using the fixed-ratio extract method [30] and the total exchangeable cations extracted using the ammonium acetate method [31]. The CEC of the sample increased with increasing zeolite (clinoptilolite and mordenite) and montmorillonite contents in the sample. Sample B had the highest CEC (178.5 meq/100 g) and zeolite content (73.2%) of the samples. The exchangeable cation of all samples tested was dominated by Ca^{2+} ranging from 90.2 to 138.6 meq/100 g followed in order by Na^{+} and Mg^{2+} .

The specific surface areas of the samples were measured using the BET method (model: ASAP 2020) in the Kyeonggi Technopark of Korea. Fig. 1 shows the specific surface areas of the samples as a function of the particle size. The specific surface area of the samples ranged from 24.5 to 41.6 m^2/g . These results were consistent with those reported by Castaldi et al. [25]. Sample B had the largest specific surface area, followed in order by samples A and C, regardless of the particle size. In addition, with exception of the sample

Table 1
Physical and chemical properties of the zeolitic rock samples.

Materials	Source	Specific gravity	Paste pH	Mineral component (%)				Exchangeable cations (meq/100 g)			Cation exchange capacity (meq/100 g)		
				Clinoptilolite	Mordenite	Plagioclase	Opal/CT	Quartz	Montmorillonite	Na		Ca	Mg
Sample A	Nasan valley mine, Kyungju	2.19	7.6	39.4	14.3	37.3	0.7	8.4	-	36.5	105.5	6.5	142.8
Sample B	Kuryungpo mine, Pohang	2.29	8.5	66.6	6.6	21.0	-	5.8	-	32.5	138.6	7.3	178.5
Sample C	Dongshinjanggi mine, Pohang	2.29	7.7	29.5	14.5	20.0	16.4	7.5	12.1	29.3	90.2	7.5	124.9

A, there were no significant changes in the specific surface area for the range of particle size tested, regardless of the type of sample used.

2.2. Chemical solutions

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich) was used to examine the Zn removal behavior of zeolitic rocks. A Zn solution (1000 mg/L) was prepared by dissolving $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DI water as a stock solution. Zn solutions at various concentrations were prepared by diluting 1000 mg/L of the Zn solution using DI water to determine the effect of the Zn concentration on the Zn removal behaviors. A concentrated nitric acid solution was used to adjust the pH of the Zn solutions to determine the effect of pH on the Zn removal characteristics.

2.3. Batch kinetic tests

A series of batch kinetic tests were conducted on samples A, B, and C with three different particle sizes for each sample (total nine samples) to determine the reaction time required to establish equilibrium and the sorption kinetics for Zn using an initial concentration of 100 mg/L at various pH conditions. The pHs of the solutions were adjusted to 2.0, 4.0, and 5.7 by adding a nitric acid solution to determine the effect of pH. A 2 g sample of zeolitic rock was placed in a 50 mL-polypropylene copolymer centrifuge tube containing 40 mL of a 100 mg/L Zn solution. The tube was then tumbled at $20 \pm 3^\circ\text{C}$ for various reaction times ranging from 10 to

480 min using a rotation shaker at 30 rpm (rotations/minutes). The suspension collected at designated sampling times (i.e., 10, 20, 40, 60, 120, 240, 360, and 480 min). The pH of the suspension was measured immediately after tumbling using a pH meter (DDK-TOA Co., Japan). The suspension was filtered through a $0.45 \mu\text{m}$ -filter paper, stored in a polyethylene bottle, and acidified to $\text{pH} < 2$ with a nitric acid solution before the chemical analyses.

2.4. Batch sorption tests

A series of batch sorption tests were conducted on samples A, B, and C with three different particle sizes for each sample (total nine samples) to evaluate the sorption characteristics of Zn. A 2 g sample was placed in a 50 mL-polypropylene copolymer centrifuge tube containing 40 mL of the Zn solution. Initial Zn concentrations ranging from 5 to 434 mg/L at pH 5.7 were used. The tube was then tumbled at $20 \pm 3^\circ\text{C}$ for 4 h, which was found to be sufficient time to reach equilibrium in the batch kinetic tests, using a rotation shaker at 30 rpm. After tumbling, the pH of the suspension was measured immediately using a pH meter. The suspension was filtered through $0.45 \mu\text{m}$ -filter paper, stored in a polyethylene bottle, and acidified to $\text{pH} < 2$ with a nitric acid solution before the chemical analyses.

2.5. Column sorption tests

The column sorption tests were conducted on samples A, B, and C with a particle size, ranging between 0.84 and 2.00 mm to determine the Zn sorption behavior of the samples under more realistic

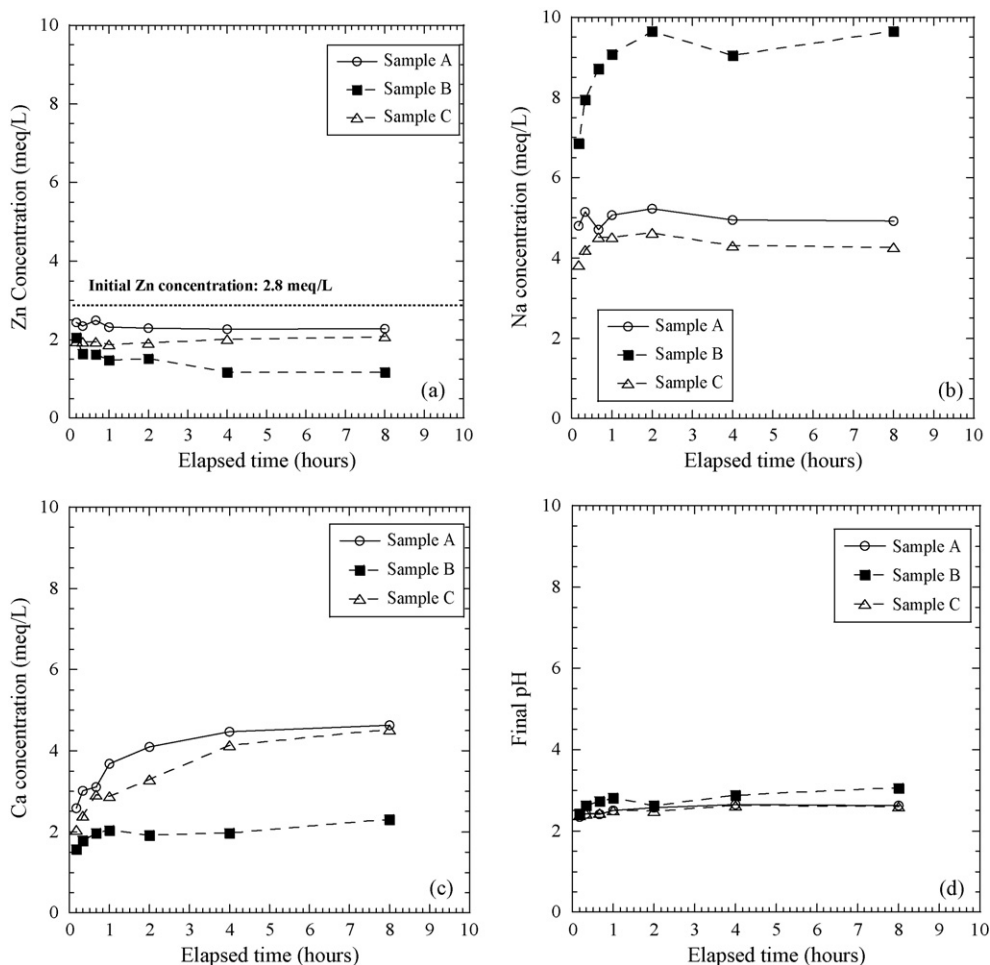


Fig. 2. Zn (a), Na (b), and Ca (c) concentrations and pH (d) as a function of the elapsed time from the batch kinetic tests at the initial pH 2.0.

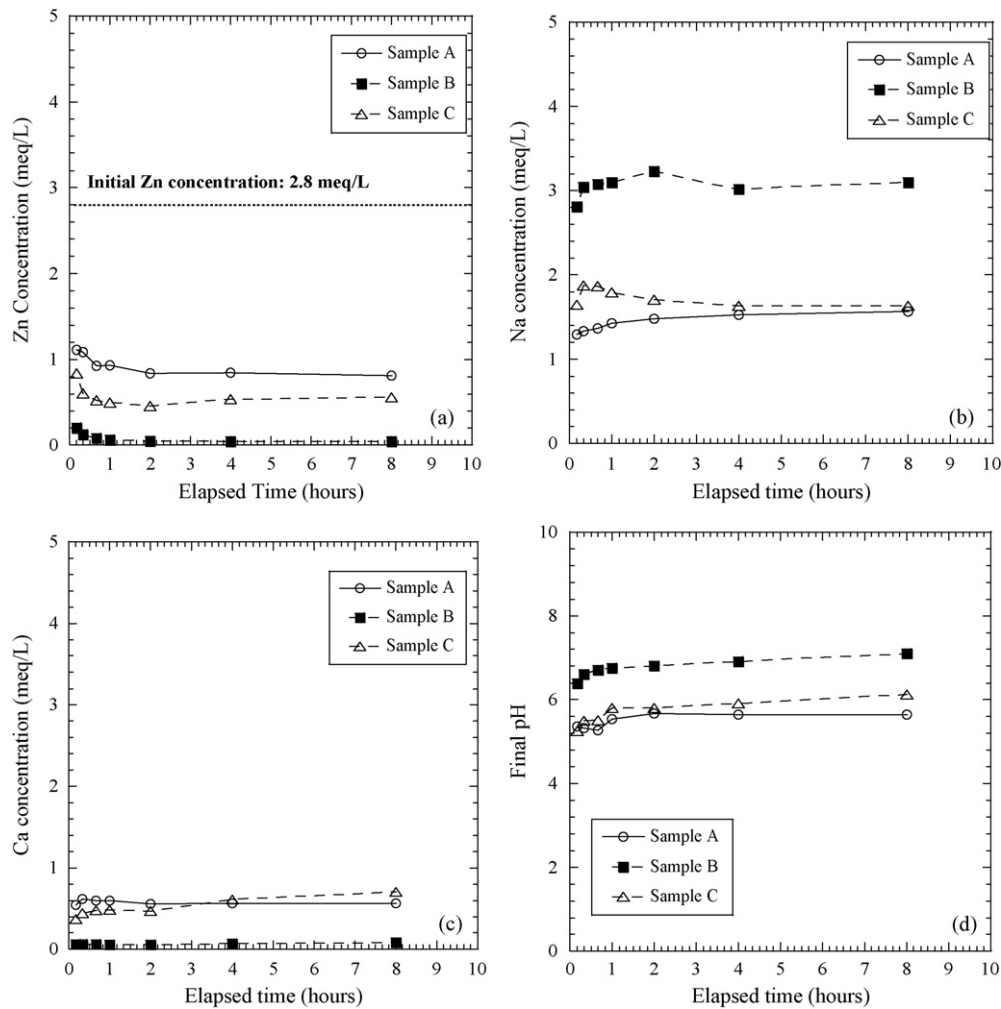


Fig. 3. Zn (a), Na (b), and Ca (c) concentrations and pH (d) as a function of elapsed time from batch kinetic tests at the initial pH 4.0.

flow-through conditions. The material was packed into a glass column, 2.4 cm in diameter and 10 cm in height, to simulate the dry density under potential field conditions (i.e., 1.0 g/cm^3). Glass filter disks, 0.4 cm thick, were placed on the top and bottom of the material to prevent clogging during permeation. A 800 mg/L of Zn solution at pH 5.7 was used as the influent with a 2 L mass flask used as the influent reservoir.

To minimize material consolidation, the influent solution was injected into the bottom of the column (i.e., upward flow) using a metering pump (Model GG50/Q2, USA) at various flow rates. The effluent samples were collected at a given period during permeation. The pH of the effluent samples was measured immediately after sampling using a pH meter. The effluent sample was then filtered through $0.45 \mu\text{m}$ -filter paper, stored in a polyethylene bottle, and acidified to $\text{pH} < 2$ with a nitric acid solution prior to the chemical analysis.

2.6. Hydraulic conductivity tests

Hydraulic conductivity tests were conducted on samples A, B, and C with three different particle sizes for each sample (total nine samples) to determine the effect of the particle size and montmorillonite content on the hydraulic conductivity of the sample.

A falling-head hydraulic conductivity test was conducted using a rigid-wall glass column, 2.4 cm in diameter and 20 cm in height. The material was packed into the glass column to the desired dry den-

sity (1.0 g/cm^3), as used in the column sorption test. The specimen was then permeated with DI water with an average hydraulic gradient of 10. The tests were continued until the hydraulic conductivity became steady and the inflow and outflow volumes were equal.

2.7. Chemical analyses

Inductivity Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was used to determine the elemental concentrations (e.g., Zn, Na, and Ca) of filtered samples from the batch and column tests. The analyses were carried out at the National Center for Inter-University Research Facilities, Seoul National University in Korea.

3. Results and discussion

3.1. Zn removal efficiency

3.1.1. Effect of reaction time

A series of batch kinetic tests were conducted on samples A, B, and C with particle sizes ranging from 0.84 to 2.00 mm using 100 mg/L ($=2.8 \text{ meq/L}$) $\text{Zn}(\text{NO}_3)_2$ solutions to determine the sorption kinetics and time to reach equilibrium for Zn at various initial pHs (i.e., 2.0, 4.0, and 5.7). The acidic solutions (i.e., pH 2.0 and 4.0) were used to mimic acid mine drainage conditions. Figs. 2–4 show the results of the batch kinetic tests.

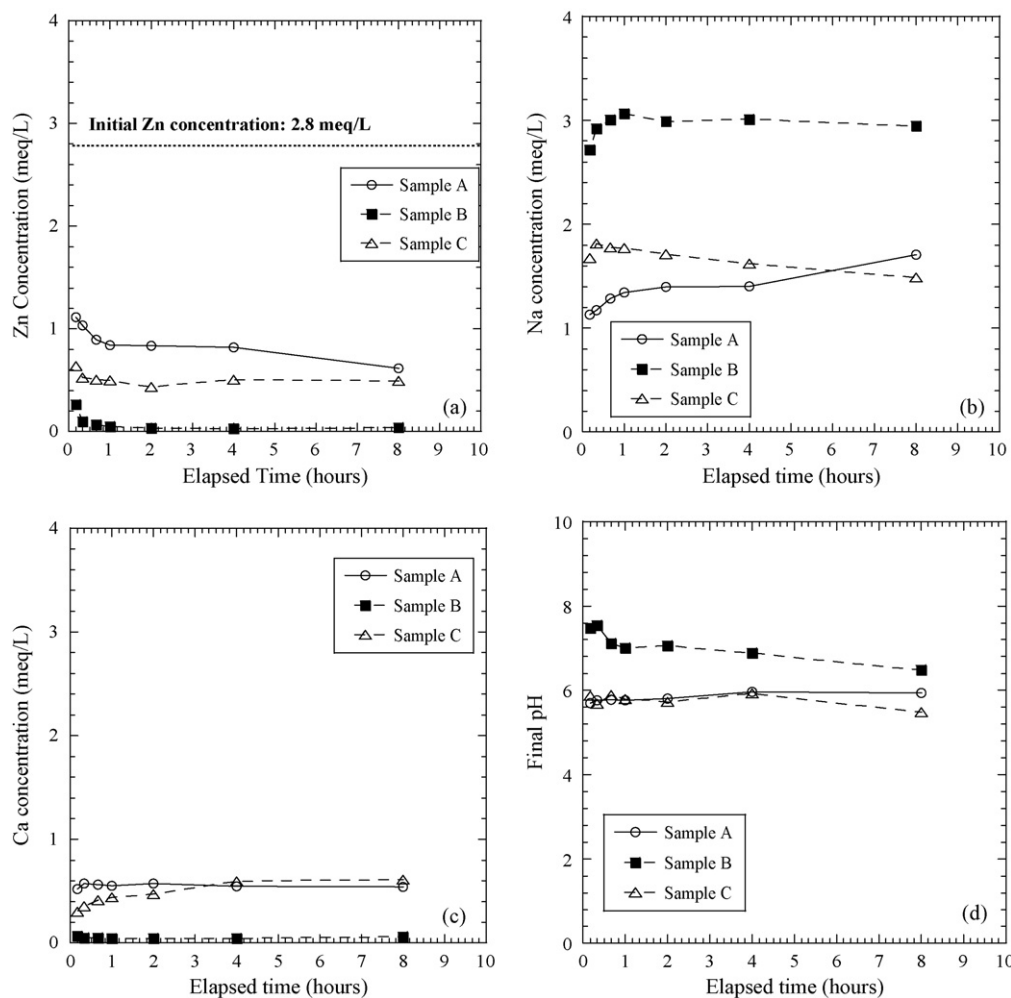


Fig. 4. Zn (a), Na (b), and Ca (c) concentrations and pH (d) as a function of elapsed time from the batch kinetic tests at the initial pH 5.7.

The Zn concentration in the leachate decreased initially and became stable after 2 h (i.e., equilibrium condition), regardless of the initial pH and samples used. At the same time, the Na and Ca concentrations in the leachate increased and reached a plateau after approximately 2 h. This indicates that Zn^{2+} ions were exchanged for Na^+ and Ca^{2+} ions. The slow rate of equilibrium is probably due to the limited rate at which cations come in and out of the micropores of zeolitic rock samples as suggested by Sprynskyy et al. [18].

Although the Ca^{2+} content was higher than the Na^+ content on the exchange sites of the samples (Table 1), the Na concentration was higher than the Ca concentration in the leachate (Figs. 2–4). For example, for sample B at pH 5.7, no Zn was found in the leachate after 2 h. On the other hand, the Na concentration was approximately 3.0 meq/L, which is comparable to the initial Zn concentration (2.8 meq/L), and there was no Ca in the leachate (Fig. 4). These results were caused by the higher preference of Zn^{2+} ions to Na^+ ions than Ca^{2+} ions on the exchange sites because divalent Zn^{2+} ions can easily exchange for monovalent Na^+ ions [10,32].

The final solution pH also became stable after 2 h, regardless of the initial pH and sample used. The final solution pH increased slightly within 2 units after 2 h, indicating that the samples had some buffering capacity due to silicate dissolution. However, at an initial pH of 5.7, the final solution pH increased to <7.0, indicating no precipitation of Zn ions from the solution. These results are comparable to those reported by Wingensfelder et al. [16], who reported that natural zeolite can increase the solution pH by up to 2 units.

3.1.2. Effect of particle size

A series of batch sorption tests were conducted on samples A, B, and C with various particle sizes at intervals of 0.15–0.42, 0.42–0.84, and 0.84–2.00 mm, respectively, using a 100 mg/L $Zn(NO_3)_2$ solution at pH 5.7. No significant change in the removal of Zn occurred with increasing particle size at pH 5.7, regardless of the samples as shown in Fig. 5. This suggests that the particle size of zeolites used in this study had no significant effect on Zn removal from solution. These results are comparable to those of the specific surface area measurement, which showed no significant change in the specific surface area with increasing particle size (Fig. 1). Some studies reported that the particle size had a small or significant effect on heavy metal removal depending on type of zeolite [16,17,33–35].

3.1.3. Effect of pH

A series of batch sorption tests were conducted on samples A, B, and C with a particle size ranging from 0.84 to 2.00 mm using a 100 mg/L $Zn(NO_3)_2$ solution at various initial pHs (i.e., 2.0, 4.0, and 5.7). Fig. 6 shows the removal of Zn as a function of the initial solution pH. The particle size in the interval of 0.84 and 2.00 mm was only used in the tests because the particle size of the zeolite used in this study was shown to have no significant effect on Zn removal (Fig. 5).

In general, the removal of Zn increased with increasing initial pH but there was almost no change in the Zn removal observed at $pH \geq 4$, regardless of the sample used, which are comparable to results obtained at $pH < 7$ reported by Ören and Kaya [17]. Ören and

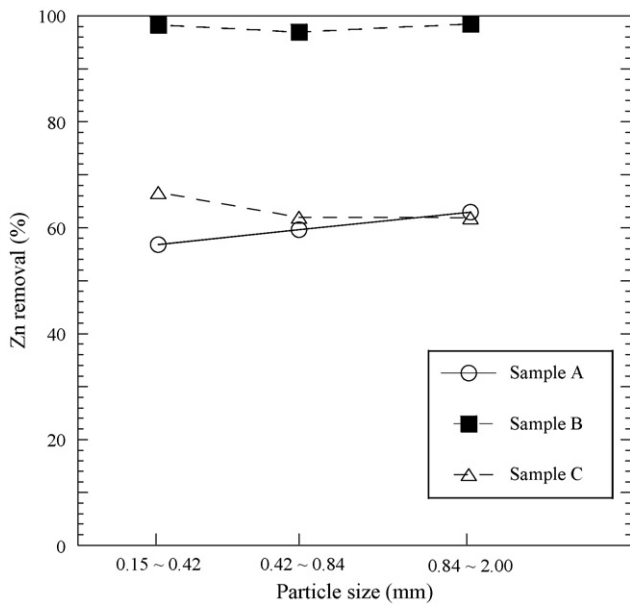


Fig. 5. Zn removal as a function of the particle size (pH 5.7).

Kaya [17] showed that the effect of pH on Zn removal was insignificant at pH between 4 and 7, whereas was significant at pH > 7. This indicates that pH has no significant effect on Zn removal at pH between 4 and 7. The Zn removal decreased to approximately 40–60% with decreasing initial pH from 4.0 to 2.0. For sample B, 100% of the Zn was removed at an initial pH 4.0, which then decreased by 60% at an initial pH of 2.0. On the other hand, for samples A and C, the Zn removal was approximately 70–80% at an initial pH of 4.0, and decreased by 20% at an initial pH of 2.0. The decrease in Zn removal with decreasing pH was attributed to competition between H^+ and Zn^{2+} ions for the exchange sites of the zeolite [17,36]. The H^+ concentration increased with decreasing pH. This suggests that zeolitic rocks cannot be used as reactive media to remove Zn from groundwater contaminated by acid mine drainage with a low pH (<2.0). Wingenfelder et al. [16] also reported that Zn removal by natural zeolite decreased from 93.6% at pH 5.5 to 23.4% at pH 2.2.

3.1.4. Effect of initial concentration

A series of batch sorption tests were conducted on the samples A, B, and C with a particle size ranging from 0.84 and 2.00 mm using various initial Zn concentrations ranging from 5 to 434 mg/L at pH 5.7. Fig. 7 shows Zn removal as a function of the initial Zn concentration and sorption isotherms from batch sorption tests. The sorbed concentration (C_s) was calculated using the following equation (Eq. (1)):

$$C_s = \frac{(C_e - C_i)V_s}{M_s} \quad (1)$$

where C_e is the equilibrium Zn concentration (mg/L), C_i is the initial Zn concentration (mg/L), V_s is the volume of the Zn solution (mL) and M_s is the mass of the sample (g).

In general, the removal efficiency of Zn decreased with increasing initial Zn concentration for all samples (Fig. 7a), as shown in Erdem et al. [37]. The decrease in Zn removal with increasing initial Zn concentration suggests that the primary mechanism for Zn removal can be a cation exchange process, as shown in the batch kinetic tests. Favorable exchange sites for Zn^{2+} ions on the samples decreased with increasing Zn concentration in the solutions [24,32].

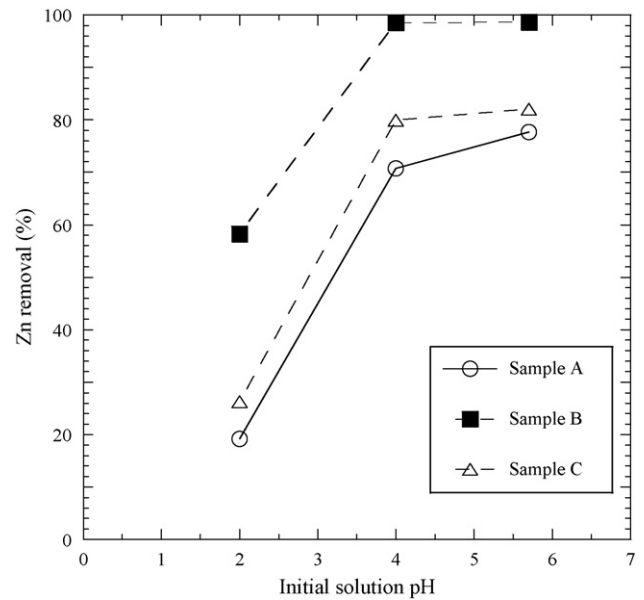


Fig. 6. Zn removal as a function of the initial solution pH.

The isotherms showed generally a non-linear sorption behavior of the zeolite samples for Zn (Fig. 7b). However, the C_s increased linearly at lower equilibrium Zn concentrations (0–302 mg/L) and became stable with increasing C_e . For sample B, C_s increased linearly with increasing C_e to approximately 50 mg/L, and then became stable at 6 mg/kg (= 18.1 meq/100 g), which represents the maximum sorption capacity. On the other hand, for samples A and C, C_s

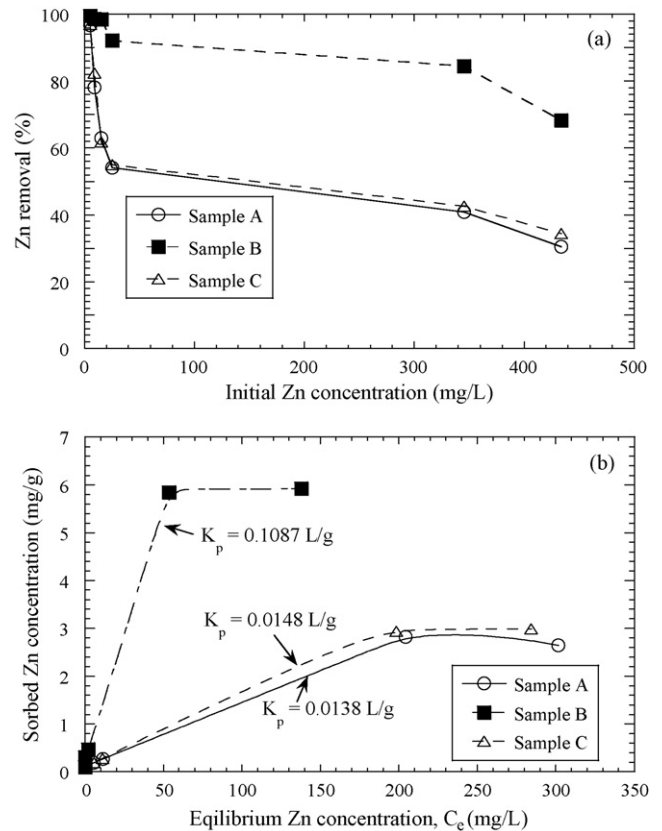


Fig. 7. Zn removal as a function of the initial Zn concentration (a) and sorbed Zn concentrations (C_s) as a function of equilibrium Zn concentrations (C_e) at an initial solution pH 5.7 (K_p = partition coefficient).

increased linearly with increasing C_e to approximately 200 mg/L, and then became stable at 3 mg/kg (= 9.1 meq/100 g), which represents the maximum sorption capacity.

The partition coefficients (K_p) were obtained from batch sorption tests at lower Zn equilibrium concentrations (0–200 mg/L). Over the range of concentrations, the data obtained from the batch sorption tests fitted well to the linear model with a zero intercept. The K_p was estimated using the following equation over the range of concentrations used (Eq. (2));

$$K_p = \frac{C_s}{C_e} \quad (2)$$

The K_p for sample B (0.1087 L/g) was higher than those for samples A and C (0.0138 and 0.0148 L/g, respectively) (Fig. 7b). This suggests that sample B has a higher sorption capacity for Zn than the other samples. The higher sorption capacity of sample B may be due to its higher content of minerals involved in the sorption of Zn, including clinoptillogite, mordenite, and montmorillonite (Table 1).

3.1.5. Effect of zeolitic rock properties

Fig. 8 shows the Zn removal as functions of the CEC and of zeolite and montmorillonite contents at various pH conditions. In general, the Zn removal increased with increasing CEC and zeolite (i.e., clinoptillogite and mordenite) and montmorillonite content. However, the effect of the CEC and zeolite and montmorillonite contents on Zn removal was more significant at pH 2.0 than at pH 4.0 and 5.7. At pH 2.0, the Zn removal increased from approximately 20 to 60% with increasing the CEC and zeolite and montmorillonite contents from 125 to 178 meq/100 g and from 50 to 71%, respectively. On the other hand, at pH 5.7, the Zn removal increased from 80 to 100% with increasing CEC and zeolite and montmorillonite contents from 125 to 178 meq/100 g and from 30 to 65%, respectively.

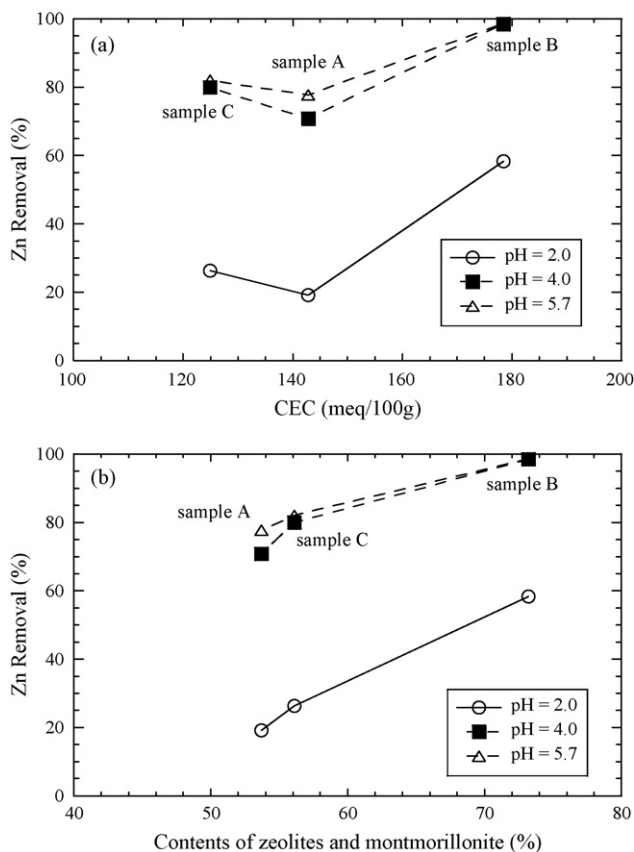


Fig. 8. Zn removal as a function of the CEC (a) and zeolites and montmorillonite contents (b).

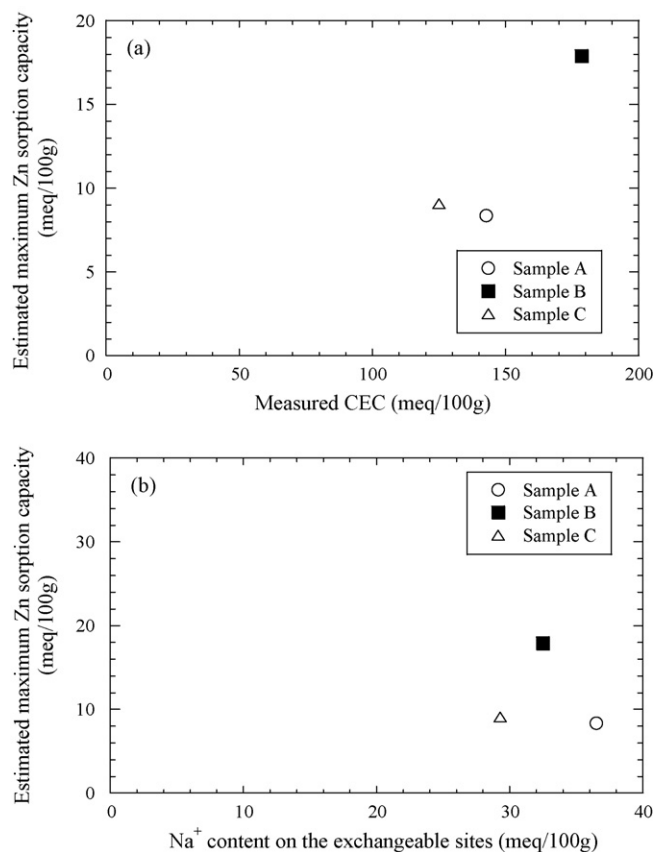


Fig. 9. Relationships between the estimated maximum Zn sorption capacity from the batch tests and measured CEC from the CEC tests (a) and Na^+ content on the exchange sites (b).

This suggests that zeolitic rock with higher zeolite content has a stronger sorption capacity than that with lower zeolite content at low pH.

There was a strong correlation between the CEC of the sample and the zeolite and montmorillonite contents (Table 1). The CEC increased from 125 to 178 meq/100 g with increasing zeolite and montmorillonite contents from 50 to 71%. The zeolites and montmorillonite have negative charges that are balanced by exchangeable cations due to the isomorphous substitution of Si^{4+} ions by Al^{3+} ions in the three-dimensional lattice of the minerals. The exchangeable cations can be exchanged easily by other cations, resulting in a higher CEC [11,16,32].

The estimated maximum Zn sorption capacities obtained from the batch sorption tests were considerably lower than the measured CEC from the CEC tests, as shown in Fig. 9a. The estimated maximum Zn sorption capacities for samples A, B, and C obtained from the batch sorption tests were approximately 8.4, 18.0, and 9.1 meq/100 g, respectively. On the other hand, the measured maximum Zn sorption capacities for samples A, B, and C obtained from the CEC tests were approximately 142.8, 178.5, and 124.9 meq/100 g, respectively (Table 1). Fig. 9b shows the correlation between the Na^+ content on the exchange sites and the estimated maximum sorption capacity of the samples. These results may be caused by the different preferences of the zeolitic rock samples for the different cations. Divalent cations (Zn^{2+}) easily exchange with monovalent cation (Na^+) but there is less exchange on the exchange sites of zeolites between Zn^{2+} with higher hydration energy and Ca^{2+} with lower hydration energy, as suggested by Wingfelder et al. [16] and Colella [38]. Zn^{2+} ion (–1955 kJ/mol) has a higher hydration energy than Ca^{2+} ion (–1505 kJ/mol), which

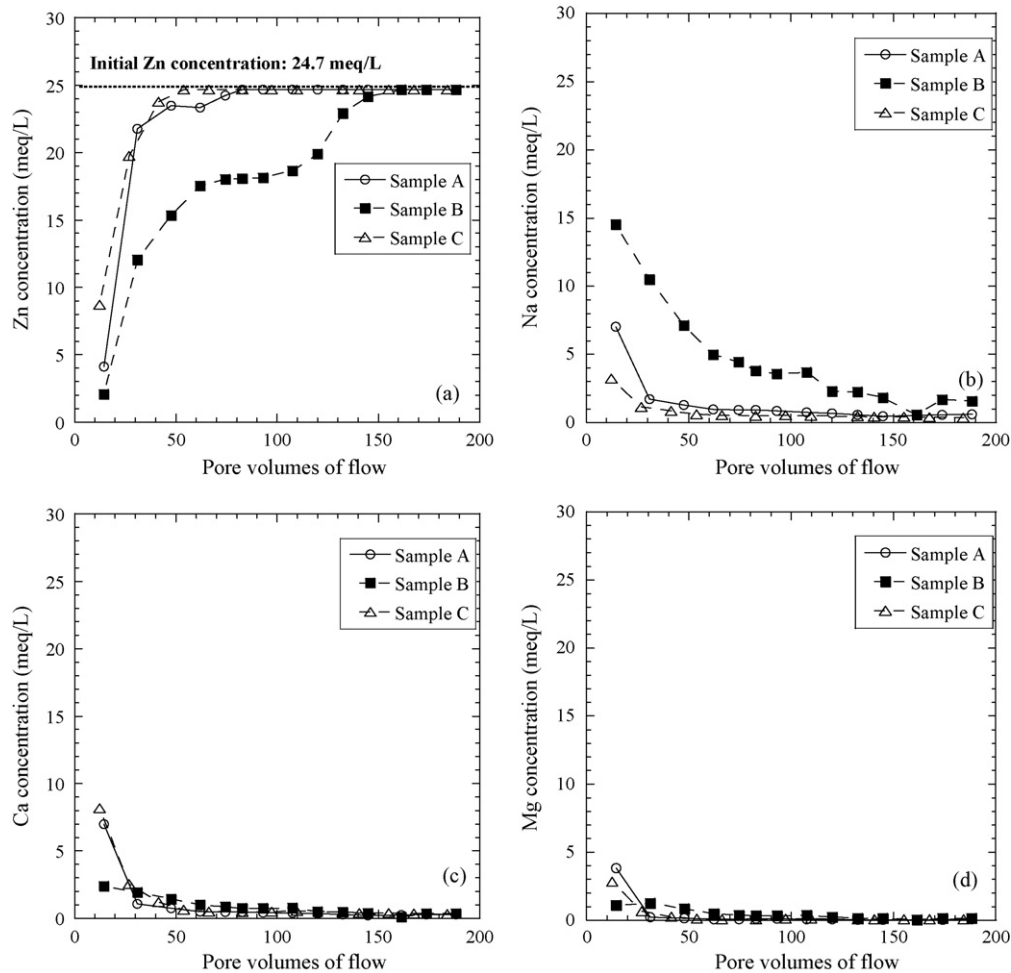


Fig. 10. Zn (a), Na (b), Ca (c), and Mg (d) concentrations in the effluents from the column tests using an 800 mg/L (24.7 meq/L) Zn solution at a flow rate of 1.0 mL/min.

is a primary exchangeable cation on the exchange sites of the samples [39].

3.1.6. Effect of flow rate

Column sorption tests were conducted on the samples A, B, and C with particle sizes ranging from 0.84 and 2.00 mm using a 800 mg/L (24.7 meq/L) $\text{Zn}(\text{NO}_3)_2$ solution with pH 5.7 at various flow rates to determine the sorption behavior of the samples under more realistic flow-through conditions. The dry density of the specimen (1.0 g/cm^3) used in the column tests was consistent with that of the specimen used in the hydraulic conductivity tests.

Fig. 10 summarizes the results of the column tests conducted at the flow rate of 1.0 mL/min. The Na, Ca, and Mg (desorbing cations) concentrations decreased gradually with increasing Zn (sorbing cation) concentration in the effluent solution, regardless of samples used. These results suggest that the exchange of Zn^{2+} ions for Na^+ , Ca^{2+} , and Mg^{2+} ions on the exchange sites occurred gradually during the permeation process. Although the primary exchangeable cation on the exchange sites of the samples was Ca^{2+} ion, as shown in Table 1, the mass of eluted Na^+ ion on the exchange sites was greater than the other cations (i.e., Ca^{2+} and Mg^{2+}), indicating that Zn^{2+} ions exchange more easily with Na^+ ions than Ca^{2+} and Mg^{2+} ions. These results are comparable to those obtained from the batch kinetic tests, as shown in Figs. 2–5. Zn^{2+} ion has a higher replacing capacity for Na^+ ion, but a lower replacing capacity for Ca^{2+} and Mg^{2+} because Na^+ is a monovalent cation, and Ca^{2+} and Mg^{2+} have lower hydration energies than Zn^{2+} [16,38].

Earlier breakthrough (i.e., almost complete exchange) of the Zn (sorbing cation) occurred from the test with sample B than with samples A and C. For sample B, the breakthrough of Zn occurred after approximately 150 PVF, whereas breakthrough for samples A and C occurred after approximately 80 and 60 PVF, respectively. These results are comparable to those obtained from the batch sorption tests in that the removal of Zn with sample B was higher than those with the other samples at a given initial Zn concentration (Fig. 7). These results were attributed to the higher availability of sorption sites on sample B, which depends on the CEC and Na^+ content on the exchange sites. Therefore, breakthrough of Zn occurs more slowly as the availability of sorption sites increases, and the tailing in the elution curves (Na, Ca, and Mg) becomes more significant. The tailing in the elution curves may be caused by slow rate at which cations come in and out of the micropores of zeolitic rock samples.

The Zn, Na, Ca, and Mg concentrations in the effluent solutions from the column tests conducted on sample B with a particle size ranging from 0.84 to 2.00 mm at various flow rates (i.e., 1.0, 2.0, and 4.0 mL/min) were measured as a function of the PVF, as shown in Fig. 11. Increasing the flow rate caused the earlier breakthrough of Zn and a more rapid reduction in the effluent concentrations of Na, Ca, and Mg because Zn was delivered to the exchange sites more rapidly. For the test at a flow rate of 4.0 mL/min, complete breakthrough of Zn occurred after approximately 70 PVF had been passed through the specimen, whereas at a flow rate of 1.0 mL/min, the breakthrough of Zn occurred after approximately 120 PVF had passed through the specimen.

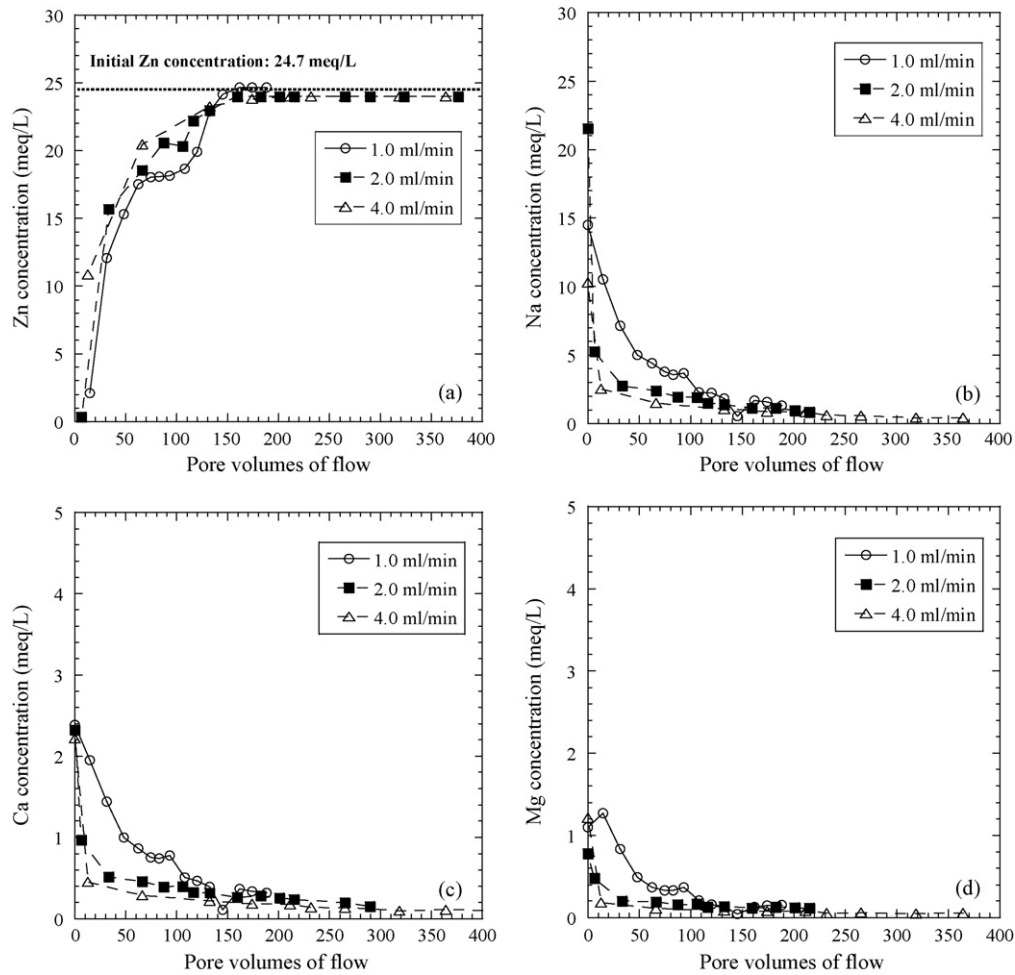


Fig. 11. Zn (a), Na (b), Ca (c), and Mg (d) concentrations in the effluents from the column tests using an 800 mg/L (24.7 meq/L) Zn solution at various flow rates.

3.2. Hydraulic conductivity

Hydraulic conductivity tests were conducted on samples A, B, and C with three different particle sizes for each sample (total nine samples) to determine the effect of the particle size and montmorillonite content on the hydraulic conductivity of the sample. The dry density of all samples was 1.0 g/cm^3 . Fig. 12 shows the results of the hydraulic conductivity tests.

In general, the hydraulic conductivity decreased by approximately two orders of magnitude (i.e., from $\sim 10^{-3}$ to $\sim 10^{-5}$ cm/s) when the particle size decreased from 0.84–2.00 to 0.15–0.42 mm, regardless of the samples used. For example, the hydraulic conductivity of sample A decreased from 9.0×10^{-3} to 9.3×10^{-6} cm/s with decreasing the particle size from 0.84–2.00 to 0.15–0.42 mm. However, the hydraulic conductivity was insensitive to the type of material, indicating that montmorillonite had no significant effect on the hydraulic conductivity of the sample. The highest hydraulic conductivity was obtained from samples B, A and C at particle sizes of 0.84–2.00, 0.42–0.84, and 0.15–0.42 mm, respectively.

The difference in hydraulic conductivity for the samples was largest at the intermediate particle size (0.42–0.84 mm). At the large particle size (0.84–2.00 mm), almost the same hydraulic conductivity was obtained regardless of the sample. At the intermediate particle size (0.42–0.84 mm), the hydraulic conductivity of sample A (3.4×10^{-4} cm/s) was approximately three orders of magnitude lower than that of sample B (1.1×10^{-6} cm/s). The type of material apparently affects the hydraulic conductivity at the intermediate particle size (0.42–0.84 mm), but is insignificant at

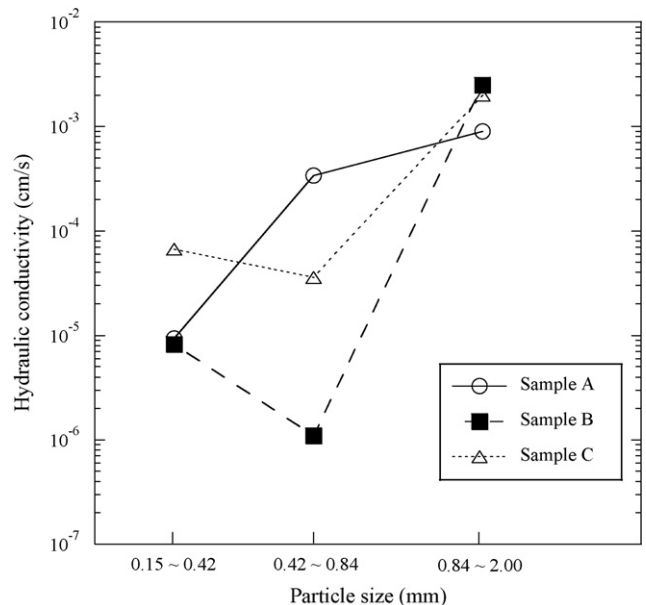


Fig. 12. Hydraulic conductivities as a function of the particle sizes.

low (0.15–0.42 mm) or high (0.42–2.00 mm) particle sizes. However, the difference in hydraulic conductivity may not be caused by the presence of montmorillonite but may be caused by the non-uniform particle size. Sample C contained only montmorillonite but sample B had the lowest hydraulic conductivity of all samples at the particle sizes of 0.15–0.42 and 0.42–0.84 mm. The insensitivity of the hydraulic conductivity to the montmorillonite content may be because the primary exchangeable cation of the montmorillonite is a divalent cation (Ca^{2+}) resulting in less swelling of the montmorillonite. Particles of the sample B at the particle size ranged between 0.42 and 0.84 mm may have more various sizes than those of the other samples, resulting in the lowest hydraulic conductivity.

4. Conclusions

The equilibrium to achieve the maximum sorption from the batch kinetic tests was reached within approximately 2 h, regardless of the initial pH and samples used. The final solution pH increased by 2 units after 2 h (i.e., less than 7.0), indicating no precipitation of Zn ions in the solution.

The particle size had no significant effect on the Zn removal for the zeolites used in this study. However, sample B had the highest removal capacity, which was attributed to its higher CEC, higher specific surface area, higher initial Na^+ content on the exchange sites, and higher zeolite (i.e., clinoptilolite and moronite) and montmorillonite contents. In general, the Zn removal increased with increasing initial solution pH, with almost complete Zn removal ($\sim 100\%$) at $\text{pH} \geq 4$, regardless of the samples used. On the other hand, the Zn removal decreased to approximately 20% at an initial pH 2.0.

The results from the column tests were comparable to those from the batch tests. The earlier breakthrough of Zn occurred from the test with sample B than with samples A and C. In addition, increasing the flow rate caused an earlier breakthrough of Zn and a more rapid decrease in the effluent concentration of Na, Ca, and Mg due to the rapid delivery of Zn to the exchange sites.

The hydraulic conductivity of the medium in PRB needs to be at least that of the aquifer. Zeolitic rock needs to be selected with a comparable hydraulic conductivity to that of the aquifer materials in which the PRB is to be installed. In addition, the medium should have strong reactivity. The hydraulic conductivity of the samples varied according to the particle sizes but Zn removal was not affected by the particle size. Therefore, sample B with the particle size ranged between 0.84 and 2.00 mm is suitable for permeable aquifers with a hydraulic conductivity of 10^{-3} cm/s because it has the highest Zn sorption capacity of the samples tested. On the other hand, sample B with the particle size $< 0.42\text{--}0.84$ mm is suitable for aquifers with hydraulic conductivity ranging from 10^{-5} to 10^{-6} cm/s.

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