Kinetic and isothermal adsorption properties of strontium and cesium ions by zeolitic materials synthesized from Jeju volcanic rocks

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ABSTRACT

The study focused on the removal of Sr and Cs ions in aqueous solutions by zeolitic materials synthesized from Jeju volcanic rocks using a fusion/hydrothermal method. The synthesis of the zeolitic materials was carried out using the fusion/hydrothermal method to reduce crystallization time. Morphological structures of the zeolitic materials could be confirmed to be the Na-A zeolite structure and crystalline with the chamfered-edged structure. In the adsorption experiment, as the initial concentrations of the Sr and Cs ions increased, it took longer to reach adsorption equilibrium. The adsorption kinetics and isotherms of Sr and Cs ions were predicted well by the pseudo-2nd-order and Langmuir isotherm models, respectively. The maximum adsorption capacities of Sr and Cs ions by the Langmuir isotherm model were 154.8 mg/g and 144.0 mg/g, respectively. The zeolitic materials prepared in this study is considered as an effective adsorbent for removing Sr and Cs ions in aqueous solutions.

Keywords: Adsorption, Cesium, Strontium, Volcanic rock, Zeolitic material

1. Introduction

Due to the nuclear power plant accidents in Fukushima (2011) and in Chernobyl (1986) a large amount of radioactive materials such as ¹³⁷Sr and ⁹⁰Cs ions are entering the water environment and destroying the aquatic ecosystem [1]. They have a long half-life and high solubility in water, so it is known that they remain for a long time. When the cells of the body bind to Sr and Cs ions, they can cause many kinds of diseases such as leukemia and skin cancer [2]. Several methods for example adsorption [3], solvent extraction [4], and chemical precipitation [5] have been proposed as treatment methods for wastewater solutions containing radioactive ions. The adsorption for removing their ions has attracted attention because it has advantages such as its convenient operation, non-pretreatment and low waste generation. Adsorbents such as natural minerals [6, 7], modified minerals [8, 9], natural zeolite [10, 11], and zeolitic materials [12, 13] have been applied to remove radioactive ions. The zeolitic materi-

als has been widely used in metal ion adsorption because of their unique chemical and physical properties (thermal stability, cage structure, crystallinity, ion-exchange capacity, etc) [14]. The zeolitic materials generally have a higher adsorption capacity than the natural zeolites, however, it has the disadvantage of being expensive. Recently, many studies have focused on the search of inexpensive and efficient adsorbents, zeolitic materials, fabricated from various natural minerals and industrial wastes. The zeolitic materials such as Na-X, Na-A, Na-P1, and cancrinite were synthesized from the Italian Crotone Basin [15] and Jeju volcanic rocks [16] by the hydrothermal method. In addition, the zeolitic materials prepared from various natural minerals (i.e., bentonite, diatomite, kaolinite, and clay) and coal fly ash have been proposed [17-21].

The zeolitic materials have been efficiently used to remove the radioactive ions in aqueous solutions [10, 13, 22]. The adsorption mechanisms of Sr, Ca, Ba, and Cd on the Na-A zeolite were strongly influenced by the binding affinity of individual cations for the zeolite surface [23]. The maximum adsorption capacities of Co,

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Cs, and Sr ions by Langmuir adsorption model on a natural zeolite (clinoptilolite) were 2.93 mg/g, 49.0 mg/g, and 9.8 mg/g, respectively [10]. The removal performance of Cs and Sr ions by a synthetic Na-A zeolite (commercial product) showed that the equilibrium data was well estimated by the Langmuir model more than the Freundlich model. The maximum adsorption capacities of the Cs and Sr ions were 90.7 mg/g and 69 mg/g, respectively [13]. The Na-P1 zeolite prepared from Jeju volcanic rocks has the Sr adsorption capacity of 57.0 mg/g [22]. On the other hand, we were able to synthesize zeolitic materials with coal fly ash via a fusion/hydrothermal method [21], and the synthesized zeolitic materials showed high adsorption capacities of 156.4 mg/g for Sr ion.

Previous studies have been many cases in which the removal of Sr and Cs ions was evaluated using a zeolite material. However, there have been very few cases where volcanic rocks were synthesized with zeolite materials to remove Sr and Cs ions. Therefore, the aims of this study are to synthesize zeolitic materials (Z-S1) from Jeju volcanic rocks in Korea by the fusion/hydrothermal reaction, and to study the adsorption kinetic and equilibrium properties for Sr and Cs ions by the Z-S1. To do this, the effects of different parameters for example initial concentration, contact time, pH, and temperature were evaluated through batch experiments. The kinetic data was evaluated by applying it to the pseudo-2nd order and pseudo-1st order rate models. The results of adsorption equilibrium experiments were modeled by applying isotherms of Dubinin–Radushkevitch (DR), Freundlich, and Langmuir. In addition, the thermodynamic parameters were calculated.

2. Material and Methods

2.1. Synthesis of Zeolitic Materials

Jeju volcanic rocks were collected and crushed from the scoria mine in Hanrim-eup, Jeju Island. The samples sieved by 0.425 mm or less were dried at 110°C for 24 h and then used in the synthesis of zeolitic materials. The synthesis of the zeolitic materials was carried out using the fusion/hydrothermal method which is the same procedure as the previous study [24]. The molar ratio of SiO₂/Al₂O₃ was fixed to 2.5, and then the mixture adjusted to have a NaOH/Jeju volcanic rocks ratio of 1.8 was fused at 550°C for 1 h. The fused sample was aged at 30°C for 5 h and crystallized at 90°C for 5 h while stirring in aqueous solutions to prepare the zeolitic materials. The prepared zeolitic materials were washed several times with deionized water. They dried at 105°C for 2 h and pulverized to a size of 170 mesh or more.

2.2. Adsorption Experiments for Sr and Cs Ions

The experiment was carried out batch wise. 500 mL of Sr and Cs ions solutions and 0.1 g of zeolite were placed in a 1,000 mL Erlenmeyer flask and stirred at 180 rpm using a horizontal shaker (Johnsam, JS-FS-2500). Initial concentrations of Sr and Cs ions were adjusted at the range of 20 – 100 mg/L and 10 – 100 mg/L, respectively. 2.0 mL of the sample was taken at regular intervals and treated with a centrifugal machine (Eppendorf, centrifuge 5415c) for 10 min at 10,000 rpm

simultaneously. After centrifugation, the supernatant was filtered and then the Sr and Cs ions concentrations were analyzed. The Sr and Cs ions concentrations were measured by an atomic absorption spectrophotometer (Shinmadzu, AA-7,000). The pH in the solutions was adjusted using 0.01 M NaOH and 0.01 M HCl with a pH meter (Orion, 420A). The samples morphologies were characterized using a scanning electron microscopy (SEM, Hitachi S-4200). The characterization of the samples was identified using an X-Ray diffractometer with a Cu K α radiation of $\lambda = 1.54 \text{ \AA}$ (XRD, D8 Advance, Bruker AXS). The acceleration current and voltage of XRD were set to 40 mA and 40 kV, respectively. Diffraction angle of 2θ in the range from 5 to 50° in 0.02° steps was scanned.

XRD patterns were identified by searching the International Centre for Diffraction Data (ICDD) powder diffraction file database using Joint Committee on Powder Diffraction Standards (JCPDS) files.

The Sr and Cs ions adsorption capacity adsorbed by the Z-S1 were calculated as follows:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

where q_t is the adsorption capacity (mg/g) at time t , C_0 is the initial concentration (mg/L), C_t is the concentration (mg/L) at time t , V is the volume (L) of solutions, and m is the amount (g) of the Z-S1 used.

3. Results and Discussion

3.1. Characterization of Zeolitic Materials

Fig. 1 shows the XRD patterns of Jeju volcanic rocks, and the zeolitic materials (Z-S1) synthesized with the Jeju volcanic rocks. Jeju volcanic rocks mostly consist of quartz and mullite as shown in Fig. 1(a). The main XRD peaks of the Z-S1 are observed at the 2θ (CuK α /deg) values of 7.18, 23.96, 27.08 and 29.91 as seen in Fig. 1(b), and they are consistent with the positions of major diffraction peaks of standard Na-A zeolite (Fig. 1 (c)). Thus, it

Fig. 1. XRD patterns of (a) Jeju volcanic rocks, (b) Z-S1, and (c) JCPDS card (No. 11-0590).

Fig. 2. SEM images of (a) the Jeju volcanic rocks and (b) the Z-S1.

can be identified as the Z-S1 has the morphological properties of Na-A zeolite. The XRD peaks of the Z-S1 match the standard XRD peaks for the Na-A zeolite ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27.4\text{H}_2\text{O}$) suggested by Treacy and Higgins [25]. SEM images of the Jeju volcanic rocks and the Z-S1 are presented in Fig. 2. The Jeju volcanic rocks have many amorphous particles in Fig. 2 (a). Fig. 2 (b) shows that the Z-S1 has lots of botryoidal cubic crystals with the formation of chamfered-edged. The structure of the cubic crystals corresponds to Na-A zeolite. These results showed that the Z-S1 was synthesized with Jeju volcanic rocks using the fusion/hydrothermal method. The crystals structures of the Z-S1 in this study and the zeolitic materials synthesized with fly ash by Lee et al. [21] and Tanaka et al. [26] were similar.

3.2. Effect of pH

The effect of pH on the Sr and Cs ions adsorption capacities by the Z-S1 was examined in the pH range of 2 - 10. The form of Cs and Sr species in aqueous solutions exist in the form of Sr^{2+}

Fig. 3. Effect of initial pH on the Sr and Cs ions adsorption capacities by the Z-S1 (adsorbent = 0.2 g/L, temperature = 20°C).

and Cs^+ at the pH range of 2-12 [27, 28]. As seen in Fig. 3, the Cs and Sr ions adsorption capacities by the Z-S1 are dependent on the solutions initial pH. The Sr and Cs ions adsorption capacities at above pH 6 were almost constant as about 120 mg/g and 90 mg/g, respectively, however, they decreased rapidly at below pH 4. In general, at a lower pH 4, the hydrogen ions in the solution increases and the hydrogen ions compete with the Sr and Cs ions for the Z-S1 binding sites that the adsorption capacities of the Sr and Cs ions decreased.

The pH of the acids affects the zeolite structure. In the zeolite framework, the Si-O-Al is weaker than Si-O-Si and can easily be attached by H^+ ions affecting the zeolite structure [29]. The Na-A zeolite structure with low Si/Al ratios may collapse in the presence of acids with pH lower than 5.0. In fact, pH less than 5.0 is not recommended for zeolites [30]. Therefore, all subsequent experiments for adsorption kinetics and isotherms were examined at the initial pH of 6.0.

3.3. Adsorption Kinetics

The adsorption rate should be considered for the rational design of the adsorption process. In order to investigate the Sr and Cs ions adsorption kinetics by the Z-S1, the applicability of the pseudo-1st and the pseudo-2nd order models were evaluated from the experimental data.

The pseudo-1st order model is expressed as [10]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

where k_1 is the pseudo-1st order rate constant (1/h), and q_e is the adsorption capacity (mg/g) at equilibrium.

The pseudo-2nd order model is expressed as [13]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 is the pseudo-2nd order rate constant (g/mg·h).

Fig. 4. Effect of contact time for the adsorption of (a) Sr and (b) Cs ions by the Z-S1 (adsorbent = 0.2 g/L, pH = 6, temperature = 293 K).

The experimental and calculated values for the Sr and Cs ions adsorption kinetics by the Z-S1 are seen in Fig. 4(a) and 4(b), respectively. The Sr and Cs ions adsorption capacities by the Z-S1 increased sharply up to 10 min, and it took longer to reach adsorption equilibrium for higher Sr and Cs ions initial concentrations, however, all cases reached equilibrium within 120 min. The rapid adsorption in the initial stage is because of the abundant binding sites on the pores of the zeolitic materials and it reaches equilibrium because of the occupation gradually on these binding sites as the contact time elapses. The kinetic parameters obtained by applying the experimental data to Eqs. (2) and (3) are summarized in Table 1. The decision coefficient (r^2) of the pseudo-1st and pseudo-2nd order rate equations for the adsorption of Sr ions were 0.6652 – 0.8220 and 0.9985 – 0.9999, respectively. The r^2 for the adsorption of Cs ions were 0.4010 – 0.8075 and 0.9995 – 1.0000, respectively. As seen in Fig. 4 and Table 1, the adsorption capacity ($q_{e,exp}$) obtained from the experiment did not agree with the q_e values estimated by the pseudo-1st order rate model, indicating that the pseudo-1st order model does not reproduce the Sr and Cs ions adsorption kinetics by the Z-S1. However, the $q_{e,exp}$ are similar to the q_e values calculated from the pseudo-2nd order rate model, and the r^2 values are also very close to unity. From the results, the Sr and Cs ions adsorption process by the Z-S1 beads could be accurately explained by the pseudo-2nd order rate model rather than pseudo-1st order rate model.

Similar results could be found in the adsorption of various metal ions with volcanic rocks as an adsorbent [10, 31], and also could be found in the adsorption of divalent ions by zeolites synthesized from volcanic rocks [22] and coal fly ash [21].

3.4. Adsorption Isotherm and Thermodynamic Properties

The three well known adsorption isotherm models such as Langmuir, Freundlich, and D-R isotherms were applied to investigate the adsorption equilibrium data.

The Langmuir model is expressed as [32]:

Table 1. Kinetic Parameters Calculated for The Sr and Cs Ions Adsorption by The Z-S1

Ion	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-1 st order			Pseudo-2 nd order		
			q_e (mg/g)	k_1 (1/h)	r^2	q_e (mg/g)	k_2 (mg/g·h)	r^2
Sr	20	94.5	34.8	0.0501	0.7269	95.0	0.0109	0.9999
	30	122.8	40.1	0.0548	0.8220	123.7	0.0065	0.9998
	50	147.0	35.3	0.0313	0.6667	147.7	0.0030	0.9985
	70	152.7	35.6	0.0382	0.6652	153.7	0.0032	0.9994
	100	152.7	34.7	0.0386	0.7700	154.2	0.0027	0.9992
Cs	10	51.3	4.1	0.0557	0.4010	51.3	0.0686	1.0000
	20	82.7	18.3	0.0358	0.5728	82.9	0.0105	0.9996
	30	114.1	26.6	0.0366	0.5705	114.4	0.0074	0.9996
	50	122.6	27.7	0.0807	0.8075	123.3	0.0128	1.0000
	70	137.0	40.0	0.0378	0.6335	137.5	0.0049	0.9995
	100	135.8	29.2	0.0483	0.6017	136.3	0.0084	0.9999

$$q_e = \frac{k_L q_m C_e}{1 + k_L C_e} \quad (4)$$

where q_m is the maximum adsorption capacity (mg/g), C_e is equilibrium concentration of adsorbate (mg/L), (C_e) and k_L is Langmuir constant (L/mg).

The Freundlich model is expressed as [33]:

$$q_e = k_F C_e^{1/n} \quad (5)$$

where k_F is the Freundlich constant ((mg/g)(L/mg)^{1/n}), and $1/n$ is a constant indicating the adsorption strength.

The D-R isotherm is a Gaussian energy distribution at the surface, which is applied for describing the adsorption mechanism. The D-R model is expressed as [34]:

$$q_e = q_m \exp(-\beta \varepsilon_p^2) \quad (6)$$

where β is the Freundlich constant (mol²/kJ²), and ε_p is a Polanyi potential (kJ/mol).

The ε_p is expressed as:

$$\varepsilon_p = RT \ln(1 + 1/C_e) \quad (7)$$

where R is an ideal gas constant (kJ/mol·K), and T is an absolute temperature (K).

The average adsorption energy E (kJ/mol) is calculated as follows:

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

As seen in Fig. 5, the experimental data and calculated values for the Sr and Cs ions adsorption isotherms by the Z-S1 at the solution temperatures of 293, 308, and 323 K were compared. The isotherm parameters and decision coefficients (r^2) obtained by fitting the experimental data to Eqs. (4) - (8) in Fig. 5 to the isotherm models are listed in Table 2. The r^2 of the Langmuir, the Freundlich, and the D-R isotherms were 0.9984-0.9998, 0.8800-0.9754, and 0.9573-0.9868, respectively. As observed from Table 2 and Fig. 5, the equilibrium data fit the Langmuir adsorption isotherms well, more than Freundlich and the D-R isotherms.

As shown in Table 2, the maximum Sr and Cs ions adsorption capacities (q_m) calculated from the Langmuir model increased from 154.8 mg/g to 175.1 mg/g and from 144.0 to 176.6 mg/g as the solution temperature increased from 293 to 323 K, respectively. El-Kamash [13] also reported that the q_m from the Langmuir model for the Sr and Cs ions adsorption by synthetic zeolite increased as the solution temperature increases. These results could be explained by the fact that the mobility of the Sr and Cs ions in an aqueous solution increases with temperature. Therefore, mass transfer with the Sr and Cs ions proceeds actively on the zeolite surface.

In the D-R isotherm, when the value of E is in the range of 8 - 16 kJ/mol, the adsorption process should proceed with chemisorption or ion-exchange, while the value of E is 8 kJ/mol or less, the adsorption process occurs physically [35]. As shown in Table 2, the E values of the Sr and Cs ions adsorption were between 10.4 - 12.7 kJ/mol and 6.9 - 11.0 kJ/mol, respectively. Therefore, the adsorption of the Sr and Cs ions by the Z-S1 seems to be governed by the ion exchange or chemisorption. This result is consistent with that of Abusafa and Yücel [36].

Many studies have reported the adsorption capacities for metal ions from aqueous solutions by various adsorbents (Table S1). The adsorption capacities of Sr and Cs ions by natural zeolites such as clinoptilolite and bentonites, were 9.8 mg/g - 28.4 mg/g and 49.0 mg/g - 73.1 mg/g, respectively [10, 41, 42]. The adsorption capacities by a Na-A zeolite [21] synthesized from a fly ash were 156.4 mg/g for Sr ions and 101.5 mg/g for Cs ions, and the adsorption capacity of Sr ions by a Na-P1 zeolite [22] synthesized from Jeju volcanic rocks was 57 mg/g. On the contrary, the Sr and Cs ions adsorption capacities by the Z-S1 in this study were 154.84 mg/g and 144.01 mg/g, respectively, which were superior to other adsorbents reported in the literature.

Fig. 5. Adsorption isotherms for (a) Sr and (b) Cs ions by the Z-S1 at different temperatures.

Table 2. Isotherm Parameters for the Sr and Cs Ions Adsorption by Z-S1

Ion	T (K)	Langmuir			Freundlich			D-R			
		k_L (L/mg)	q_m (mg/g)	r^2	k_F $\text{mg/g} \cdot (\text{L/mg})^{1/n}$	n	r^2	q_m (mg/g)	β (mol^2/kJ^2)	E (kJ/mol)	r^2
Sr	293	0.72	154.8	0.9998	101.2	9.36	0.9754	153.6	0.0035	11.9	0.9827
	308	1.06	166.3	0.9995	98.5	7.70	0.8979	167.1	0.0046	10.4	0.9794
	323	1.09	175.1	0.9994	106.7	7.91	0.9701	172.6	0.0031	12.7	0.9573
Cs	293	0.26	144.0	0.9984	47.9	3.66	0.8822	152.9	0.0106	6.9	0.9737
	308	0.36	160.9	0.9995	58.0	3.82	0.8800	174.8	0.0086	7.6	0.9847
	323	0.57	176.6	0.9992	82.5	5.11	0.9654	175.0	0.0041	11.0	0.9868

Fig. 6. Application of Van't Hoff plot for the adsorption of Sr and Cs ions by the Z-S1.

The thermodynamic parameters of change in Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) can be calculated by the formula as follows [44]:

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where ΔG° (kJ/mol), ΔH° (kJ/mol) and ΔS° (J/mol K) are changes of Gibbs free energy, enthalpy and entropy, respectively. T is the absolute temperature (K), k_L is the Langmuir constant (L/mg), and R is the ideal gas constant (J/mol K). The ΔG° at given temperatures were obtained from Eq. (9). The values of ΔH° and ΔS° in Eq. (10) were calculated by the slope and intercept on the plot of $\ln k_L$ versus $1/T$ (Fig. 6). These thermodynamic parameters for the Sr and Cs ions adsorption are given in Table S2. The ΔH° and ΔS° values for the Sr ions were 21.2 kJ/mol and 74.0 J/mol·K, and Cs ions were 27.5 kJ/mol and 109.2 J/mol·K, respectively. The ΔG° values for the Sr and Cs ions at 293 - 323 K were from -0.54 to -2.76 kJ/mol and from -4.51 kJ/mol to -7.79 kJ/mol, respectively. Therefore, the ΔH° values for the Sr and Cs ions adsorption by the Z-S1 were positive because of the endothermic characteristic

of the adsorption process. ΔS° values were found to be positive due to the ion exchange of the Sr and Cs ions with more mobile ions, Na^+ ions [45, 46], present on the Z-S1. The ΔG° values for the Sr and Cs ions were negative at 293 - 323 K and the negative values indicate the feasibility and the spontaneous characteristic of the adsorption process by the Z-S1. These results were similar to those of Panayotova [47] who studied the removal of Cu ions from wastewater by use of zeolite.

4. Conclusions

The zeolitic materials, Z-S1, could be synthesized from Jeju volcanic rocks using a fusion/hydrothermal method. The morphological structures of the Z-S1 were confirmed to be highly crystalline with the chamfered-edged structure by a XRD and a SEM. Batch experiments were performed to study the adsorption kinetic and equilibrium properties for Sr and Cs ions by the Z-S1. The Sr and Cs ions adsorption kinetics were predicted well by the pseudo-2nd order rate equation rather than the pseudo-1st order rate equation. The Sr and Cs ions adsorption isotherms were fit by the Langmuir isotherm better than those of the Freundlich and the D-R isotherms at 293 - 323 K. The maximum adsorption capacities by the Langmuir isotherm model were 154.8 mg/g for Sr ions and 144.0 mg/g for the Cs ions. The ΔH° and ΔS° values for the Sr and Cs ions were 21.2 kJ/mol and 74.0 J/mol·K and 27.5 kJ/mol and 109.2 J/mol·K, respectively. The ΔG° values of the Sr and Cs ions at 293 - 323 K were from -0.54 to -2.76 kJ/mol and from -4.51 to -7.79 kJ/mol, respectively. The Sr and Cs ions adsorption processes by the Z-S1 synthesized from the Jeju volcanic rocks have an endothermic and spontaneous nature. Therefore, the Z-S1 prepared in this study is considered as effective adsorbents for removing Sr and Cs ions in aqueous solutions.

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Author Contributions

M.G.L. (Professor) conducted the adsorption experiments and wrote

the manuscript; S.K.K. (Professor) supplied Jeju volcanic rocks and wrote the manuscript; C.H.L. (Professor) synthesized adsorbents and wrote the manuscript.

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