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Preparation of novel adsorbent PSf-SZ beads via immobilization of zeolite prepared from volcanic rocks with polysulfone and their Sr ion removal characteristics

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ABSTRACT

Scoria zeolite (SZ), synthesized from volcanic rocks, was immobilized with polysulfone (PSf) to fabricate PSf-SZ beads. The prepared PSf-SZ beads were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) analysis. The optimum PSf/SZ ratio to prepare PSf-SZ beads was 1.25. The diameter of the prepared PSf-SZ beads was about 3 mm. Batch experiments were conducted to investigate the adsorption characteristics of Sr ions by the PSf-SZ beads. A pseudo-second-order model fit the kinetic data for the Sr ion adsorption by PSf-SZ beads well. The equilibrium data fit well with Langmuir isotherm model and the maximum adsorption capacity was 65.4 mg/g. The thermodynamic parameters such as enthalpy change ($\Delta H°$), entropy change ($\Delta S°$) and Gibbs free energy change ($\Delta G°$) were evaluated. The positive values of $\Delta H°$ revealed the endothermic nature of the adsorption process and the negative values of $\Delta G°$ were indicative of the spontaneity of the adsorption process. Also, the distribution coefficients (K_d) of Sr ion in the presence of Na^+, K^+, Mg^{2+} and Ca^{2+} were in order of $Sr^{2+} > K^+ > Ca^{2+} > Mg^{2+} > Na^+$, indicating high selectivity for Sr ions even in the presence of coexisting ions. The PSf-SZ beads were found to have a remarkably high selectivity for Sr ions and high adsorption capacity because the K_d value of the Sr ion was higher than those of other metal ions. These results showed that the PSf-SZ beads prepared in this study could be effective adsorbents for removing Sr ions in aqueous solutions.

Keywords: Adsorption; Polysulfone; Strontium; Volcanic rock; Zeolite

1. Introduction

Nuclear power has been used in various fields such as medical, agricultural and industrial fields etc. as well as power plants. A large amount of liquid waste is generated in the course of using nuclear power. Especially, the problem of liquid waste disposal is a very important issue due to the explosion in the Chernobyl nuclear power plant and nuclear accident in Fukushima, Japan. Generally, radioactive materials have a long half-life and have high solubility in water, so it is known that if they leak into the natural environment, they will remain for a long time and adversely affect the ecosystem. Radioactive materials such as Cs and Sr ions generated in the nuclear industry can cause diseases such as skin disease, bone cancer, leukemia, etc. [1].

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Adsorption is widely used for the removal of radioactive materials such as Sr ions, and natural clay minerals such as kaolin, bentonite and clay are widely used as adsorbents for removing radioactive materials because they have high physico-chemical and thermal stability and low cost. However, these natural minerals have a disadvantage of low adsorption capacity. Therefore, many researchers have been working on synthesizing zeolites from various natural minerals such as bentonite [2], diatomite [3], kaolin [4] and clay [5] and using them as adsorbents. Smičiklas et al. [6] reported that the adsorption capacity of Sr ions by clinoptilolite, a natural zeolite, was 11.6 mg/g and Ma et al. [7] reported that the adsorption capacity of Sr ions by montmorillonite was 57.0 mg/g. On the other hand, El-Kamash [8] reported that the adsorption capacities of Cs and Sr ions by the commercial zeolite A were 69.0 mg/g and 90.7 mg/g, respectively, and Lee et al. [9] reported that adsorption capacities of Cs and Sr ions by the commercial zeolite A were 234.7 mg/g and 160.2 mg/g, respectively. Synthetic zeolites have better adsorption capacity than natural zeolites, but have a disadvantage of high price. Different kinds of zeolite are produced depending on the ingredient of the raw material and the adsorption performance is also different. Recently, many researches have been conducted to synthesize zeolite using industrial wastes such as fly ash as a low-cost raw material. Sinha et al. [10] studied the removal of Cs ions by the synthetic zeolite ZSM-5, El-Dessouky et al. [11] studied the removal of Cs and Sr ions using Na-A and Na-X mixed zeolites synthesized with fly ash from the Cairo thermal power plant in Egypt, and Lee et al. [12] studied the removal characteristics of Sr and Cs ions by Na-A zeolite synthesized from fly ash from the Ulsan industrial area, Korea. Also, Lee et al. [13] studied the removal characteristics of Sr ions by the Na-A zeolite synthesized from fly ash from a thermal power plant. Lee et al. [14] studied the removal characteristics of Sr and Cs ions using Na-A zeolite synthesized from volcanic rocks.

However, since adsorbents such as zeolite are generally used in the form of nano-sized powder, it is difficult to separate and recover the adsorbents after use, and there is a disadvantage that a pressure drop occurs when the adsorbent is charged in a column. In order to solve these problems, some researchers have been studied the removal of heavy metals and pollutants by immobilizing adsorbents or extractants using polymer substances such as alginate [15], chitosan [16], polyacrylonitrile (PAN) [17], and polysulfone (PSf) [18,19], etc. They reported that the prepared beads not only effectively removed metal ions but also reduced pressure drop, which enabled the recovery (solid-liquid separation) and reuse of the used beads. However, the studies on the removal of Sr and Cs ions in aqueous solutions by immobilizing zeolite on PSf are rare. PSf is a thermoplastic polymer with thermal decomposition temperature of 600 °C and is well known to have thermal stability at elevated temperatures. Also, the PSf has higher thermal stability than the alginate, the chitosan and the PAN, which have thermal decomposition temperature in the range of 110–310°C [19,20]. Thus, the adsorbent prepared by immobilizing zeolite on the polymer PSf is expected to be an adsorbent having higher thermal stability for the removal of radioactive ions such as Sr and Cs ions.

Therefore, in this study, we synthesized the PSf scoria zeolite (PSf-SZ) beads as a new adsorbent by immobilizing scoria zeolite (SZ) synthesized from natural volcanic rocks on PSf, and the synthesized PSf-SZ beads were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis. The effects of PSf/SZ ratio, Na-ion, pH, and coexisting ions were investigated to examine the adsorption characteristics of Sr ions by the synthesized PSf-SZ beads. The adsorption process was also evaluated in kinetic, isotherm, and thermodynamic aspects.

2. Materials and methods

2.1. Materials and chemicals

The reddish brown scoria (volcanic rocks) was collected and crushed from the scoria mine in Hanrim-eup, Jeju Island, Korea. The samples sieved by 0.425 mm or less were dried at 110°C for 24 h and then used in the synthesis of zeolite. PSf was purchased from Sigma-Aldrich. Hydrogen chloride (HCl), sodium hydroxide (NaOH), 1-methyl-2-pyrrolidone (NMP), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and strontium nitrate ($Sr(NO_3)_2$) were used extra pure grade reagents purchased from Samchun Co. in Korea. The Sr ion solution was prepared by dissolving $Sr(NO_3)_2$ in deionized water (Milli-Q Millipore 18.2 Mcm^{-1} conductivity) to prepare 1,000 mg/L stock solution.

2.2. Preparation of adsorbent

In this study, the synthesis of the SZ using volcanic rocks was carried out by the same procedure as the previous study [14]. The molar ratio of SiO_2/Al_2O_3 was fixed to 2.5, and the mixture adjusted to have a ratio of NaOH to scoria of 1.8 was melted at 550°C for 1 h. The sintered sample was aged and crystallized while stirring in an aqueous solution to synthesize the SZ. The synthesized SZ was washed several times with deionized water, dried at 105°C for 2 h and then pulverized to a size of 170 mesh or more.

PSf-SZ beads were prepared by dissolving 1.25 g of PSf in 10.0 mL of NMP, and then 1 g of the synthesized SZ powder was added and sufficiently mixed to obtain homogeneous slurry. The PSf-SZ beads were synthesized by dropping the mixed slurry into distilled water using a 1 mm diameter syringe. The PSf-SZ beads were prepared by changing the content of PSf to 1.0 g, 1.25 g, 1.5 g, and 1.75 g at the fixed SZ content of 1.0 g. Also, they were prepared by changing the content of the SZ to 0.5 g, 0.75 g, 1.0 g, 1.5 g, 2.0 g, and 3.0 g at the fixed PSf content of 1.0 g. The PSf-SZ beads were prepared by varying the PSf/SZ ratios from 0.33 to 1.75. The PSf-SZ beads were washed several times with deionized water and used in the experiment.

2.3. Characterization of materials

The morphologies of the PSf-SZ beads were observed using a scanning electron microscope (SEM, Hitachi S-2700, Japan). The samples were coated with a thin layer of platinum and mounted on a copper slab using double-sided tape for the SEM measurements. FTIR spectra of the PSf-SZ beads were analyzed using a FTIR spectrometer (Bruker Vertex 70, USA). TGA analysis of the PSf-SZ beads was conducted with a thermogravimetric analyzer (Perkin Elmer TGA 7, USA) and experiments were carried out on approximately 10 mg of samples in flowing air (flowing rate = 50 mL/min) at a heating rate of 10°C/min. Zeta potentials of the PSf-SZ beads were measured under the pH range of 2–10 with a Brookhaven Zeta plus (Brookhaven Instruments, USA). The concentrations of metal ions in samples were measured by an atomic absorption spectrophotometer (AAS) (Shinmadzu AA-7000, Japan).

2.4. Adsorption experiments

The adsorption experiment was carried out batch wise. 200 mL of a given concentration of Sr ion solution and 2 g of PSf-SZ beads were placed in a 500 mL Erlenmeyer flask at 20°C and stirred at 180 rpm using the horizontal shaker (Johnsam JS-FS-2500, Korea), and 1 mL of the sample was collected at regular intervals and centrifuged for 10 min at 10,000 rpm with a centrifugal machine (Eppendorf centrifuge 5415c, Germany). After centrifugation, the concentrations of metal ions in the supernatant were analyzed by the AAS.

2.4.1. Effect of pH

The pH change experiments were conducted with 100 mg/L of Sr ion solution at 20°C. 2 g of the PSf-SZ beads was transferred into a 500 mL Erlenmeyer flask containing 200 mL of Sr ion solution. The initial pH of the Sr ion solution was adjusted from 3 to 10 by using 0.1 M HCl and 0.1 M NaOH solutions and measured using a pH meter (Istek AJ-7724, Korea).

2.4.2. Adsorption kinetic, isotherms and thermodynamic studies

The adsorption kinetics were carried out by adding 2 g of the PSf-SZ beads into 200 mL solution with initial Sr ion concentration from 100 to 300 mg/L at initial pH of about 6 and at 20°C. At appropriate time intervals, samples were collected and analyzed after centrifugation.

The adsorption isotherms were studied by adding 2 g of the PSf-SZ beads into 200 mL solution with initial concentration from 100 to 300 mg/L. After the mixed solutions were shaken for 96 h, the equilibrium concentration of Sr ion in the solution was determined.

The adsorption thermodynamic experiments were conducted with 2 g of the PSf-SZ beads and initial Sr ion solution of 100 mg/L at three different temperatures of 293 K, 308, and 323 K. After the suspensions were shaken for 96 h, they were centrifuged and the supernatant were analyzed. The adsorption capacity q_t (mg/g) of the Sr ions adsorbed by the PSf-SZ beads and the partition coefficient (K_d) were calculated by the following formula [21].

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

$$K_d = \frac{(C_o - C_t)V}{C_o \times m} \tag{2}$$

where q_t is the adsorption capacity (mg/g) of the Sr ions adsorbed by the PSf-SZ bead at time t, C_0 is the concentration (mg/L) at the beginning, C_t is the concentration (mg/L) at time t, m is the amount (g) of the beads used, and $V(L)$ is the volume of solution.

2.4.3. Effect of coexisting ions

To investigate the adsorption characteristics of the Sr ions by the PSf-SZ beads in the presence of coexisting, the adsorption experiments were carried out with a multi-component mixed solution in which Na^+, K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} ions coexisted at concentrations of 1 mmol/L. The multi-component mixed solution with the concentration of 1 mmol/L per each coexisting ion was prepared by dissolving NaCl, KCl, $CaCl_2$, $MgCl_2$, and $Sr(NO_3)_2$ in deionized water. After the multi-component mixed solution was shaken for 96 h, the equilibrium concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} ions in the solution were determined by the AAS.

3. Results and discussion

3.1. Characterization of materials

3.1.1. FT-IR analysis

Fig. 1 shows the results of the FT-IR analysis of SZ, PSf and PSf-SZ beads. As shown in Fig. 1a, the peaks of SZ located at 556 cm^{-1}, 1004 cm^{-1}, and 1651 cm^{-1} are related to the presence of Si-O-Al, Si-O-Al, and HOH, respectively [22]. Also, as shown in Fig. 1(b), the peaks of the polymer PSf located at 1151 cm^{-1} and 2967 cm^{-1} are related to the presence of O=S=O and C-H peaks, respectively [23]. And in the case of the PSf-SZ beads shown in Fig. 1(c), the peaks of PSf-SZ beads located at 558 cm^{-1}, 1012 cm^{-1}, and 1647 cm^{-1} were maintained without reduction, in addition to the peaks of the PSf located at 1151 cm^{-1} and 2967 cm^{-1} observed in Fig. 1(b). From these observations, it was confirmed that the SZ was successfully immobilized on the polymer PSf.

3.1.2. TGA analysis

The thermal stability of SZ, PSf, and PS-SZ beads was evaluated by TGA analysis. Thermograms of SZ, PSf, and PS-SZ beads are shown in Fig. 2. As shown in Fig. 2, a weight loss at the range of 100–200°C can be due to the loss of water molecules on the SZ. The major weight loss at 600°C was associated thermal decomposition of organic PSf compound [23]. In the case of the PSf-SZ beads synthesized in this study, weight loss by water contained in the SZ in the range of 100–200°C and weight loss by the PSf at 600°C were observed. These results indicated that the SZ was immobilized in the PSf-SZ beads.

3.1.3. SEM analysis

A digital photograph and SEM images for PSf-SZ beads prepared are presented in Figs. 3(a)–(d). Fig. 3(a) shows

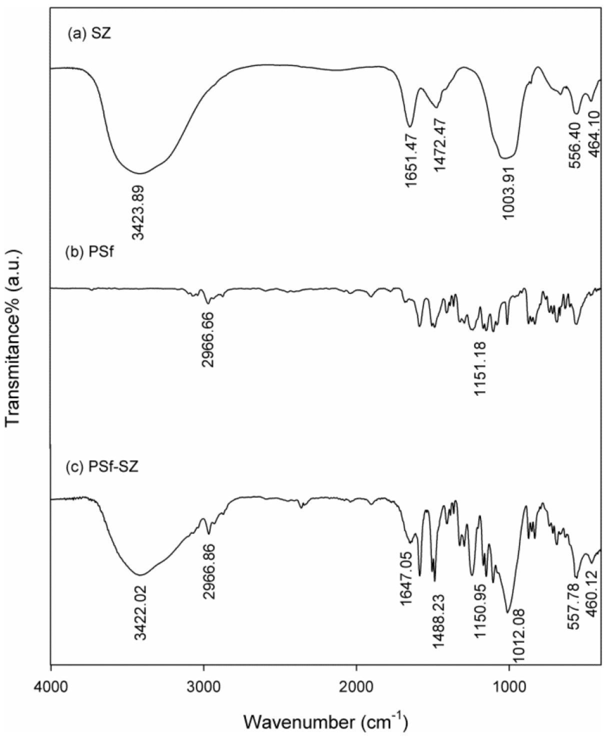


Fig. 1. FT-IR spectra of (a) SZ, (b) PSf, and (c) PSf-SZ beads.

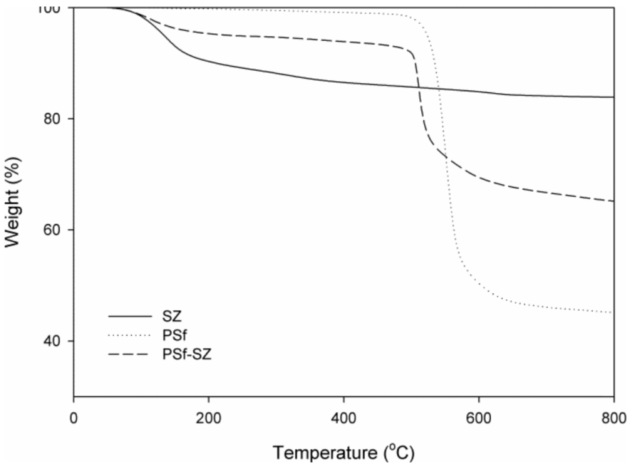


Fig. 2. Thermograms of SZ, PSf and PSf-SZ beads.

the whole shape of the PSf-SZ beads, and the PSf-SZ beads were spherical with the sizes of about 3 mm. Figs. 3(b)–(d) show the cross-section of the PSf-SZ beads synthesized by varying the content of the polymer the PSf and the SZ. It is observed that porous pores produced by PSf exist inside the bead, and SZ is adhered and immobilized on the surface of the polymer. Figs. 3(b) and 3(c) show SEM images of the PSf-SZ beads prepared by varying PSf/SZ ratios of 0.42 and 1.25, respectively. As the PSf/SZ ratios decreases from 1.25 to 0.42, more amounts of zeolites were observed inside the bead. Also, Figs. 3(b) and 3(d) show SEM images of the PSf-SZ beads prepared at PSf/SZ ratios of 0.42 and 1.75, respectively. It is observed that the pores decreased more as the PSf/SZ ratio increased to 1.75.

3.2. Adsorption of Sr ion

3.2.1. Effect of PSf/SZ ratio

Fig. 4 shows changes in the adsorption capacity of the Sr ions by the PSf-SZ beads according to varying the content of PSf and SZ. In the Fig. 4, the open symbol shows the adsorption capacity of the PSf-SZ beads prepared by increasing the content of PSf to 1.0 g, 1.25 g, 1.5 g, and 1.75 g

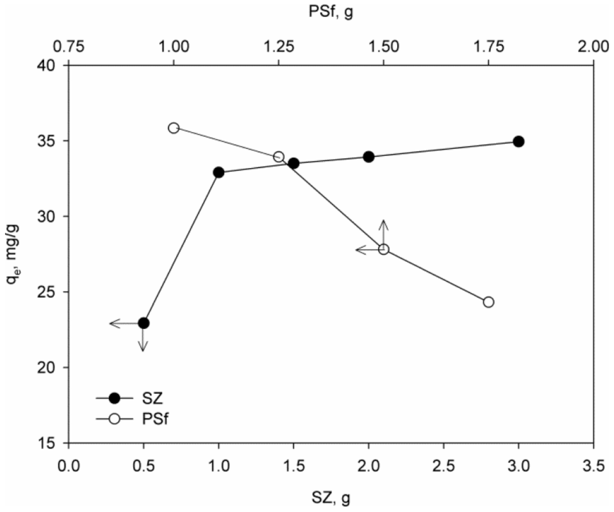
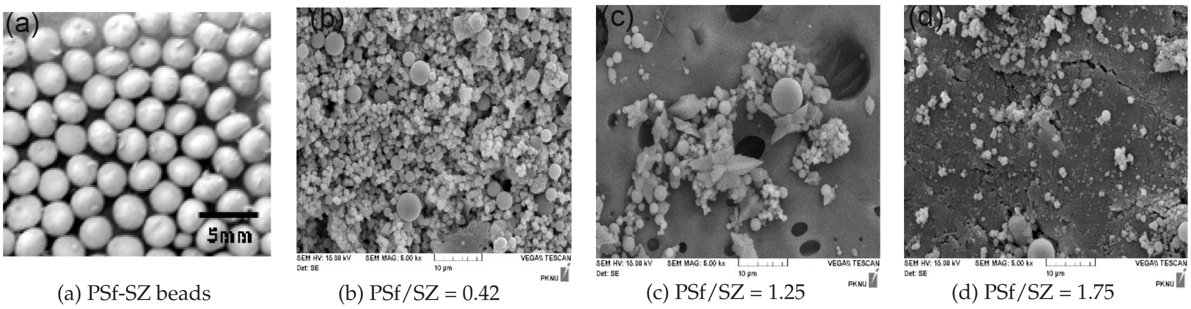


Fig. 4. Adsorption capacity of Sr ion for different PSf and SZ contents (PSf-SZ beads = 2.0 g/0.2 L, concentration = 100 mg/L, pH = 6, temperature = 293 K).



(a) PSf-SZ beads (b) PSf/SZ = 0.42 (c) PSf/SZ = 1.25 (d) PSf/SZ = 1.75

Fig. 3. A digital photograph and SEM images for PSf-SZ beads prepared.

at the constant content of SZ of 1.0 g, and the closed symbol shows the adsorption capacity of the PSf-SZ beads prepared by increasing the content of SZ to 0.5 g, 0.75 g, 1.0 g, 1.5 g, 2.0 g, and 3.0 g at the fixed PSf content of 1.0 g. As shown in the Fig. 4, when the content of PSf was 1.0 g and the constant content of SZ of 1.0 g, the PSf-SZ beads could be formed but the SZ was released from beads. However, when the content of PSf was 1.25 g or more the SZ was not released from the PSf-SZ beads. As the content of PSf increased from 1.25 g to 1.75 g, the adsorption capacity decreased from 33.9 mg/g to 24.3 mg/g. The similar trend was reported by Lee et al. [24] who studied the adsorption capacities of Cs and Sr ions by the SAN-Zeolite beads prepared by immoblizing zeolite on SAN. This is because the pores of the beads become smaller as the content of PSf increases (see Fig.3 (d)) and the solution cannot flow easily. On the other hand, when the content of PSf was kept constant at 1.25 g and the content of SZ was increased from 0.5 g to 1.0 g, the adsorption capacity rapidly increased. Yurekli [25] also reported that metal exchange capacity of the membrane increased with the zeolite NaX content in the study of the removal of Pb and Ni ions in wastewater by using zeolite nano-particles impregnated PSf membranes. When the content of SZ became 1.0 g or more the adsorption capacity was almost constant. This result indicated that the adsorption capacity increases due to increase the content of SZ in the PSf-SZ beads. However, when the amount of SZ is larger than a certain amount in the unit volume, the distance between the adsorbent SZ becomes closer and the active sites become coalesced or interfered with each other. Therefore, further experiments were carried out using PSf-SZ beads prepared with 1.25 g of PSf and 1.0 g of SZ.

3.2.2. Effect of Na ion

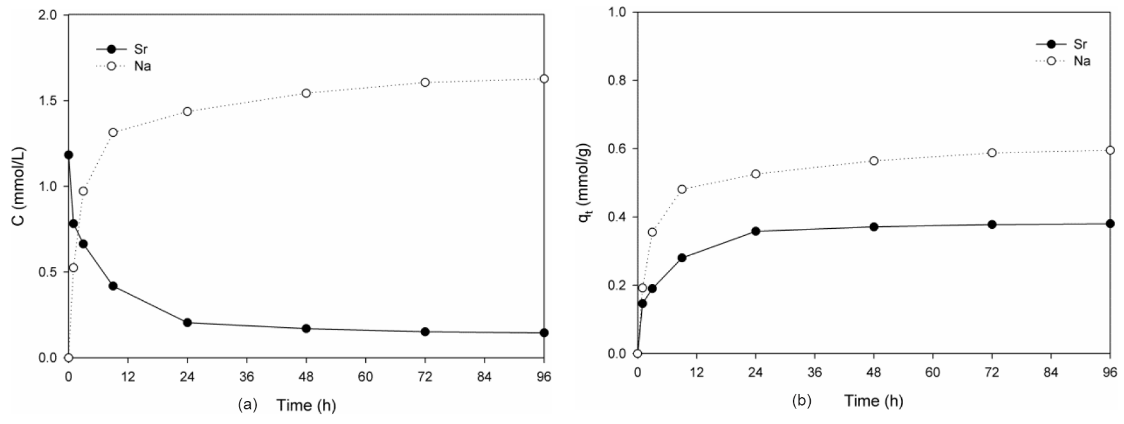
In the adsorption of Sr ions by the PSf-SZ beads, the following ion exchange reaction occurs between Na^+ ions present in the SZ of the beads and Sr ions in the solution [26].

$$2\overline{Na^{+}_{Solid}} + Sr^{2+}_{aq} \Leftrightarrow 2Na^{+}_{aq} + \overline{Sr^{2+}_{Solid}} \tag{3}$$

In order to investigate the relationship between the Sr ions adsorbed on the PSf-SZ beads and the Na^+ ions released from the PSf-SZ beads, changes in concentration and adsorption capacity with time are shown in Fig. 5. As shown in Fig. 5(a), the concentration of the Sr ions gradually decreased with time, but the concentration of the Na ions increased proportionally with the concentration decrease of the Sr ions. Fig. 5(b) shows that the adsorption capacity of the Sr ions adsorbed by the PSf-SZ beads was 0.38 mmol/g and the amount of Na ions released from the PSf-SZ beads was 0.6 mmol/g. If the removal of the Sr ions by the PSf-SZ beads is due to only ion exchange, 0.3 mmol/g of Sr ion should be removed since the equivalence ratio of Sr ions to Na ions is 1:2 and 0.6 mmol/g of Na ions was released. The 0.38 mmol/g of Sr ions adsorbed by the PSf-SZ beads was slightly higher than 0.3 mmol/g of the equivalence capacity of Sr ions. It seems that the adsorption of Sr ions is occurred by ion exchange with Na^+ on the zeolite (SZ) of the PSf-SZ beads, and the PSf used for immobilizing the SZ also affects the adsorption.

3.2.3. Effect of pH

It is generally known that the pH of a solution has a large influence on the adsorption process because the ionic form of the adsorbate in aqueous solutions and the surface charge of the adsorbent change as the pH of the solution changes. The effect of pH on the adsorption of Sr ions from aqueous solutions using the prepared PSf-SZ beads was investigated at pH range of 2–10. Fig. 6 shows the changes in the adsorption capacity and the zeta potential value of the PSf-SZ beads with the pH change in the solution. As shown in Fig. 6, the zeta potential gradually decreased as the pH value increased. The isoelectric point of the PSf-SZ beads was approximately 6. This indicated that the PSf-SZ beads were positively charged at pH < 6 and negatively charged at pH > 6. The adsorption capacity of the Sr ions by the PSf-SZ beads decreased with decrease in the pH value at pH less than 6. At lower pH values (pH < 6), the low adsorption capacity can be explained due to electrostatic repulsion between the Sr ions and the adsorbent with



(a) concentration

(b) adsorption capacity

Fig. 5. Comparison of (a) concentration and (b) adsorption capacity for the adsorbed Sr ions and the released Na ions during the adsorption of Sr ions by PSf-SZ beads (PSf-SZ beads = 2.0 g/0.2 L, pH = 6, temperature = 293 K).

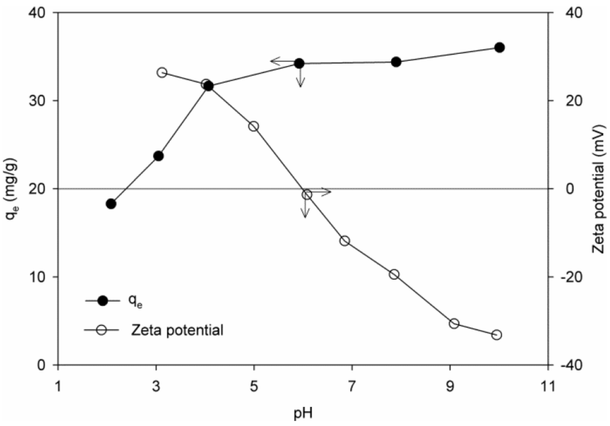


Fig. 6. Effect of pH on the adsorption of Sr ions and zeta potential of PSf-SZ beads (PSf-SZ beads = 2 g/0.2 L, concentration = 100 mg/L, temperature = 293 K).

positive charge and inhibition by the presence of H_3O^+ ions competing with the Sr ions for the surface sites [8]. The high adsorption capacity of about 35 mg/g was observed at pH range from 6 to 10. Thus, all subsequent experiments in this study were carried out at pH 6.

3.2.4. Effect of contact time

Fig. 7 shows the variation of the adsorption capacity of Sr ions by the PSf-SZ beads with contact time. It is shown that the adsorption rate at the beginning of 24 h is fast due to the presence of many active sites on the surface of the PSf-SZ beads and then slowdown after 96 h due to be saturated active sites with contact time. The adsorption gradually reaches equilibrium. In our previous study [12], the adsorption equilibrium time was 2 h for the adsorption of Sr ions from an aqueous solution using powdered Na-A zeolite synthesized from coal fly ash, but it was as long as 96 h for the adsorption of Sr ions by the PSf-SZ beads in this study. Lee et al. [24] also reported that the adsorption capacities of Sr and Cs ions increased gradually within 12 h and then reached to adsorption equilibration after 72 h in the study of adsorption of Sr and Cs ions using SAN-zeolite beads. This result suggests that the mass transfer resistance on the surface of the zeolite immobilized inside the PSf-SZ beads was higher than that of the powder Na-A zeolite due to be the diffusion through the structure formed by the polymerization of PSf. On the other hand, as the Sr ion concentration increased from 100 mg/L to 300 mg/L, the adsorption capacity increased from 43.0 mg/g to 62.9 mg/g. The increase of the adsorption capacity is thought to be caused by the increase of the concentration difference which is the driving force of adsorption as the concentration increases.

3.2.5. Adsorption kinetics

In order to investigate the adsorption mechanism of Sr ion by the PSf-SZ beads, three kinetic models such as the pseudo-first-order, the pseudo-second-order, and intraparticle diffusion models were applied to the experimental data.

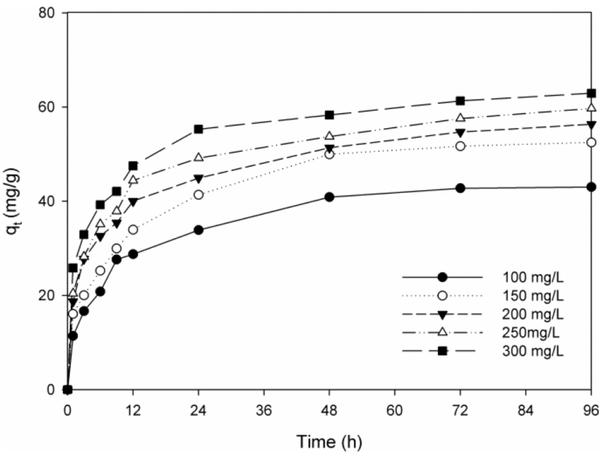


Fig. 7. Effect of contact time for the adsorption capacities of Sr ions by PSf-SZ beads (PSf-SZ beads = 2 g/0.2 L, pH = 6, temperature = 293 K).

The pseudo-first-order model is represented as [27]:

$$In\left(q_e - q_t\right) = In\left(q_e\right) - K_1 t \quad (4)$$

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

The pseudo-second-order model is expressed as [28]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 is a pseudo-second-order rate constant (g/mg·h).

Table 1 summarizes the parameter values obtained by applying the experimental results in Fig. 7 to Eqs. (4) and (5). As shown in Table 1, the values of correlation coefficient (r^2) applied to the pseudo-first-order model and the pseudo-second-order model are 0.9331–0.9928 and 0.9973–0.9989, respectively. In addition, the adsorption capacity ($q_{e,exp}$) obtained by the experiment of Sr ions by the PSf-SZ beads are similar to the calculated q_e values from the second-order rate model. These results indicate that the adsorption process of Sr ions by the PSf-SZ beads can be explained more accurately by the pseudo-second-order model rather than pseudo-first-order model and that the overall adsorption rate is controlled by the chemical sorption process [16,22]. Similar trends were reported by other researchers [17,24,29].

The above two kinetic models could not definitely explain the adsorption mechanism, so the intra particle diffusion model proposed by Weber and Morris [30] was applied in this study.

The intra particle diffusion model is expressed as [31]:

$$q_t = K_d t^{1/2} \quad (6)$$

where k_d is the intra particle diffusion rate constant (mg/g·$h^{1/2}$).

Fig. 8 plots the results by applying Eq. (6) into the data in Fig. 7 and the calculated parameters are summarized in Table 2. As shown in the figure, the plots diverged two linear parts before and after 3.43 $h^{1/2}$, which indicated two

Table 1
Kinetic data calculated for the adsorption of Sr ions by PSf-SZ beads

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_e (mg/g)	k_1 (1/h)	r^2	q_e (mg/g)	k_2 (g/mg·h)	r^2
100	43.0	34.8	0.0649	0.9843	45.7	0.0037	0.9980
150	52.5	40.1	0.0558	0.9928	55.9	0.0028	0.9973
200	56.3	35.3	0.0430	0.9618	58.1	0.0036	0.9977
250	59.7	35.6	0.0401	0.9362	61.3	0.0036	0.9980
300	62.9	34.7	0.0445	0.9331	64.5	0.0155	0.9989

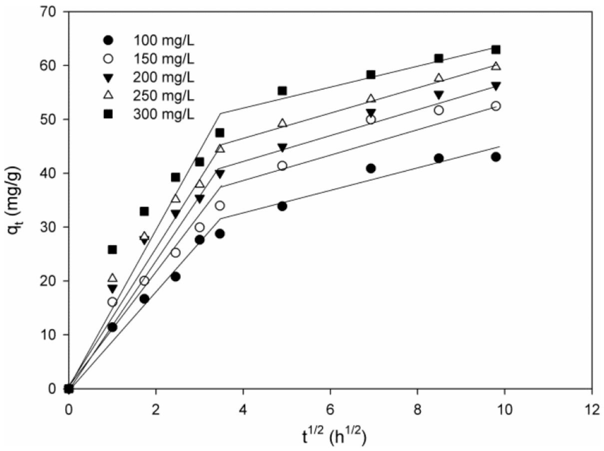


Fig. 8. Webber-Morris linear plot for the adsorption of Sr ion by PSf-SZ beads at different initial Sr ion concentrations (PSf-SZ beads = 2 g/0.2 L, pH = 6, temperature = 293 K).

Table 2
Parameters of intra particle diffusion model

C_0 (mg/L)	First linear part		Second linear part	
	k_d (mg/g·$h^{1/2}$)	r^2	k_d (mg/g·$h^{1/2}$)	r^2
100	8.2700	0.9824	2.3373	0.9151
150	9.1671	0.9637	2.9551	0.9041
200	10.9159	0.9432	2.6290	0.9765
250	11.9704	0.9561	2.4058	0.9903
300	12.5924	0.9151	2.2656	0.9179

steps occurred in the adsorption process. Hamdaoui et al. [31] explained that the first linear part is due to the external mass transfer and the second linear part is due to the intra particle diffusion. The rate constants in the first linear part are 8.27–12.59 mg/g·$h^{1/2}$, while the values in the second part are 2.34–2.96 mg/g·$h^{1/2}$ and are about 4–5 times lower than those in the first part. This result indicates that the external mass transfer step in the adsorption of Sr ions by the PSf-SZ beads is very fast, but the adsorption reaction by intra particle diffusion proceeds slowly. The above results showed that the adsorption behavior of Sr ions by the PSf-SZ beads is controlled by intra particle diffusion together with the pseudo-second-order kinetic model. This means that the chemical adsorption and intra particle diffusion resistance of Sr ions inside the PSf-SZ beads affect both the rate of adsorption. It is considered that the rapid film diffusion of Sr ions to the external surface is followed by the slow intra particle diffusion along the micropores of the PSf-SZ beads [19,32].

3.2.6. Adsorption isotherms

In this study, the two-well known adsorption isotherm models such as Langmuir isotherm and Freundlich isotherm were used to investigate the adsorption equilibrium data.

Langmuir model is as follows [33]:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

where q_m is the maximum adsorption capacity (mg/g) and k_L is Langmuir constant (L/mg).

Freundlich model is expressed as [34]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{7}$$

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

Table 3 shows the parameter values obtained when the experimental results of isothermal adsorption at different temperatures are applied to Langmuir and Freundlich models. The r^2 values for Langmuir model were found to be higher than that for Freundlich model. This indicates that Langmuir model represents a better fit to the experimental data than Freundlich model. Also, as shown in Table 3, the maximum adsorption capacity (q_m) increased from 65.4 mg/g to 67.6 mg/g and Langmuir constant (k_L) increased from 0.1172 L/mg to 0.2446 L/mg. This is thought to be due to the fact that, as the solution temperature increases, the movement of the ions in the solution becomes more active and the mass transfer becomes faster [35]. Fig. 9 compares the equilibrium data for the PSf-SZ beads in this study and the equilibrium data for scoria zeolite (SZ) obtained from our previous study. As shown in Fig. 9, the q_m value for the PSf-SZ beads and the SZ are 65.4 mg/g and 154.8 mg/g, respectively. The PSf-SZ beads prepared in this study showed about 40% of the adsorption capacity of Sr ions by the SZ powder adsorbents. This result suggests that the prepared PSf-SZ beads could be a useful adsorbent not only having high adsorptivity of up to 40% of the adsorption capacity of the SZ powder but also having the advantage of easy separation and recovery of the

Table 3
Comparison of adsorption isotherm constants for the adsorption of Sr ions by PS-SZ beads

Temperature	Langmuir			Freundlich		
	q_m (mg/g)	k_L (L/mg)	r^2	k_F ((mg/g)(L/mg)$^{1/n}$)	$1/n$	r^2
293 K	65.4	0.1172	0.9984	30.9694	0.1397	0.9805
308 K	66.7	0.1623	0.9960	38.8963	0.0984	0.9740
323 K	67.6	0.2446	0.9970	38.2063	0.1117	0.9956

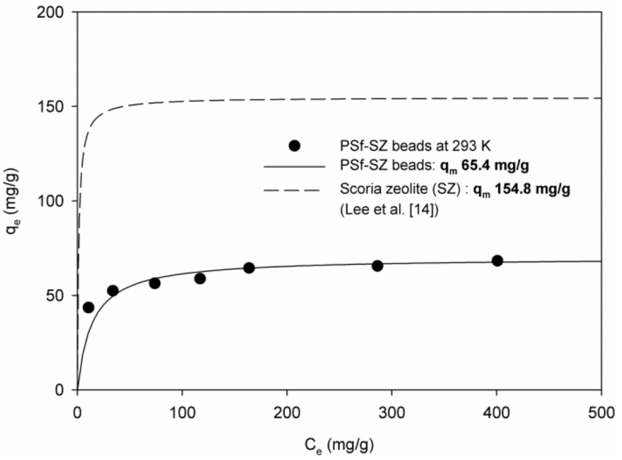


Fig. 9. Isotherm plots for the adsorption of Sr ions by PSf-SZ beads and SZ (scoria zeolite).

Table 4
Thermodynamic parameters for the adsorption of Sr ions by PSf-SZ beads

ΔH° (kJ/mol)	ΔS° (J/mol·K)	ΔG° (kJ/mol)		
		293 K	308 K	323 K
19.28	84.97	–5.63	–6.90	–8.18

Table 5
Adsorption selectivity of Sr ions

Solution	Ion	q_e		K_d (L/g)
		(mg/g)	(mmol/g)	
Single	Sr^{2+}	34.46	0.393	2.885
Mixed	Sr^{2+}	24.03	0.274	0.861
	Ca^{2+}	2.09	0.052	0.068
	Mg^{2+}	0.65	0.027	0.035
	Na^+	–6.54	–0.285	–0.151
	K^+	4.26	0.109	0.172

adsorbent from the aqueous solution after the use in the adsorption process.

3.2.7. Thermodynamic analysis

The thermodynamic parameters can be determined by using the following relationships [36].

$$InKL = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

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 Gibb's free energy change (ΔG°) at given temperatures are obtained from Eq. (9). ΔH° and ΔS° are calculated from the slope and intercept of the plot of ln k_L versus 1/T. The calculated values of the thermodynamic parameters were given in Table 4. The ΔH° value for the adsorption of Sr ions by the PSf-SZ beads was positive due to the endothermic nature of the adsorption process. The values of ΔG° were negative at all temperatures and the negative values confirm the feasibility of the adsorption process of Sr ions by the PSf-SZ beads and the spontaneous nature of adsorption. The increase of the absolute value of ΔG° as temperature increases implies that the affinity of Sr ions on the PSf-SZ beads was higher at a high temperature. The positive value of ΔS° reflects the affinity of the PSf-SZ beads for Sr ions and an increased randomness at the solid-solution interface during adsorption [8,12,17,29,37].

3.2.8. Effect of coexisting ions

Various cations such as Na^+, K^+, Mg^{2+}, and Ca^{2+} can exist in seawater contaminated with radioactive materials. The presence of these coexisting ions in seawater may affect the adsorption characteristics of the Sr ions by the PSf-SZ beads. Table 5 shows the adsorption capacity (q_e) and the partition coefficient (K_d) of the Sr ions obtained from the experimental results. K_d indicates the interaction between metal ions coexisting as a mobility index of metal ions present in the aqueous solutions, which means that the larger the K_d, the higher the selectivity. As shown in Table 5, when Na^+, K^+, Mg^{2+}, and Ca^{2+} ions coexist in the Sr ion solution, the value of K_d value was in the order of Sr^{2+} (0.861 L/g) > K^+ (0.172 L/g) > Ca^{2+} (0.068 L/g) > Mg^{2+} (0.035 L/g). At this time, the value of q_e was in the order of K^+ 4.26 mg/g (0.109 mmol/g) > Ca^{2+} 2.09 mg/g (0.052 mmol/g) and Mg^{2+} 0.65 mg/g (0.027 mmol/g), which is proportional to the order of the K_d values. The q_e and K_d values for Na ions are negative at –6.54 mg/g (–0.285 mmol/g) and –0.151 L/g, respectively. This result is because the SZ immobilized on the PSf-SZ beads is a Na-A zeolite having Na ions in the structure, so Na^+ ions are ion-exchanged with Sr ions and released into the aqueous solution. The K_d value of Sr ions when Sr ions exist alone is 2.885 L/g, but the value in the presence of coexisting ions is 0.861 L/g, which shows a tendency to decrease in the presence of coexisting ions. However, the adsorption capacity of Sr ions in the presence of coexisting ions is 24.03 mg/g, which is about 6–30 times higher than the adsorption capacity of other ions. This suggests that the adsorption of Sr ions by the PSf-SZ beads is selective even in the presence of other ions.

4. Conclusion

PSf-SZ beads were prepared by immobilizing scoria zeolite (SZ) synthesized from volcanic rocks with polysulfone (PSf). FT-IR, TGA and SEM analysis confirmed that the SZ was immobilized well on the PSf-SZ beads. The optimum PSf/SZ ratio to prepare the PSf-SZ beads was 1.25. SEM images showed that the prepared PSf-SZ beads had a spherical shape of about 3 mm in diameter and had a porous structure inside the beads. In order to investigate the adsorption characteristics of the Sr ions by the PSf-SZ beads, the effects of various parameters such as the initial concentrations of the Sr ions, contact time, and solution pH were investigated in a batch mode. A pseudo-second-order model fitted well the kinetic data for the Sr ion adsorption by the PSf-SZ beads. Langmuir model fitted the adsorption isotherm data better than Freundlich model. The maximum adsorption capacity of the Sr ions, as determined by Langmuir model, was 65.4 mg/g, and it was equivalent to about 40% of powdered zeolite (SZ). The calculated thermodynamic parameters of $\Delta H°$ and $\Delta G°$ showed that the adsorption of Sr ions by the PSf-SZ beads occurred through a spontaneous and an endothermic reactions. The PSf-SZ beads showed high selectivity for Sr ions even in the presence of Na^+, K^+, Mg^{2+} and Ca^{2+} ions. Therefore, the PSf-SZ beads prepared in this study are considered to be effective adsorbents for removing Sr ions in the aqueous solutions.

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