Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2018.22752

124 (2018) 184–192
August

Removal of strontium ion from aqueous solution by PS-D2EHPA beads prepared by immobilizing di-2-ethylhexyl phosphoric acid (D2EHPA) with polysulfone (PS)

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Received 20 December 2017; Accepted 4 July 2018

ABSTRACT

PS-D2EHPA beads were prepared by immobilizing di-2-ethylhexyl-phosphoric acid (D2EHPA) with polysulfone (PS). The prepared PS-D2EHPA beads were characterized by using a Fourier transform infrared spectrometer (FTIR) and scanning electron microscopy (SEM). The removal characteristics of Sr(II) from an aqueous solution by the prepared PS-D2EHPA beads was investigated in a batch system. The kinetic data followed the pseudo-second-order kinetic model. Equilibrium data fit the Langmuir isotherm model well and the removal capacity of Sr(II) by the PS-D2EHPA beads obtained from the Langmuir model was 1.71 mg/g at 298 K. The removal process of Sr(II) by the PS-D2EHPA beads is dependent on the initial pH of the solution. The optimum removal of Sr(II) by PS-D2EHPA beads was observed in the range of pH 6–10. The values of the thermodynamic parameters such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) showed that the adsorption of Sr(II) by the PS-D2EHPA beads was feasible, spontaneous and endothermic at 298–328 K. The results implied that the prepared PS-D2EHPA beads could be an interesting alternative material for the removal of Sr(II).

Keywords: Strontium; Polysulfone; Di-(2-ethylhexyl) phosphoric acid; Immobilization; Extractant

1. Introduction

The radioactive waste containing radio nuclides have been considered the most hazardous environmental pollutant, and its treatment has received much attention. Cesium and strontium are the most abundant radio nuclides in nuclear fission products that are routinely or accidentally released. They have a relatively long half-life of about 30 years and are considered hazardous elements for the environment [1,2].

In general, many methods such as precipitation [3], ion exchange [4], solvent extraction [5] and adsorption [6] in the removal of Sr(II) from aqueous solutions are being used. Among these methods, solvent extraction is widely used to remove heavy metal ions from aqueous solutions because of its high selectivity and rapid removal rate. Mishra and Devi [7] reported that Cyanex 921 can effectively remove Cu(II) from aqueous solutions. Nejad and Kazemeini [8] conducted a study to remove platinum ions using trioctylphosphine oxide (TOPO) as an extractant. Kidani and Imura [9] studied the removal of Cu(II) using the extractant thenoyltrifluoroacetone (TTA). Sarangi et al. [10] reported

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that extractants such as tri-n-butyl phosphate (TBP), LIX 84I and Cyanex 923 can effectively remove Cu(II), Fe(III), and Zn(II) in aqueous solutions. Ren et al. [11] suggested that di (2-ethylhexyl) phosphoric acid (D2EHPA) can effectively remove Cu (II) from aqueous solutions. Belkhouche et al. [12] investigated the removal characteristics of Ni(II) and Cu(II) when using D2EHPA as the extractant. Dozol et al. [13] studied the removal of SR(II) and Cs(I) in aqueous solutions using dicarbollides, crown ethers and calixarenes with functional groups. Kocherginsky et al. [5] studied the removal of Sr(II) by D2EHPA in very high pH wastewater. Various extraction agents have been used in the removal of heavy metals in water by the solvent extraction method. Among these extracting agents, D2EHPA is known to have high efficiency and selectivity for removing heavy metal ions from aqueous solutions and is widely used commercially [14]. However, liquid-liquid extraction requires a large amount of organic solvent and the spillage of the organic solvent in water is a problem [15].

Thus, many studies have been carried out using impregnated porous materials such as supported liquid membranes [16], ion exchange resins [17], and carbon nano tubes [14]. However, when a porous material is impregnated with an extraction agent, it is known to have a short life span because the extraction agent is lost from the membrane or resin [18,19]. Recently, to overcome these problems, many studies have been carried out to recover or remove metal ions by encapsulating an extractant with a polymer material [20,21]. If the liquid extractant is encapsulated using a polymeric material, the extractant is present inside the capsule and isolated from the surroundings by the thin capsule wall. Thus it is possible to use a small amount of organic solvent compared to liquid-liquid extraction and also it can be recovered and reused after use.

Nishihama et al. [22] used micro capsules consisting of styrene–divinylbenzene copolymer containing bis(2-ethylhexyl) phosphinic acid for the separation of rare earth metals, Yang et al. [21] prepared and used polystyrene microcapsules containing Aliquat 336 for the separation of metal ions. Ozcan et al. [19] investigated the removal of Cr(VI) from aqueous solutions using polysulfone microcapsules containing Cyanex 923 as the extraction reagent. Zhang et al. [23] prepared PVA–alginate gel beads containing [A336] [MTBA] as novel solid-phase extractants for the recovery of Hg(II) from aqueous solutions. Lee and Lee [24] studied for the enhanced adsorption of Sr(II) from aqueous solutions using solid-phase extractants containing TTA and TOPO. Also, Yang et al. [20] reported that a microcapsule of size 80 μm was prepared by immersing the extractant D2EHPA in polysulfone and that the prepared PS-D2EHPA microcapsules could remove Cu(II) from aqueous solutions. Ciopec et al. [25] performed the removal of Cu(II) with PS-D2EHPA microcapsules prepared by immobilizing D2EHPA in polysulfone and Davidescu et al. [26] used DEHPA impregnated XAD7 copolymer resin for the removal of Cr(III) from water. Singh et al. [27] studied uranium sorption using D2EHPA-impregnated polymeric beads containing D2EHPA on polyethersulfone polymer matrix and Kanagare et al. [28] synthesized the D2EHPA extractant encapsulated polymeric beads and investigated for the sorption of Zn (II) from aqueous solutions.

Even micro capsules can prevent the leakage of the organic solvent, but the phase separation and the handling are not easy and problems such as pressure drop may occur during continuous operation because the particle size of the micro capsules is small. It is considered that it is more effective to make beads with larger size than micro capsules in field application.

Therefore, in this study, PS-D2EHPA beads were prepared by immobilizing D2EHPA in PS for the removal of radioactive Sr(II) from aqueous solutions. The prepared PS-D2EHPA beads were characterized by SEM and FTIR analysis. The removal of Sr(II) by PS-D2EHPA beads were carried out batch wise and the removal performance evaluated in terms of solution pH, contact time and initial Sr(II) concentration. The kinetic parameters and the isotherm parameters were calculated and discussed.

2. Materials and methods

2.1. Materials and chemicals

PS-D2EHPA beads were prepared by an immobilization method as used in our previous study [27]. All the chemicals and reagents used in the present study were of analytical grade and used without further purification. Polysulfone (PS) was purchased from Sigma–Aldrich and N-methyl-2-pyrrolidone (NMP) was purchased from Samchun Pure Chemical. The pH value of the solution was adjusted with hydrochloric acid (Samchun Pure Chemical, EP) and sodium hydroxide (Shinyo pure chemicals Co, GR). Stock solution of Sr(II) (1,000 mg/L) was prepared by dissolving strontium nitrate anhydrous (Shimakyu's pure chemicals Co, EP) in deionized water. All the working solutions were obtained by diluting the stock solution with deionized water.

2.2. Preparation of PS-D2EHPA beads

1.5 g of PS was put into a beaker (50 mL), and 10 mL of NMP (density = 1.03 g/mL) was added. After 1 h of stirring, 1 mL of D2EHPA (density = 0.965 g/mL, molecular weight = 322.42 g/mol) was added, and the mixture was stirred for 1 h at 150 rpm using magnetic stirrer at room temperature. PS-D2EHPA beads were prepared by dropping this mixed slurry into a mixed solution of 150 mL of distilled water and 350 mL of ethanol using a 1 mm-diameter syringe, and the obtained PS-D2EHPA beads were washed with deionized water several times. D2EHPA was not detected in the residual solution after the preparation of the beads.

2.3. Instrumentation

The morphologies of the PS-D2EHPA beads were observed with a microscope (SV-55, SOMETECH). Fourier transform infrared spectroscopy (FT-IR spectroscopy, Bruker Vertex 70) was used for the IR spectral studies of PS, D2EHPA and PS-D2EHPA. The thermogravimetric analysis (TGA) was analyzed with a thermogravimetry (Perkin Elmer, TGA 7) at a heating rate of 10°C/min in the range of 50°C to 700°C in a N_2 atmosphere. The concentration of

Sr(II) was measured with an atomic absorption spectrometer ((AAS) Shimadzu, AA-7000).

2.4. Batch experiment

Batch experiments were performed at 298 K in a 1,000 mL Erlenmeyer flasks containing 300 mL of Sr(II). The solution was stirred at 170 rpm using a shaker (Johnsam Co., Js-Fs-2500) and sampled at certain time intervals. To investigate the effect of pH on the removal of Sr(II) by the PS-D2EHPA beads, it was varied from 2.5 to 10.5 by gradually adding 0.1 M HCl/NaOH. The solution's pH was measured with a pH meter (Istek, AJ-7724). The required quantity of PS-D2EHPA beads was added to each flask, and the mixtures were stirred for 2 h, which was enough time to achieve equilibrium. For kinetic studies, Sr(II) concentrations were varied between 5 and 100 mg/L. The thermodynamic parameters were studied at 298, 313, and 328 K. After each experiment, each sampled solution was centrifuged at 10,000 rpm for 5 min by using a centrifuge (Eppendorf, Centrifuge 5415c). After centrifugation, the concentrations of Sr(II) in the supernatant were analyzed by the AAS.

The reusability experiment was carried out as follows. 5 g of the equilibrated PS-D2EHPA beads through the contact with fresh solution (5 mg/L of Sr(II) ion) were added to 1000 mL of 2 M HNO_3 and stirred at 150 rpm for 300 min, and the loaded Sr(II) ions were leached out. The stripped PS-D2EHPA beads were washed with deionized water and re-equilibrated again with fresh feed solution. These processes were repeated five times.

The amount of Sr(II) removed by the PS-D2EHPA beads was calculated using Eq. (1)

$$q = \frac{\left(C_o - C_t\right)V}{W} \tag{1}$$

where q (mg/g) is the removal capacity at time t, C_0 (mg/L) is the initial concentration, C_t (mg/L) is the solution concentration at time t, W (g) is the dosage of the PS-D2EHPA beads, and V (L) is the volume of the solution.

3. Results and discussion

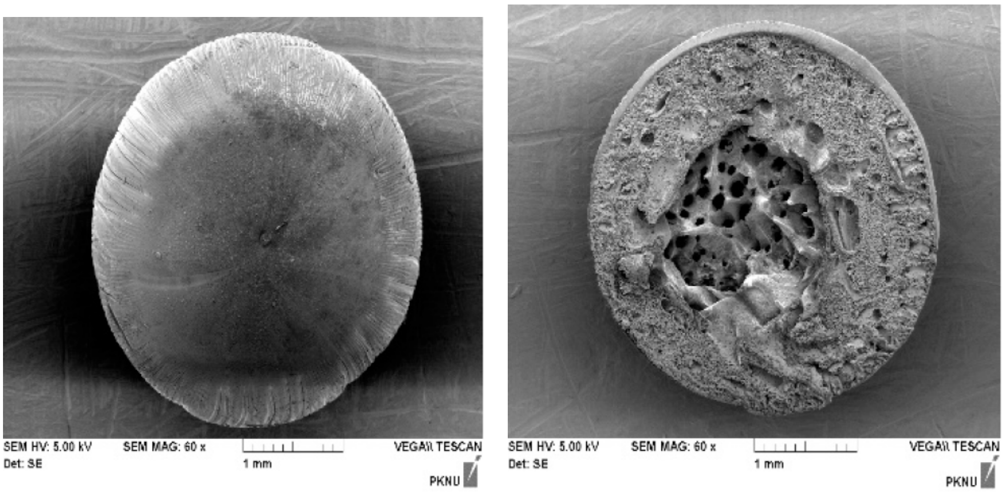
3.1. Characterization of PS-D2EHPA beads

Fig. 1 shows the microscopic images of a PS-D2EHPA bead. As shown in Fig. 1a, the prepared PS-D2EHPA beads exhibited a spherical shape with a mean diameter of about 2.5 mm. These PS-D2EHPA beads were bigger than the micro capsules of size 80 μm prepared by Yang et al. [20]. The cross sectional view in Fig. 1b shows the cavity surrounded by a porous membrane. During the curing of the PS-D2EHPA beads, D2EHPA does not diffuse into the water-ethanol solution but remains in the inner space of the bead. On the other hand, NMP diffuses into the solution through the outer wall from the inside of the bead, so that the outer wall of the bead forms a porous structure in which the objective solution flows smoothly [29]. The prepared PS-D2EHPA beads were calculated to contain 1.21 mmol D2EHPA (0.39 g D2EHPA)/g PS-D2EHPA beads by the immobilization method in this study. Ciopec et al. [30] prepared XAD7-D2EHPA beads by impregnating XAD7 with extractant D2EHPA, and reported that the extractant content of the beads produced was 0.35 g D2EHPA/g SIR. This value is comparable to the result of 0.39 g D2EHPA/g beads for the PS-D2EHPA beads prepared in this study.

Fig. 2 shows the FT-IR spectra of PS, D2EHPA, and PS-D2EHPA. As shown in Fig. 2a, the spectra of D2EHPA had a P=O stretching band at 1,223.46 cm^{-1} and P-O-C at 1,014.89 cm^{-1} [14]. The specrtra of PS in Fig. 2b had O=S=O and aromatic C=C at 1147.28 cm^{-1} and 1485.82 cm^{-1}, respectively. The spectra of PS-D2EHPA in Fig. 2c show a P=O peak (1,223.46 cm^{-1}) observed in the spectra of D2EHPA, and also showed C=O (1,014.89 cm^{-1}) and O=S=O (1,151.01 m^{-1}) peaks observed in the spectra of PS. This result indicated that D2EHPA was successfully immobilized in the PS-D2EHPA beads.

3.2. Effect of pH

Fig. 3 shows the distribution of the ion species of Sr (II) as a function of pH using a chemical equilibrium model



(a) (b)

Fig. 1. SEM images of (a) the whole shape and (b) the cross-section of PS-D2EHPA bead.

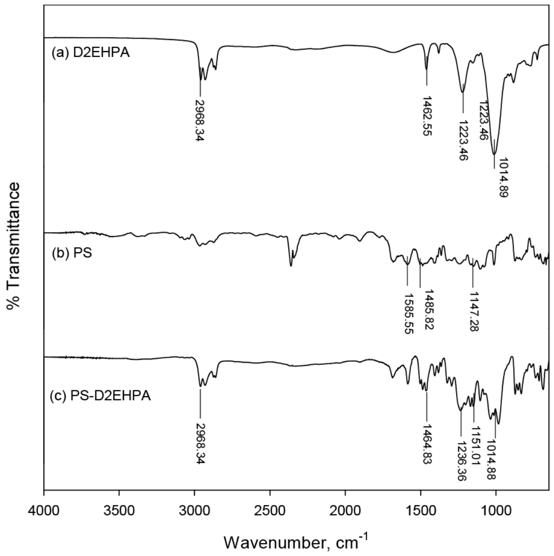


Fig. 2. FTIR spectra of (a) D2EHPA, (b) PS, and (c) PS-D2EHPA.

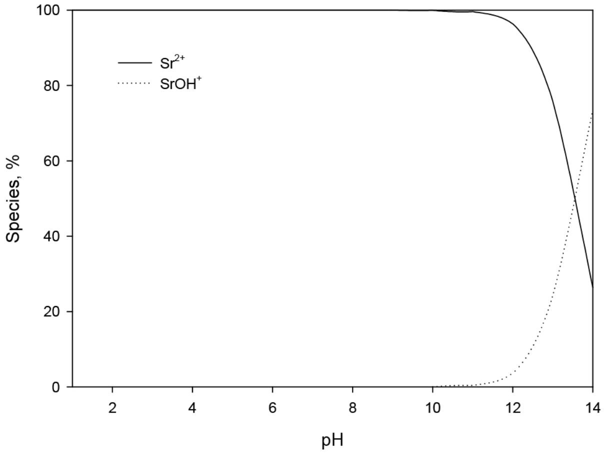


Fig. 3. Example of Sr speciation as a function of pH.

program (Visual MINTEQ ver. 3.0). As shown in Fig. 3, Sr(II) is present as a free ion at below pH 10, however, it is present in the form of $SrOH^+$ complex at above pH 10.5. Therefore, the effect of pH was investigated over the pH range of 2.5–10.5. As shown in Fig. 4, it was observed that the removal process of Sr(II) by PS-D2EHPA beads is dependent on the initial pH of the solution. The removal efficiency of Sr(II) by the PS-D2EHPA beads was constant at about 55% in the range of pH 6–10, but decreased abruptly at below pH 4. To reduce the removal of Sr(II) at a lower pH than pH 4 is due to the fact that the hydrogen ions in the solution increase at under pH 4 and these hydrogen ions compete with Sr (II) ions at the binding sites of PS-D2EHPA beads. The test of the experiments in this study was conducted at pH 6.

3.3. Effect of initial Sr(II) concentration

The removal efficiency of Sr(II) is also largely affected by the initial Sr(II) concentration in the aqueous solutions.

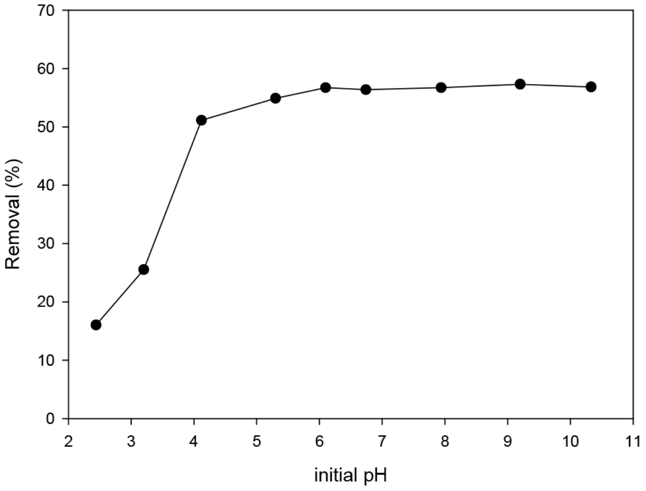


Fig. 4. Effect of initial pH for the removal of Sr(II) by PS-D2EHPA beads (PS-D2EHPA = 5 g/0.3 L (20.7 mmol D2EHPA/L), agitation speed = 170 rpm, concentration = 10 mg/L, temperature = 298 K).

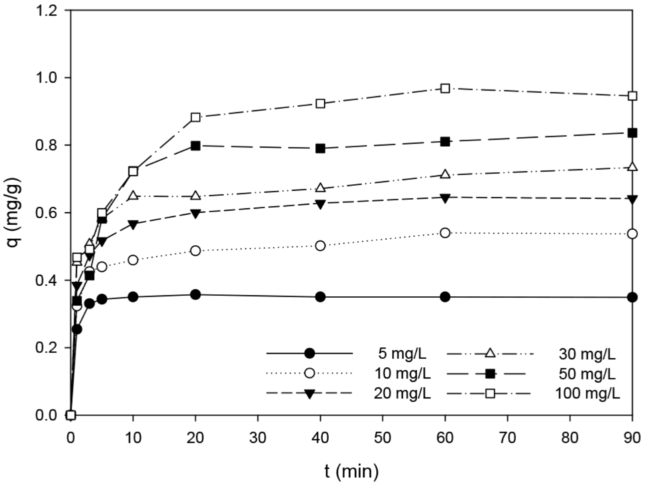


Fig. 5. Effect of contact time for the removal of Sr(II) by PS-D2EHPA beads (PS-D2EHPA = 5 g/0.3 L (20.7 mmol D2EHPA/L), agitation speed = 170 rpm, temperature = 298 K).

The initial concentration of Sr(II) in the aqueous solutions was varied (5–100 mg/L) with varying contact times (0–90 min). Fig. 5 shows the changes in concentrations at different time intervals. As shown in Fig. 5, the removal capacity of Sr(II) by the PS-D2EHPA beads increased with increasing initial Sr(II) concentration. Also, the removal of Sr(II) was very rapid in the first 10 min, slowed down from 20 min and reached the equilibrium state after about 40 min.

3.4. Kinetic studies

To describe the changes in the removal capacity of Sr(II) by the PS-D2EHPA beads with time, the pseudo-first-order and the pseudo-second-order kinetic models were investigated.

The linear form of the pseudo-first-order kinetic equation is described as follows [31]:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{K_1 t}{2.303} \tag{2}$$

where q_t (mg/g) and q_e (mg/g) are the amount of Sr(II) removed by the PS-D2EHPA beads at time t (min) and at equilibrium, respectively. k_1 (1/min) is the pseudo-first-order rate constant. The pseudo-first order kinetic constants can be determined experimentally by plotting $log(q_e - q_t)$ vs. t

The linear form of the pseudo-second-order equation is expressed as follows [32]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where k_2 (g/mg·min) is the pseudo-second-order rate constant. The removal rate constant (k_2) can be determined experimentally by plotting t/q_t vs. t.

Figs. 6 and 7 show the linearized plots of pseudo-first-order kinetic model and pseudo-second-order kinetic model, respectively. The kinetic parameters for the removal of Sr(II) by the PS-D2EHPA beads are summarized in Table 1. As shown in Table 1, the values of correlation coefficient (R^2) obtained for the pseudo-second-order kinetic model are higher than those of the pseudo-first-order kinetic model. This indicates that the removal of Sr(II) by the PS-D2EHPA beads does not follow the pseudo-first-order kinetic model and that the pseudo-second-order model best fits the removal kinetic data. Similar results were found by Ciopec et al. [30], Singh et al. [27], and Kanagare et al. [28].

To investigate the kinetic model further, an intra particle diffusion model was also applied. This model is based on the theory proposed by Weber and Morris [33].

$$q_t = K_d t^{\frac{1}{2}} + C \tag{4}$$

where q_t (mg/g) is the amount adsorbed at time t (min), K_{id} is the intra particle diffusion rate constant (mg/g min$^{-0.5}$) and C is the intercept that gives an idea about the thickness of the boundary layer.

Fig. 8 shows that initially the linear portion reflects the film or boundary layer diffusion effect and the subsequent linear portion attributed to the intra particle diffusion effect [34]. Table 2 shows that K_{id} values were obtained from the slope of the linear portion of the curve at each solute concentration. The K_{id} values in the second linear portion were about 100 times lower than those in the first linear portion. This suggests that the adsorption of Sr(II) by the PS-D2EHPA beads is governed by the diffusion within the pores of the adsorbent. Kanagare et al. [28] reported that the intra-particle diffusion is not the sole rate determining parameter controlling the sorption of Zn(II) in the study of the removal of Zn(II) from zinc-rich waste liquor by D2EHPA impregnated polymeric beads. Ciopec et al. [30] reported that intra particle diffusion was the rate-controlling step after rapid saturation of surface and big pores of XAD7-D2EHPA beads in the study of the removal of Cd(II) and Zn(II) from aqueous solutions by D2EHPA-impregnated XAD7 resin.

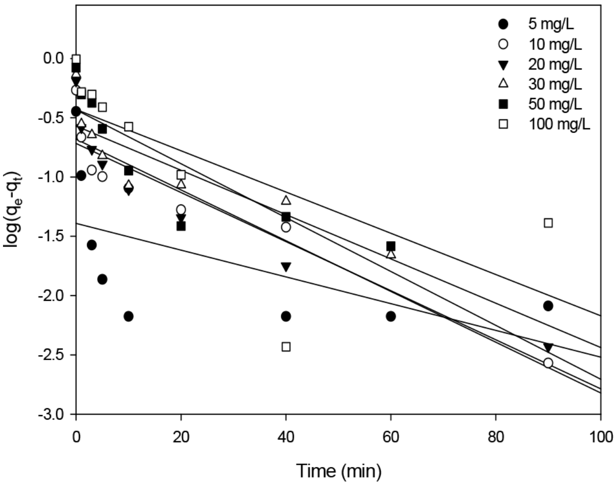


Fig. 6. Pseudo-first-order kinetic plots for the removal of Sr(II) by PS-D2EHPA beads.

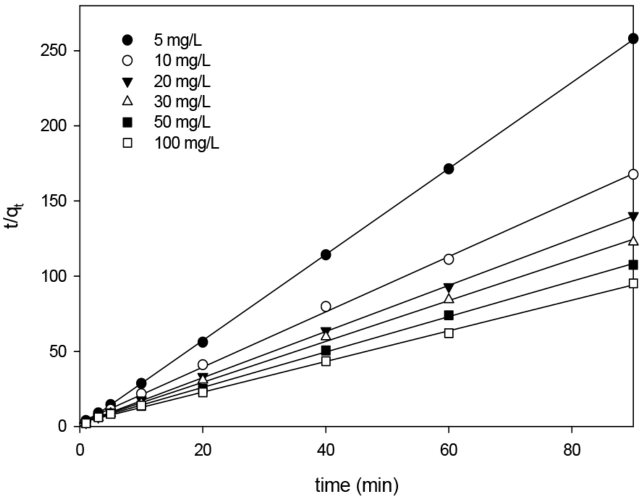


Fig. 7. Pseudo-second-order kinetic plots for the removal of Sr(II) by PS-D2EHPA beads.

3.5. Equilibrium isotherms

To study the effect of temperature, the removal of Sr(II) by the PS-D2EHPA beads were carried out at three different temperatures of 298, 313, and 328 K. The results are shown in Fig. 8. The equilibrium data was applied to the Langmuir and Freundlich isotherm models to examine the relationship between the sorbate concentration and the maximum removal capacity of the sorbent at equilibrium.

The linearized form of the Freundlich isotherm is as follows [35]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where q_e (mg/g) is the equilibrium Sr(II) concentration on the sorbent PS-D2EHPA beads, k_F((mg/g)(L/mg)$^{1/n}$)

Table 1
The calculated parameters of the pseudo-first-order and pseudo-second-order kinetic models for the removal of Sr(II) by PS-D2EHPA beads with different initial concentrations

Concentration, mg/L	Pseudo-first-order			Pseudo-second-order		
	$q_{e,cal}$, mg/g	k_1, 1/min	R^2	$q_{e,cal}$, mg/g	k_2, g/mg·min	R^2
5	0.0406	0.0260	0.3444	0.3499	6.0012	0.9999
10	0.1918	0.0477	0.8965	0.5437	1.2424	0.9991
20	0.2087	0.0493	0.8738	0.6518	1.2470	0.9998
30	0.2692	0.0431	0.7712	0.7362	0.7916	0.9987
50	0.3685	0.0523	0.7498	0.8508	0.5334	0.9994
100	0.4339	0.0387	0.8155	0.9824	0.4054	0.9990

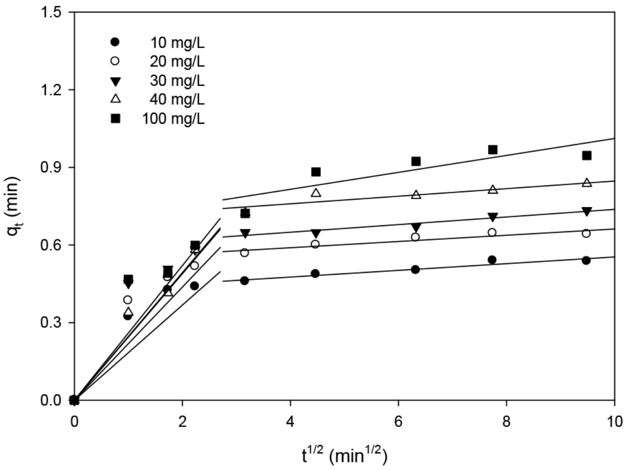


Fig. 8. Plot of q_t vs. $t^{1/2}$ for the adsorption of Sr(II) by PS-D2EHPA beads.

Table 2
The calculated parameters of intra-particle diffusion model for the removal of Sr(II) by PS-D2EHPA beads

Ion	C_0 (mg/L)	First linear line		Second linear line	
		k_{d1} (mg/g·min$^{1/2}$)	R^2	k_{d2} (mg/g·min$^{1/2}$)	R^2
Sr	10	0.1839	0.6822	0.0129	0.9127
	20	0.2187	0.7439	0.0121	0.8646
	30	0.2444	0.9580	0.0147	0.9300
	50	0.2465	0.7438	0.0147	0.7740
	100	0.2600	0.8165	0.0328	0.7058

is a constant relating the removal capacity and *1/n* is an empirical parameter relating the sorption intensity. C_e (mg/L) is the equilibrium concentration of Sr(II) in the solution.

The linearized form of the Langmuir isotherm is as follows [36]:

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

where q_m (mg/g) is the maximum removal capacity of the sorbent PS-D2EHPA beads and k_L is the Langmuir constant related to the free energy of sorption.

The values of Langmuir and Freundlich isotherm parameters calculated from Eqs. (5) and (6) are given in Table 3. As shown in Table 3, the equilibrium data of Sr(II) fit the Langmuir and Freundlich isotherm models well. However, Fig. 9 shows that the Langmuir isotherm model fits the experimental data better than the Freundlich isotherm model. Also, the Langmuir constants q_m and k_L for the removal of Sr(II) by the PS-D2EHPA beads increased with temperature. This indicates that the removal of Sr(II) by the PS-D2EHPA beads is endothermic in nature. The increase in removal with increase in temperature may be attributed to either the increase in the number of active sites present on the surface of the sorbent or the increase in the attractive forces between the metal ions and the sorbent. These results imply that the removal capacity and intensity for the removal of Sr(II) by the PS-D2EHPA beads are enhanced at higher temperatures. The maximum removal capacity (q_m) obtained from the Langmuir isotherm was 1.07–1.64 mg Sr/g PS-D2EHPA (0.88–1.36 mg Sr/mmol D2EHPA).

The essential characteristics of the Langmuir isotherm can be described by a separation factor (R_L), which can be calculated using the following equation [37]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{7}$$

where k_L (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial concentration of Sr(II). The value of the coefficient (R_L) indicates the type of isotherm either to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

As shown in Fig. 10, the R_L values of $0 < R_L < 1$ indicate applicability of the Langmuir isotherm and suggests the monolayer coverage of Sr(II) on the surfaces of the PS-D2EHPA beads.

3.6. Thermodynamic studies

In order to evaluate the thermodynamic nature of the removal process of Sr(II) by the PS-D2EHPA beads, experiments were carried out at three different temperatures and thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change

Table 3
Isotherm model parameters for the removal of Sr(II) by PS-D2EHPA beads

Temp., K	Freundlich			Langmuir			
	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2	K_L L/mg	q_m, mg/g	q_m, mg Sr/mmol D2EHPA	R^2
298	0.4768	5.9321	0.9869	0.1866	1.0725	0.8864	0.9951
313	0.4798	4.7798	0.9694	0.1226	1.3586	1.1228	0.9963
328	0.4194	3.5050	0.9680	0.1213	1.6435	1.3583	0.9887

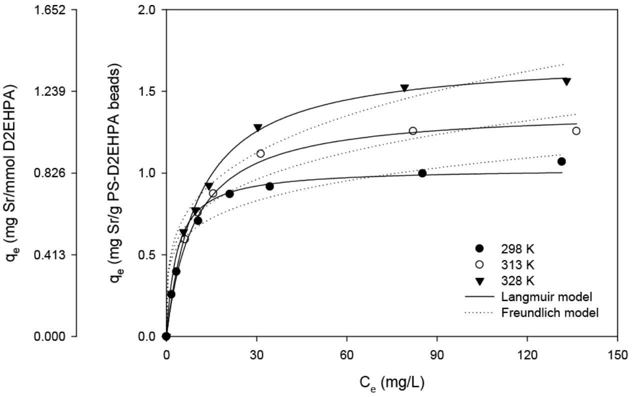


Fig. 9. Isotherm plots for the removal of Sr(II) ions by PS-D2EHPA beads at different temperatures.

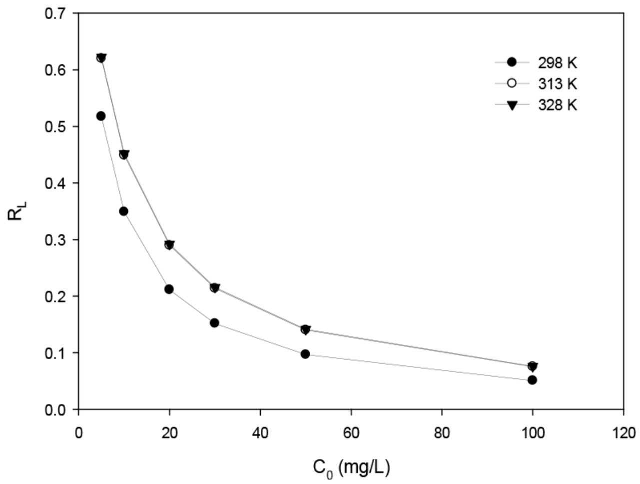


Fig. 10. Separation factor for the adsorption of Sr(II) by PS-D2EHPA beads.

(ΔS°) were determined. ΔG° was calculated from the following equation [1]:

$$\Delta G^\circ = -RT\ln K_L \tag{8}$$

where T (K) is the temperature, K_L is an equilibrium constant obtained by multiplying the Langmuir constants k_L and q_m, and R (J/mol·K) is the ideal gas constant.

ΔH° and ΔS° were calculated from experimental data at different temperatures using the following Van't Hoff thermodynamic equation [1]:

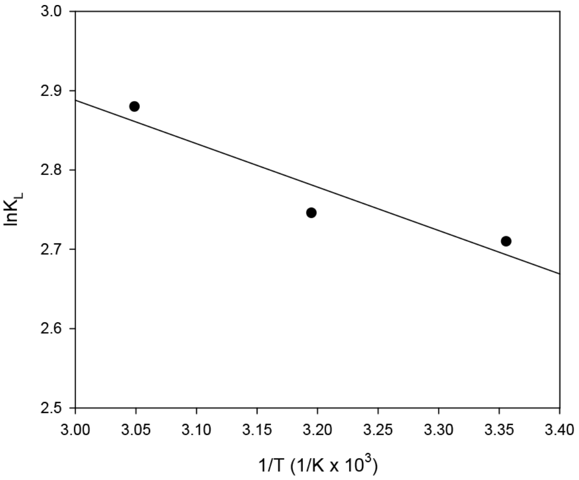


Fig. 11. Van't Hoff plot for the removal of Sr(II) by PS-D2EHPA beads.

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

Fig. 11 shows the plot of ln K_L versus 1/T. The thermodynamic values calculated from the slope and intercept in Fig. 11 are given in Table 4. As shown in Table 3, the values of ΔG° for all temperatures were negative and decreased with increasing temperature. The negative values of ΔG°suggest that the removal process of Sr(II) by the PS-D2EHPA beads is a spontaneous process and thermodynamically favorable under the experimental conditions. The positive value of ΔH° suggests that the removal process of Sr(II) by the PS-D2EHPA beads is endothermic.

3.7. Reusability of PS-D2EHPA beads

To investigate the reusability of PS-D2EHPA beads, PS-D2EHPA beads were first equilibrated with fresh Sr(II) solution, then the loaded Sr(II) were leached with nitric solution, and the stripped PS-D2EHPA beads were re-equilibrated with fresh Sr(II) solution again. These processes were repeated 5 times. Fig. 12 shows the removal efficiency of Sr(II) obtained from the reusability experiment of PS-D2EHPA beads. As shown in Fig. 12, although the removal efficiency of Sr(II) slightly decreased with reuse of the beads, it was almost constant at about 88%. In addition, the leakage of extractant from PS-D2EHPA beads or the structural damage of PS-D2EHPA beads was not observed during the repeated use of 5 times. These results suggest

Table 4
Thermodynamic parameters for the removal of Sr(II) by PS-D2EHPA beads

ΔH°, kJ/mol	ΔS°, J/mol·K	ΔG°, kJ/mol		
		298 K	313 K	328 K
4.37	37.14	–6.70	–7.26	–7.82

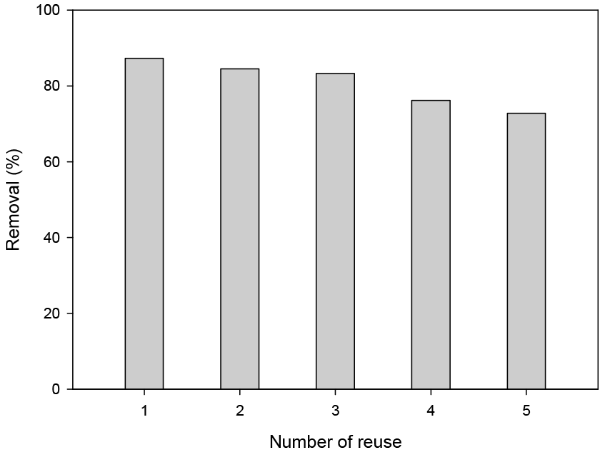


Fig. 12. Reusability of PS-D2EHPA beads for the removal of Sr(II) (PS-D2EHPA beads = 5 g/0.3 L (20.7 mmol D2EHPA/L), agitation speed = 170 rpm, concentration = 5 mg/L, temperature= 298 K).

that the PS-D2EHPA beads could be used several times with sustaining initial removal efficiencies of Sr(II).

4. Conclusion

PS-D2EHPA beads were prepared by immobilizing di-2-ethylhexyl-phosphoric acid (D2EHPA) with polysulfone (PS) and those beads exhibited a spherical shape with about 2.5 mm diameter. The removal process of Sr(II) by the PS-D2EHPA beads was dependent on the initial pH of the solution and the optimum removal of Sr(II) by the PS-D2EHPA beads was observed in the range of pH 6–10. The removal capacity of Sr(II) by the PS-D2EHPA beads increased with increasing initial concentration of Sr(II). Also, the removal of Sr(II) was very rapid in the first 10 min and reached the equilibrium state after about 40 min. The kinetic data obeyed the pseudo-second-order kinetic model and the equilibrium data fit the Langmuir isotherm model well. The thermodynamic parameters showed that the removal process of Sr(II) by the PS-D2EHPA beads is spontaneous, endothermic, and thermodynamically favorable under the experimental conditions. The PS-D2EHPA beads prepared in this study have potential as an effective adsorbent for removing Sr(II) in aqueous solutions.

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