Enhanced adsorption of strontium(II) ion from aqueous solution using solid-phase extractant containing TTA and TOPO

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ABSTRACT

Solid-phase extractant PVA[TTA][TOPO] beads containing thenoyltrifluoroacetone (TTA) and trioctylphoshine oxide (TOPO) were prepared for the removal of Sr(II) from aqueous solutions. PVA[TTA][TOPO] beads were characterized by using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and thermal gravimetry analysis (TGA). Kinetic parameters for pseudo first-order and pseudo second-order models and correlation coefficients (r^2) of the Sr(II) were calculated, so the results showed that the kinetic data of Sr(II) removal by the prepared solid-phase extractant PVA[TTA][TOPO] beads followed the pseudo-second order reaction model. The equilibrium data fitted well with Langmuir–Freundlich isotherm model and the maximum removal capacity of Sr(II) was 12.59 mgg^{-1}. The optimum pH region was in the wide range of 4–10. The result showed that PVA[TTA][TOPO] beads prepared in this study could be used as a solid-phase extractant for the removal of radioactive Sr(II) from aqueous solution.

Keywords: Strontium; Extraction; TTA; TOPO; PVA; Immobilization

1. Introduction

A growing interest in operation and development of the nuclear power program as a potential solution for global energy resulted in the creation of millions of gallons of high- and low-level radioactive waste [1,2]. Enormous amounts of low-level liquid radioactive waste (LLRW) which may raise serious environmental and health concerns are being produced [3]. Some of the important isotopes are americium, cesium, plutonium, strontium and technetium. Among these isotopes, strontium, radioactive waste from the reprocessing of nuclear fuels is one of the products of nuclear fission [4]. Since strontium has a long life, high solubility and bio-toxicity, the removal of the ion from waste solutions is imperative to reduce the risk of human exposure to radiation [4,5].

Several technologies such as thermal treatment [6], chemical precipitation [7], membrane [8], adsorption [9] and ion exchange [10] are proposed to remove radioactive waste. Among these, extraction, especially liquid-liquid extraction, is one of the major separation processes for many industrial fields. The advantages of this technique are the simplicity of equipment and operation and the reusability of the extractant [11]. However, it has not been used in new developing commercial processes because of its inherent disadvantages such as the leakage of organic solvent into the environment and the difficulty of phase separation etc., [12]. To overcome the disadvantage, the liquid-liquid extraction principle can be extended to a solid-liquid extraction by immobilizing the extractant [9]. This is based on encapsulation of extractant within solid support. The resulting advantages are that the loss of an organic solvent to the aqueous phase is reduced, and the phases after the treatment can be separated easily by filtration or sedimentation, and the continuous operation can be achieved by the employment in the process of a column packed with the extractant-containing microcapsule [12,13].

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Many researchers have demonstrated that polymeric materials from a variety of monomers which contains different functional groups are suitable for encapsulating the extractant. Particularly, a synthetic polymer, polyvinyl alcohol (PVA) is low cost and non-toxic which produces high strength and durability [14]. Its porous surface structure enables a high diffusivity of aqueous solutions [15].

Most of the researchers [12,13,16] have studied one kind of encapsulating extractant in polymeric materials. However, Xia et al. [17] and Kim et al. [18] have reported that thenoyltrifluoroacetone (TTA) with tri-octylphosphine oxide (TOPO) had enhanced the extraction efficiencies in the liquid-liquid extraction process. Therefore, a synergistic effect is expected when two kinds of extractants are immobilized in the polymeric materials.

The aim of this study is to synthesize solid-phase extractant (PVA[TTA][TOPO]) immobilizing 2 extractants, TTA and TOPO. PVA[TTA][TOPO] beads prepared were characterized by SEM, FTIR and TGA. The performance of a Sr(II) extraction by PVA[TTA][TOPO] beads is evaluated in terms of the effect of pH, contact time, and adsorption isotherm.

2. Materials and methods

2.1. Reagents

TTA, TOPO and PVA purchased from Sigma–Aldrich. Sodium alginate and xylene from Samchun, and calcium chloride, sodium hydroxide and boric acid from Shinyo Pure Chemicals were used. All chemicals above are extra pure grade. Aqueous solutions of Sr(II) at various concentrations were prepared by strontium nitrate anhydrous ($Sr(NO_3)_2$) purchased from Shimakyu's Pure Chemicals.

2.2. Synthesis of solid-phase extractant

Synthesis of solid-phase extractant was carried out by the addition of 50 mL deionized water to 4.0 g of PVA and 0.675 g of sodium alginate. The solution was heated to a temperature of around 90°C to dissolve PVA. 4 mL of xylene solution with 0.44 g of TOPO and 0.44 g of TTA solution (mole ratio of TTA to TOPO = 1:1) was prepared. It is combined with PVA and the sodium alginate solution and then stirred for an hour using a mechanical agitator (Global lab, S-10) at 500 rpm. Using a syringe, the mixture was extruded as drops into a solution of saturated boric acid containing 3% (w/v) calcium chloride. The PVA[TTA][TOPO] beads were stirred gently in this solution for 24 h to completely solidify and then washed with distilled water to remove any excess boric acid.

The surface morphology of the PVA[TTA][TOPO] bead was observed by a scanning electron microscope (SEM; Philips, XL20). The transmission FT-IR spectra were obtained with Bruker Vertex 70 atomic absorption spectrophotometer. Thermal gravimetric analysis (TGA) was performed with thermogravimetry (Perkin Elmer, TGA 7) at a heating rate of 10°C/min in the range of 50°C–700°C, in a N_2 atmosphere.

2.3. Experiment procedure

The experiments were performed as a batch type. A certain concentration of 300 mL Sr(II) solution and 4.5 g of PVA[TTA][TOPO] is inserted in a 1,000 mL Erlenmeyer flask.

The solution is stirred at 170 rpm using a shaker (Johnsae Co., Js-Fs-2500) and sampled at certain time intervals. It was centrifuged at 10,000 rpm for 5 min and the supernatant was analyzed. The concentration of Sr(II) is measured with an atomic absorption spectrophotometer (Shimadzu, AA-7000). The pH of the solution is controlled with 0.1 M of NaOH and 0.1 M of HCl and it is measured with a pH meter (Istek, AJ-7724). The removal capacity and the removal efficiency of Sr(II) were calculated using Eq. (1) below:

$$\text{Removal capacity } \left(mg/g\right) = \frac{(C_i - C_j)V/1000}{W} \tag{1}$$

where C_i and C_j are initial and final concentration of Sr(II) (mgL^{-1}), V is the volume of the Sr(II) solution (L), and W is total amount of PVA gel bead (g).

3. Results and discussion

3.1. Characterization of PVA[TTA][TOPO]

The microscopic image of the PVA[TTA][TOPO] bead was observed by a scanning electron microscope. As shown in Fig. 1(a), the size of the PVA[TTA][TOPO] bead is approximately 2 mm and it exhibits a spherical shape with a porous surface structure, which enables the solution to penetrate easily. A cross-sectional view in Fig. 1(b) illustrates the cavity and shell structure of the PVA[TTA][TOPO] bead. The large cavity volume with a thin shell possesses extractants.

Fig. 2 shows FT-IR spectra of TTA, TOPO, PVA and PVA[TTA][TOPO]. The specrtra of TTA in Fig. 2(a) have keto carbonyl C=O, -enol carbonyl C=O, and -enol C-O vibrations at 1647, 1590 and 1195 cm⁻¹, respectively (Chen et al., 2007).
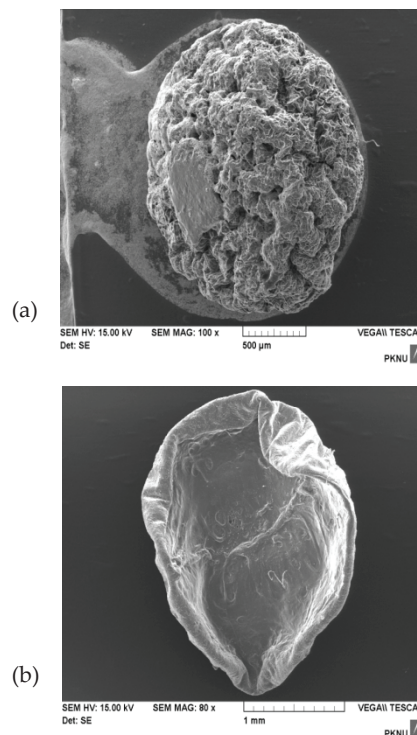

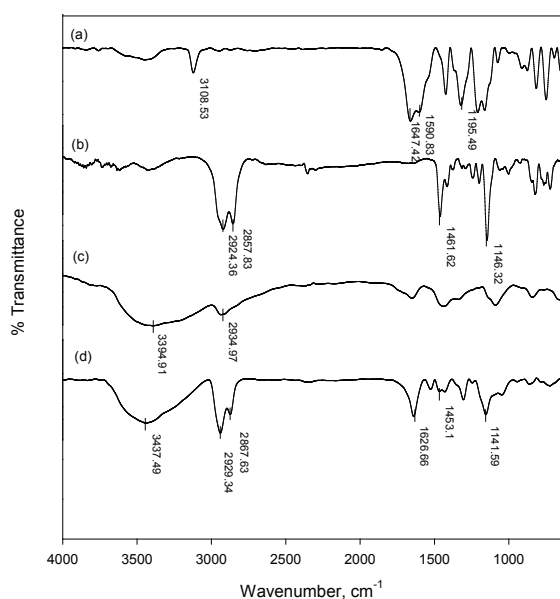Fig. 1. SEM image of (a) the surface of and (b) the cross section of PVA[TTA][TOPO] bead.

Fig. 2. FT-IR spectra of (a) TTA, (b) TOPO, (c) PVA, and (d) PVA[TTA][TOPO].

The TOPO spectra shown in Fig. 2(b) have alkyl at 1461 cm^{-1} and a P=O band at 1146 cm^{-1} [19,20]. PVA spectra in Fig. 2(c) contain O-H stretch at about 3400 cm^{-1}. In the spectra of PVA[TTA][TOPO] as shown in Fig. 2(d), the spectrum of C=O is at 1626 cm^{-1} of TTA and P-O is at 1141 cm^{-1} of TOPO, which are not observed in the PVA spectra in Fig. 2(c). Thus, this result indicates TTA and TOPO are successfully immobilized into the PVA gel bead.

Fig. 3 indicates the thermal degradation behavior of the PVA, TTA, TOPO, and PVA[TTA][TOPO] analyzed by TGA. As shown in Fig. 3, PVA degraded slowly from 300°C to 700°C, TTA completely degraded in the range of 100°C–150°C, and TOPO dissociates from 300°C to 350°C. However, the PVA[TTA][TOPO] curve contains 2 main segments of 100°C–350°C and 350°C–450°C. The first decrease in weight (approximately 40%) represents the decomposition of TTA and TOPO in the range of 100°C–350°C and the second zone of weight loss depicts the disassociation of the PVA gel bead. This result revealed that TTA and TOPO were successfully immobilized in the PVA gel bead.

3.2. Effect of pH

The pH of the aqueous solution is an important aspect for the process of removal due to its influence on both aqueous solutions and surface binding sites of the extractant [21]. Fig. 4 shows the results of Sr(II) removal efficiency on the PVA[TTA][TOPO] beads at various pH levels of the solution. The optimum pH for the removal of Sr(II) on the PVA[TTA][TOPO] beads was observed in the wide range of pH 4 to 10. However, at lower pH levels, the percentage of removal was lower. This is due to the presence of protons (H$^+$) which are considered as a competitive ion in the removal process [19].

3.3. Effect of contact time

In order to know the equilibrium time, Sr(II) removal on the PVA[TTA][TOPO] beads was investigated as a function
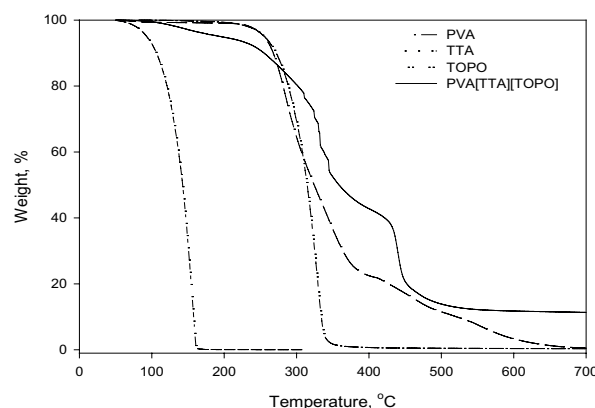

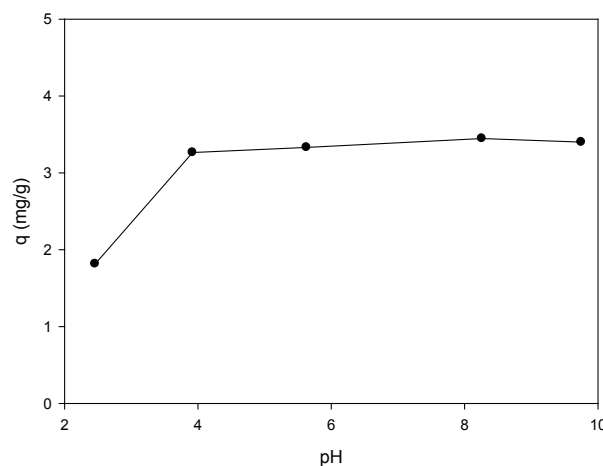Fig. 3. Thermogram of TTA, TOPO, PVA, and PVA[TTA][TOPO].

Fig. 4. Effect of pH on Sr(II) removal by PVA[TTA][TOPO] beads (solid-phase extractant: 1.5 g/0.1 L, agitation speed: 170 rpm, concentration: 10 mg/L, temperature: 302 K).

of time. The result is indicated in Fig. 5. The removal of Sr(II) is very rapid in the first 60 min, slowed down from 100 min and it reached equilibrium at about 120 min. Thus, the initial Sr(II) removal rate is high at first due to the active sites on the extractants allowing the strontium ions to reach the sorption sites. Once the site is occupied, the rate slows down because there is not enough room for the ions to attach [21].

The evaluation of Sr(II) removal kinetics were used to investigate the solid-phase extraction rates using pseudo first- and pseudo second-order rate models. Lagergen [22] suggested the pseudo-first order equation for the adsorption of a liquid/solid system based on the solid's capacity. The pseudo-first order model is expressed as Eq. (2). The value of $k_{1,\mathrm{ad}}$ was calculated from the plot of $\ln(q_e - q)$ vs. t for the Sr(II) ion Fig. 6(a).

$$\frac{dq}{dt} = k_{1,\mathrm{ad}}(q_e - q) \qquad (2)$$

Ho and McKay [23] developed a pseudo-second order equation based on the amount of sorbate adsorbed onto a
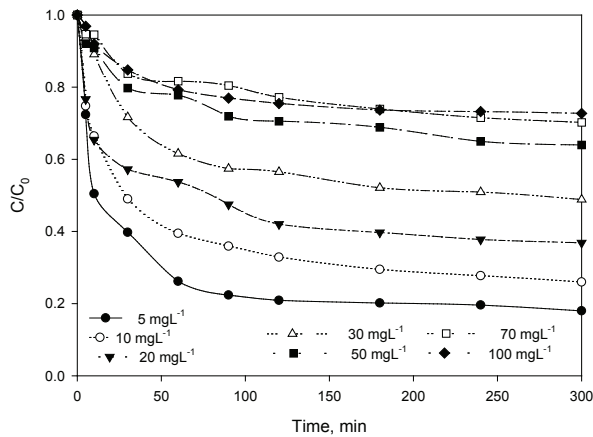
Fig. 5. Effect of contact time on the removal of Sr(II) ion (solid-phase extractant: 4.5 g/0.3 L, agitation speed: 170 rpm, temperature: 302 K, pH: 7.3).
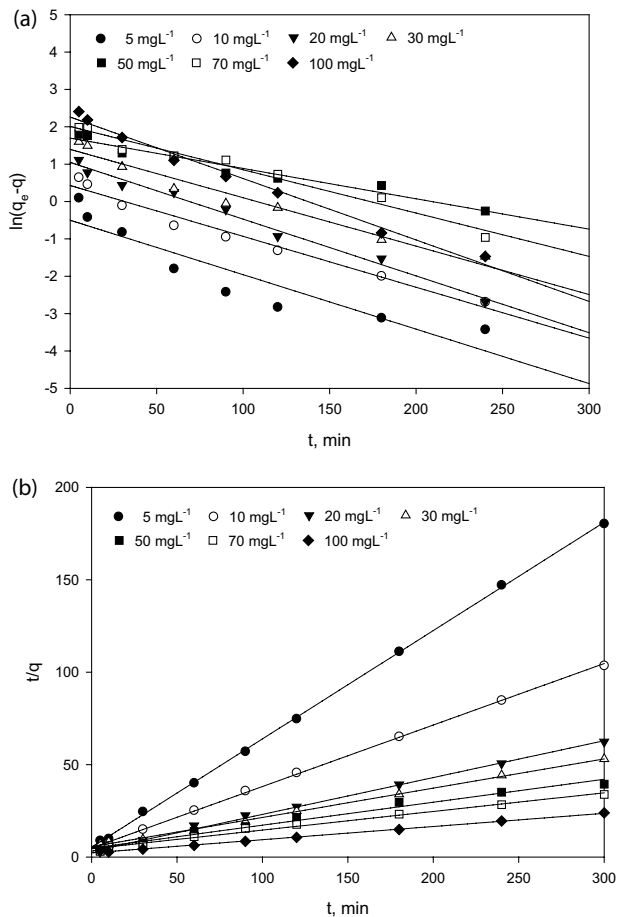

Fig. 6. Plots of pseudo first- and second- order rate equations of Sr(II) removal on by PVA[TTA][TOPO] beads: (a) pseudo first-order rate, (b) pseudo second-order rate.

sorbent. Aksu [24] studied the kinetics for Cd(II) adsorptions with the pseudo first- and pseudo second-order rates. The pseudo-second order model can be expressed as Eq. (3). The slopes and intercepts of plots from t/q versus t were used to calculate q_e and $k_{2,ad}$ Fig. 6(b).

$$\frac{dq}{dt} = k_{2,ad}(q_e - q)^2 \tag{3}$$

In this equation, q is the metal ion removal capacity (mgg^{-1}), t is the contact time (min), q_e is metal ion removal capacity at equilibrium (mgg^{-1}), $k_{1,ad}$ is the first-order rate constant (min^{-1}), and $k_{2,ad}$ is the second-order rate constant (gmg^{-1}min^{-1}).

Kinetic parameters for 2 kinetic models and correlation coefficients (r^2) of the Sr(II) ions were calculated and listed in Table 1. The values of r^2 (0.9831–0.9997) of the pseudo-second order model were higher than those of the pseudo-first order model (0.8592–0.9872) for Sr(II). The experimental value, q_e, also agreed well with the calculated value, $q_{e,cal}$ and plotted in Fig. 7. Hafizi et al. [25] suggested that the adsorption rate of Sr(II) with Dowex 50W-X Resins could be estimated with the pseudo-second order kinetic model. This model's accuracy was reasonably higher than that of the pseudo-first order kinetic model. In the Sr(II) ion removal experiment, the initial rapid removal subsequently gives way to a slow approach to equilibrium, and equilibrium is obtained after 60–120 min.

3.4. Isotherm model

The Langmuir isotherm model expressed as the following [26]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4}$$

where q_e is the amount of Sr(II) sorbed on an unit mass of the PVA[TTA][TOPO] beads at equilibrium (mgg^{-1}), q_m is the maximum amount of Sr(II) removed on an unit mass of extractant(PVA[TTA][TOPO] beads) (mgg^{-1}), C_e is the equilibrium concentration (mgg^{-1}) and b is the Langmuir constant (Lmg^{-1}).

The Freundlich isotherm model is expressed as the following [27]:

$$q_e = K_F C_e^{1/n} \tag{5}$$

In this equation, K_F is the Freundlich constants associated with the quantity of the sorbent, $1/n$ is the affinity of the binding sites.

The non-linear form of the model (Redlich–Peterson model) to improve the Langmuir and Freundlich isotherms is given by Eq. (5). It has a linear dependence on concentration in the numerator and an exponential function in the denominator [28]:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta}} \tag{6}$$

In this equation K_{RP}, α_{RP} and β are the Redlich–Peterson parameters. The exponent β lies between 0 and 1. For $\beta = 1$ Eq. (6) converts to the Langmuir form.

Langmuir–Freundlich model is another 3-parameter empirical model for the representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich models and is expressed as the following:

$$q_e = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}} \tag{7}$$

Table 1
Kinetic constants for Sr(II) on PVA[TTA][TOPO] beads

C mgL^{-1}	q_e	$k_{1,ad}$	$q_{e,cal}$	r^2	$k_{2,ad}$	$q_{e,cal}$	r^2
	mgg^{-1}	min^{-1}	mgg^{-1}		gmg^{-1}min^{-1}	mgg^{-1}	
4.87	1.66	0.0146	0.61	0.8592	0.0647	1.71	0.9997
9.40	2.90	0.0136	1.54	0.9740	0.0227	3.01	0.9994
18.29	4.81	0.0152	2.85	0.9881	0.0126	5.02	0.9972
26.55	5.66	0.0129	4.04	0.9592	0.0045	6.32	0.9980
46.83	7.61	0.0081	5.46	0.9541	0.0032	8.05	0.9831
71.50	8.87	0.0116	7.46	0.9723	0.0023	9.92	0.9871
110.48	12.55	0.0164	9.59	0.9872	0.0023	14.02	0.9976
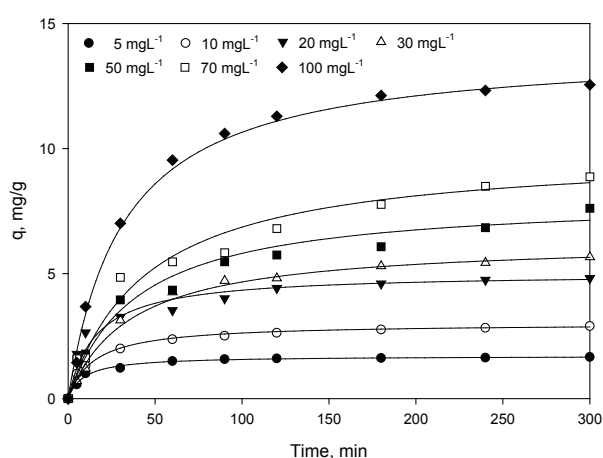
Fig. 7. Kinetics of the uptake of Sr(II) by PVA[TTA][TOPO] beads with a pseudo second-order kinetics.
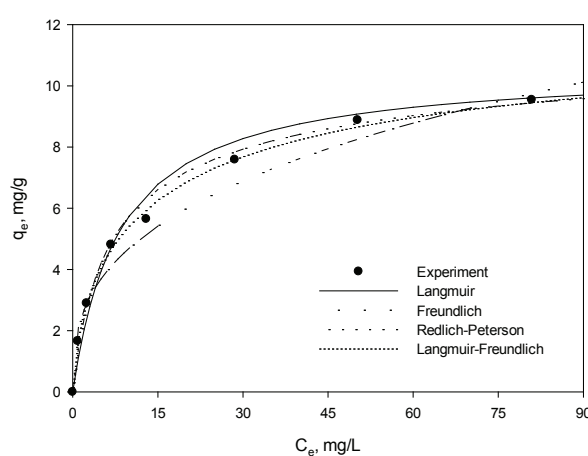

Fig. 8. The isotherms plot of Sr(II) on PVA[TTA][TOPO] beads (solid-phase extractant: 4.5 g/0.3 L, agitation speed: 170 rpm, temperature: 302 K, pH: 7.3).

where q_m, b and $1/n$ are the Langmuir–Freundlich parameters. This model is valid when $1/n > 1$.

The resulting isotherm for Sr(II) removal on the PVA[TTA][TOPO] beads is plotted in Fig. 8. The removal capacity increased with the equilibrium solution concentrations, and reached a steady point. The model parameters Q_m, b, K_F, $1/n$, K_{RP}, a_{RP} and r^2 obtained from all the isotherms are given in Table 2. The lines in Fig. 8 represent the isotherm models using Eqs. (4), (5), (6), and (7). The experimental data of the removal capacity were fitted better by the three models (Langmuir, Redlich–Peterson, and Langmuir–Freundlich models) than the Freundlich model. The removal data were represented well by the Redlich–Peterson and Langmuir–Freundlich model with a correlation coefficient of 0.9984 and 0.9985, respectively, higher than those of the Langmuir model with a correlation coefficient of 0.9963. The maximum removal capacity (q_m) obtained from the Langmuir–Freundlich isotherm was 12.59 mgg^{-1} and the Langmuir–Freundlich constant (b) was 0.17 Lmg^{-1}. Ngomsik et al. [29] found that the adsorption isotherm of nickel ion with magnetic alginate microcapsules containing an extractant fit by the Langmuir model ($r^2 = 0.9801$) well and q_m and b were 30.51 mgg^{-1} and 0.54 Lmg^{-1}, respectively. Other research for solid-phase extraction with a HA-gel, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester(HA) immobilized PVA hydrogels, suggested maximum metal loading capacities

under optimized conditions were 19 ± 0.8, 8 ± 0.4 and 11 ± 0.5 mgg^{-1} of swollen HA-gel, for U(VI), Pu(IV) and Am(III), respectively [9].

The comparisons of the experimental, q_e, and calculated values, $q_{e,cal}$, of the Sr(II) removal isotherms are presented in Fig. 9. These results can be attributed to the sensitivity of 3 models, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models, to interactive effects of the active sites existing on the surface of the PVA[TTA][TOPO] beads in solid-phase extraction. Most of the data except for the Freundlich model are distributed around the diagonal line. It indicated that the three models represented the experimental data of Sr(II) extraction well. The data of the Freundlich model is not valid for all concentrations.

The values of q_m was close to the experimental data of the removal capacity which indicated good removal on the PVA[TTA][TOPO] beads and the q_m of the PVA[TTA][TOPO] beads was the middle value as compared with some q_m values of other sorbents reported in literature (Table 3). It may be seen that the q_m values differ widely for different sorbents. Comparison of the q_m values shows that the PVA[TTA][TOPO] beads exhibits moderate capacity for Sr(II) removal from aqueous solutions. PVA materials are used to particles for immobilization, which are nano-adsorbent [34], yeast cells [35], and wastewater treatment [36], so polyvinyl

Table 2
Isotherm constants for Sr(II) on PVA[TTA][TOPO] beads

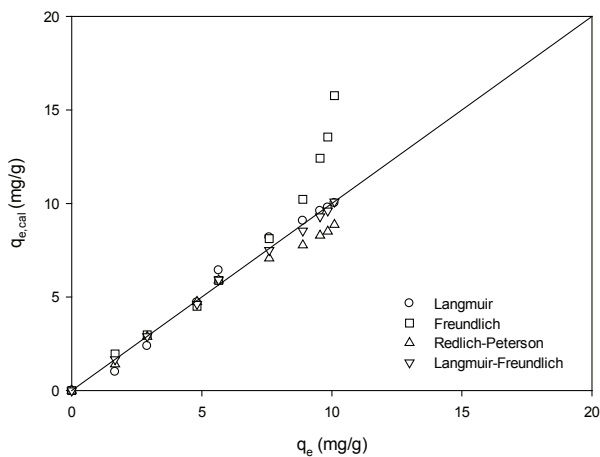| Langmuir			Freundlich			Redlich–Peterson				Langmuir–Freundlich			
q_m	b	r^2	K_F	$1/n$	r^2	K_{RP}	a_{RP}	b	r^2	q_m	b	$1/n$	r^2
mgg^{-1}	Lmg^{-1}					mgg^{-1}	Lmg^{-1}			mgg^{-1}	Lmg^{-1}		
10.61	0.12	0.9963	2.11	0.35	0.9244	2.09	0.34	0.92	0.9984	12.59	0.17	0.66	0.9985

Fig. 9. Comparison of the experimental values, q_e, with the theoretical values, $q_{e,cal}$, obtained from the Langmuir, Freundlich, Redlich–Freundlich and Langmuir–Freundlich models for Sr(II) by PVA[TTA][TOPO] beads.

Table 3
Comparison of PVA[TTA][TOPO] beads and other typical sorbents for Sr(II) removal

Sorbents	q_m (mgg^{-1})	pH	Temp (°C)	Reference
Dowex 50W-X resins	125.00	3.7	25	[25]
Hybrid gel	77.11	2.0–12.0	20	[30]
Zr-Sb oxide/PAN	43.67	4.7	60	[31]
Fe$_3$O$_4$/bis(trimethoxysilylpropyl) amine	8.76	4.0–10.0	20	[32]
Dolomite powder	1.17	5.5	20	[33]
PVA[TTA][TOPO] beads	12.31	7.3	29	In this study

alcohol (PVA) is a cheap and nontoxic synthetic polymer, and its granules can meet the mechanical mechanical and chemical stability requirements of waste water treatment [37].

4. Conclusion

The removal of Sr(II) from aqueous solutions using extractants TTA and TOPO immobilized on PVA gel beads was investigated. The optimum pH levels for the removal of Sr(II) was found to be a broad range of pH 4–10. On comparing the kinetic parameters for pseudo first-order and pseudo second-order models and correlation coefficients (r^2),

the removal of Sr(II) by the prepared in this study followed the pseudo-second order kinetics.

The 4 isotherm models of Langmuir, Freundlich, Redlich-Peterson, and Langmuir–Freundlich models were used to predict the equilibrium data of Sr(II) on the PVA[TTA][TOPO] beads. The equilibrium data of Sr(II) removal capacity fit the other three models better than the Freundlich model. The equilibrium data were represented well by the Redlich–Peterson and Langmuir–Freundlich models with a correlation coefficient higher than those of the Langmuir model. The maximum removal capacity with the Langmuir–Freundlich model was determined to be 12.59 mgg^{-1}. The result showed that the PVA[TTA][TOPO] beads prepared in this study can be used as a solid-phase extractant for removal of Sr(II) from aqueous solutions.

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