

Molecular modification of a novel macroporous silica-based impregnated polymeric composite by tri-*n*-butyl phosphate and its application in the adsorption for some metals contained in a typical simulated HLLW

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Abstract

Using tri-*n*-butyl phosphate (TBP) as a molecular modifier, a novel macroporous silica-based 4,4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) polymeric composite (DtBuCH18C6 + TBP/SiO₂-P) was synthesized. It was done by impregnating and immobilizing DtBuCH18C6 and TBP molecules into the pores of SiO₂-P particles utilizing an advanced vacuum sucking technique. The adsorption of 10 fission and non-fission products Sr(II), Ba(II), Ru(III), Mo(VI), Na(I), K(I), Pd(II), La(III), Cs(I), and Y(III) onto (DtBuCH18C6 + TBP)/SiO₂-P was investigated by examining the influence of contact time and the HNO₃ concentration in a range of 0.1–5.0 M at 298 K. It was found that at the optimum concentration of 2.0 M HNO₃ (DtBuCH18C6 + TBP)/SiO₂-P exhibited strong adsorption ability and high selectivity for Sr(II) over all of the tested elements, which showed very weak or almost no adsorption except Ba(II). Moreover, the quantity of DtBuCH18C6 leaked from (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₃, 326.2 ppm, was obviously lower than 658.4 ppm that leaked from DtBuCH18C6/SiO₂-P. This was ascribed to the effective association of DtBuCH18C6 and TBP through intermolecular interaction, i.e., hydrogen bonding. The significant reduction of DtBuCH18C6 leakage by molecular modification with TBP was achieved. It was of great benefit to application of the (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite in chromatographic partitioning of Sr(II), one of the main heat generators, from high level liquid waste (HLLW) in reprocessing of nuclear spent fuel in MAREC process developed recently.

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1. Introduction

In high level liquid waste (HLLW) produced in reprocessing process of nuclear spent fuel, a large quantity of fission products (FPs) such as the long-lived minor actinides MAs(III), two heat emitting nuclides Cs(I) and Sr(II), as well as Tc(II–VII), etc., is contained [1]. Because of the adverse impact on environment, elimination of these radionuclides from HLLW to a great extent is required.

Strontium mainly has two isotopes, Sr-89 with a half-life of 53 days and Sr-90 with a half-life of 28.6 year. It is well known that Sr-90 is one of the main heat generators produced by

the fission reaction of uranium or plutonium in nuclear reactor. It can pose a serious radiation hazard to health and environment. Especially, it is harmful for the vitrification of HLLW in final geological disposal [2]. Removal of Sr-90 from HLLW is required to produce a low-activity waste (LAW) that can be vitrified into LAW glass. On the other hand, Sr-90 is used as the source of β-radiation and energy generator. This makes the recovery of strontium from HLLW beneficial. However, the effective partitioning and recovery of strontium has been always a challenging work because of its high difficulty.

The liquid–liquid solvent extraction is one of the effective partitioning techniques. It was reported that transuranic extraction process [3,4], universal solvent extraction process [5–7], and strontium extraction process [8,9] had been efficient to separate MA(III), Tc(II–VII), Sr(II), and Cs(I) from an acidic HLLW utilizing a variety of chelating extractants in

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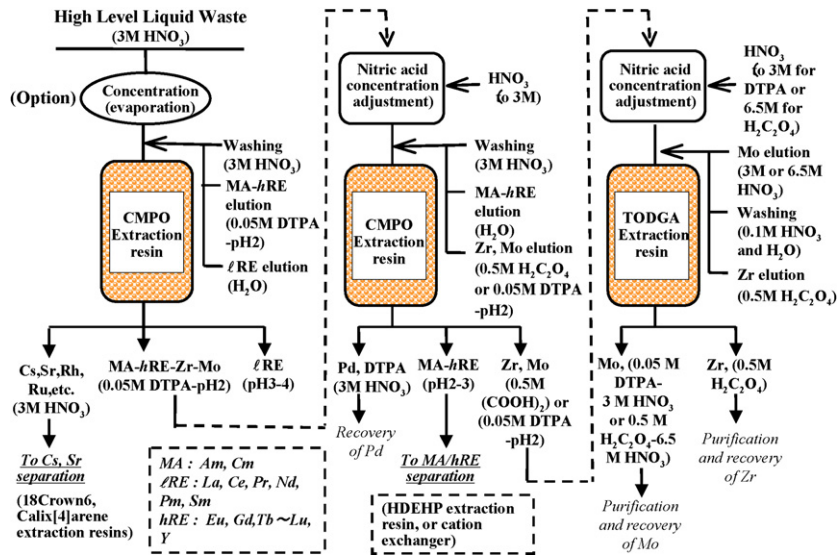


Fig. 1. MAREC process developed for minor actinides and some specific nuclides partitioning from the simulated HLLW by extraction chromatography utilizing a few macroporous silica-based polymeric composites.

hydrocarbon diluent. In these extractants, a derivative of macrocyclic crown ethers, 4,4',(5')-di(*tert*-butylcyclohexa-no)-18-crown-6 (DtBuCH18C6) dissolved in ISOPAR[®]L diluent, seemed to have excellent extraction ability and selectivity for Sr(II) [10,11]. However, because of high affinity of DtBuCH18C6 for aqueous solution, significant quantity of DtBuCH18C6 was demonstrated to be lost in solvent extraction process. This made the application of DtBuCH18C6 in the Sr(II) partitioning difficult. Moreover, the solvent extraction can generate a great amount of organic waste resulting from the hydrolytic and radiolytic degradation of extractants and diluents [12–15]. A large number of instruments and equipments are required for the multi-stage extraction, stripping and solvent washing processes. So, a minimal usage of organic solvents and compact equipments are desired for HLLW partitioning. As an alternative separation method, extraction chromatography seems to be promising.

A polymer-based extraction resin, initially called strontium specific (SrSpec) and now Sr-resin, synthesized through impregnation of 40% (w/w) of a liquid extractant solution of 1 M DtBuCH18C6 in 1-octanol into the pores of an inert polymeric support (XAD-7) was reported [16,17]. The Sr-resin exhibited excellent selectivity for Sr(II) [18]. However, the Sr(II) adsorption capacity was low, this makes the application Sr-resin in the large-scale partitioning process infeasible. On the other hand, comparison with the silica-based support, the resistance ability of polymer-based one against various irradiations, HNO₃, and high temperature is not so high. So, it is required to choose the adsorbents having much better resistance ability and the high adsorption capacity for Sr(II).

Based on the various macroporous silica-based polymeric composite, the title authors have developed recently an advanced chromatographic partitioning technology entitled Minor Actinides Recovery from HLLW by Extraction Chromatography process (MAREC) as shown in Fig. 1 [19,20].

The long-lived minor actinides such as Am(III) and Cm(III) were separated utilizing two columns packed with a macroporous silica-based octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) polymeric composite [21,22]. Sr(II) was partitioned by a novel silica-based DtBuCH18C6 or *N,N,N',N'*-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) impregnated polymeric composite (DtBuCH18C6/SiO₂-P or TODGA/SiO₂-P) packed column [23,24]. However, the significant quantity of DtBuCH18C6 that leaked from DtBuCH18C6/SiO₂-P in HNO₃ solution was observed [25]. This would make the life-time of recycle use of DtBuCH18C6/SiO₂-P short. It is adverse to the application of DtBuCH18C6/SiO₂-P in genuine partitioning of Sr(II) due to the secondary waste production and high capital in cost. So, significant reduction of the affinity of the DtBuCH18C6/SiO₂-P polymeric composite for aqueous solution is much desired. The reduction of the leakage of DtBuCH18C6 or DtBuCH18C6-containing adsorbent by molecular modifier has not been reported yet.

The objective of the present work is focused on (1) modification of DtBuCH18C6 by an organophosphorus compound, tri-*n*-butyl phosphate (TBP), and synthesis of a novel silica-based polymeric composite (DtBuCH18C6 + TBP/SiO₂-P). It was performed through impregnation and immobilization of TBP and DtBuCH18C6 molecules into the pores of the macroporous SiO₂-P particles. It was done utilizing an advanced vacuum sucking technique developed recently. (2) Investigation of the adsorption of 10 fission and non-fission products such as Na(I), K(I), Cs(I), Sr(II), Ba(II), Ru(III), Mo(VI), Pd(II), La(III), and Y(III) towards (DtBuCH18C6 + TBP)/SiO₂-P. It was conducted by the examination of the effects of contact time and HNO₃ concentration in a wide range of 0.1–5.0 M, and (3) evaluation of the leakage behavior of DtBuCH18C6 and TBP from (DtBuCH18C6 + TBP)/SiO₂-P in various experimental conditions designed.

2. Experimental

2.1. Reagents

All of the chemical reagents such as alkali metals nitrate MNO_3 ($M=Na, K, \text{ and } Cs$), $Sr(NO_3)_2$, $Ba(NO_3)_2$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and $RE(NO_3)_3 \cdot nH_2O$ ($RE=La \text{ and } Y, n=3 \text{ or } 6$) employed were of analytical grade. Two highly pure reagents, ruthenium (III) nitrosyl nitrate solution with 1.5 wt% of Ru(III) and palladium nitrate solution with 4.5 wt% of Pd(II), were provided by Strem Chemicals, the United States of America and Tanaka Noble Metal Co. Inc., Japan, respectively. La(III) and Y(III) were used to simulate the adsorption behavior of all rare earth and minor actinide elements because of their similarity in the chemical properties. The concentrations of all of the tested elements used were about $5.0 \times 10^{-3} \text{ M}$ ($M = \text{mol/dm}^3$). Various HNO_3 solutions of different concentrations employed were prepared temporarily.

4,4',(5')-Di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) with a purity greater than 97% was provided by Eichrom Technologies Inc., the United States of America. Tri-*n*-butyl phosphate with a purity more than 98% was provided by Kanto Chemical Co. Inc, Japan. Dichloromethane, methanol and other inorganic/organic reagents used in the experiments were of analytical grade were used without further purification.

The silica-based SiO_2 -P particles and macroporous inorganic/organic polymeric composite (DtBuCH18C6 + TBP)/ SiO_2 -P were synthesized in our laboratory. A letter "P" in the SiO_2 -P particles means the styrene-divinylbenzene co-polymer, which was prepared by means of a series of polymerization reactions taking place inside the macroporous SiO_2 substrate.

2.2. Synthesis of silica-based SiO_2 -P particles

Spherical silica particles with a diameter of 40–60 μm , a mean pore size of 0.6 μm , and a pore fraction of 0.69 were used. To support the organic chelating agent, an inert co-polymer of formylstyrene and divinylbenzene was synthesized and embedded in the pores of the silica particles. The preparatory flow sheet of the polymer-immobilized silicon-based particles was illustrated in Fig. 2. The silica particles were put into a glass flask was evacuated by a vacuum pump, and a mixture of monomers composed of 85 wt% of *m/p*-formylstyrene, 15 wt% *m/p*-divinylbenzene, dioctyl phthate and methylbenzoate, initiators made of α, α -azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile (V-40), and diluents consisted of 1,2,3-trichloropropane and *m*-xylene was sucked into the flask through a rubber tube. The flask was rotated continuously so that the mixture would soak completely into the pores of the silica particles and then filled with N_2 gas. The flask was maintained in a silicone-oil bath and then heated at 363 K for 20 h. The grafted material SiO_2 -P particles were washed with acetone and distilled water and then dried overnight at 323 K. The content of the inert co-polymer, formylstyrene-divinylbenzene, in the SiO_2 -P particles obtained

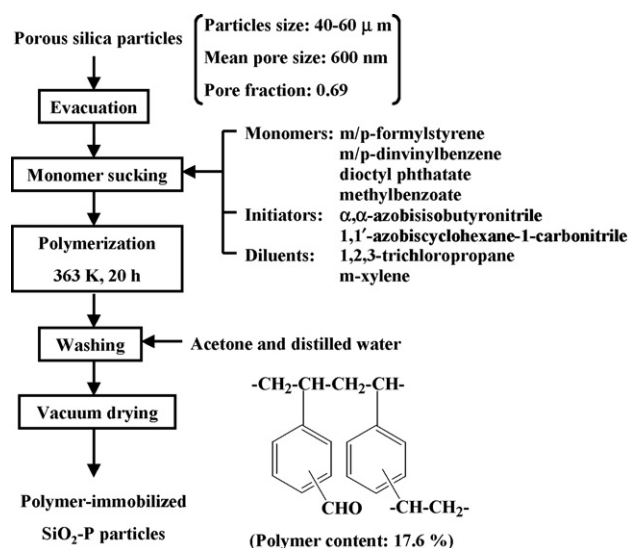


Fig. 2. Synthesis of macroporous SiO_2 -P particles by the polymerization reaction.

was 17.6 wt% measured by means of thermogravimetric analysis.

2.3. Synthesis of (DtBuCH18C6 + TBP)/ SiO_2 -P

Prior to synthesis the SiO_2 -P particles were treated actively by acetone and methanol. The active treatment method by methanol was described as follows: a weighted quantity of the SiO_2 -P particles was mixed with about 80 cm^3 of methanol into 300 cm^3 of conical flask, shaken mechanically at 120 rpm for 60 min, and then separated. Subsequently, it was dried in a vacuum drying oven at 318 K for 24 h. The identical operation was repeated three times. The purpose of this procedure was to significantly increase the affinity of co-polymer inside the SiO_2 -P particles for DtBuCH18C6 and TBP.

The synthesis procedure of (DtBuCH18C6 + TBP)/ SiO_2 -P was described as follows: the weighted quantity of colorless liquid tri-*n*-butyl phosphate and the calculated amount of sticking 4,4',(5')-di(*tert*-butylcyclohexano)-18-crown-6 were dissolved completely with $\sim 100 \text{ cm}^3$ of dichloromethane in a 300 cm^3 of glass conical flask, then, the given quantity of the activated SiO_2 -P particles was introduced under continuous shaking. After that, the mixture obtained was stirred using a rotary evaporator (EYELA N-1000, Tokyo Rikakikai Co. Ltd., Japan) over 90 min, it was then moved into a silicone-oil bath controlled using a temperature controller (EYELA OHB-2000, Tokyo Rikakikai Co. Ltd., Japan) and stirred further for about 240 min at 323 K to impregnate the DtBuCH18C6 and TBP molecules into the pores of the SiO_2 -P particles by physical evaporation and chemical immobilization. Following drying in a vacuum drying oven at around 323 K for overnight, a colorless silica-based polymeric composite (DtBuCH18C6 + TBP)/ SiO_2 -P, was obtained. It was characterized by TG-DSC and elementary analysis, respectively. The schematic diagram of synthesizing (DtBuCH18C6 + TBP)/ SiO_2 -P is shown in Fig. 3. Its physical properties are listed in Table 1.

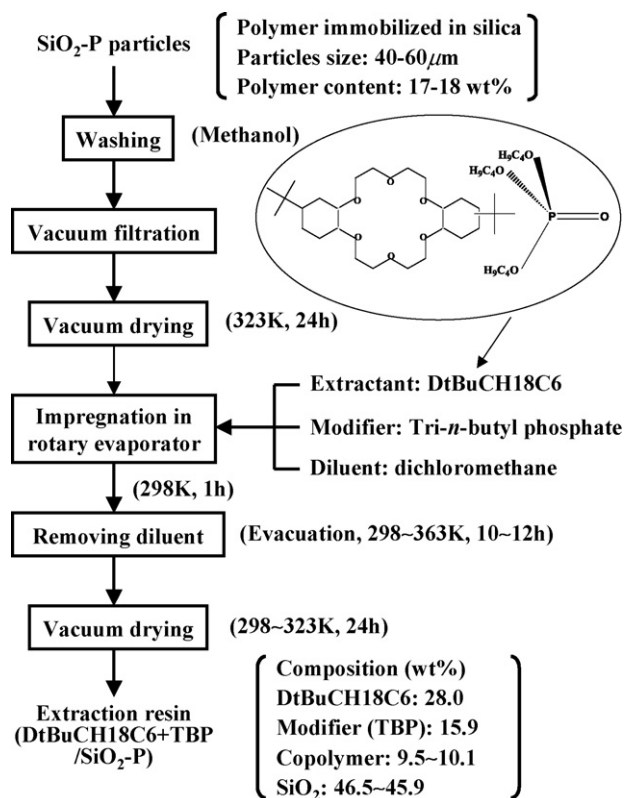


Fig. 3. Synthesis procedure of a novel silica-based DtBuCH18C6 impregnated polymeric composite modified by TBP.

2.4. Adsorption of metals towards (DtBuCH18C6 + TBP)/SiO₂-P

In batch experiment, a 5 cm³ of HNO₃ solution containing $\sim 5.0 \times 10^{-3}$ M of Na(I), K(I), Cs(I), Sr(II), Ba(II), Ru(III), Mo(VI), Pd(II), La(III), and Y(III) as an aqueous phase and the weighed amount of (DtBuCH18C6 + TBP)/SiO₂-P as a solid phase were mixed into a 50 cm³ ground glass-stopped flask. It was shaken mechanically using a TAITEC MM-10 thermostated

water bath shaker at 120 rpm for a desired contact time at 298 K. The HNO₃ concentration in aqueous phase was in the range of 0.1–5.0 M. After the phase separation through a membrane filter with ~ 0.45 μm pore, the concentrations of phosphorus and various metals in aqueous phase were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, SPS-5000, Seiko Instruments, Japan) except the content of Cs(I), Na(I), and K(I) that was analyzed using a series inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500, Agilent Technologies, Japan) or an atomic adsorption spectroscopy (AA-6800, Shimadzu, Japan). The concentration of total organic carbon (TOC) leaked from (DtBuCH18C6 + TBP)/SiO₂-P into aqueous phase was determined using a TOC-VCPN analyzer (Shimadzu 5000, Shimadzu, Japan). The concentrations of TBP and DtBuCH18C6 leaked were calculated based on the contents of phosphorus and TOC. The distribution coefficients (K_d) of various metals towards (DtBuCH18C6 + TBP)/SiO₂-P polymeric materials were calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \frac{V}{W} \quad (\text{cm}^3/\text{g}) \quad (1)$$

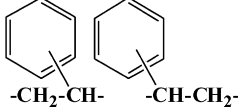
where C_o and C_e represent the initial and equilibrium concentrations of various metals in aqueous phase, respectively. W and V denote the weight of dry (DtBuCH18C6 + TBP)/SiO₂-P and the volume of aqueous phase used in the experiments.

3. Results and discussion

3.1. Dependence of (DtBuCH18C6 + TBP)/SiO₂-P adsorption on contact time

The silica-based DtBuCH18C6 polymeric composite developed is mainly used to partition and recover Sr(II). To understand the molecular modification effect of DtBuCH18C6 by TBP, the adsorption of some typically simulated fission and non-fission products Cs(I), Sr(II), Ba(II), Ru(III), Mo(VI), Pd(II), La(III), Y(III), Na(I), and K(I) towards (DtBuCH18C6 + TBP)/SiO₂-P with a continuous change in contact time was investi-

Table 1
Structure and physical properties of a novel silica-based macroporous DtBuCH18C6 impregnated polymeric composite modified by TBP

Organic/inorganic polymeric composite	(DtBuCH18C6 + TBP)/SiO ₂ -P
Chelating functional group	4,4', (5')-Di-(<i>tert</i> -butylcyclohexano)-18-crown-6
Pore fraction	0.69
Mean pore size	0.6 μm
Bead diameter	40–60 μm
Volume fraction	1.1 cm ³ /g
Molecular modifier	Tri- <i>n</i> -butyl phosphate (TBP)
Co-polymer inside SiO ₂ -P support	Macroporous SiO ₂ particles immobilized by following inert co-polymer-containing compound $\text{-CH}_2\text{-CH-CH}_2\text{-CH-}$  $\text{-CH}_2\text{-CH-CH}_2\text{-CH-}$
Appearance	Colorless powdered micro-ball
Affinity for water or acidic solution	Good

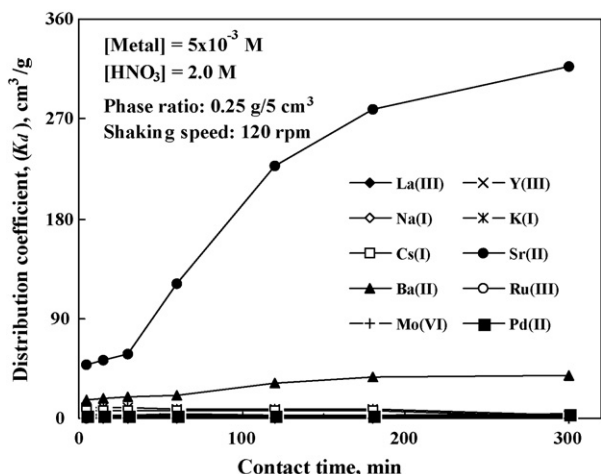


Fig. 4. Effect of contact time on the adsorption of (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₃ at 298 K. [Metal] = 5×10^{-3} M, phase ratio: 0.25 g/5 cm³, contact time: 300 min.

gated at phase ratio of 0.25 g/5 cm³, metal concentration of 5.0×10^{-3} M, HNO₃ concentration of 2.0 M, and shaking speed of 120 rpm at 298 K. La(III) and Y(III) were used to simulate the adsorption behavior of MA(III) and RE(III) elements. The results are showed in Figs. 4–6, respectively.

Fig. 4 shows the effect of contact time on the adsorption of (DtBuCH18C6 + TBP)/SiO₂-P for the tested metals in 2.0 M HNO₃ solution. As can be seen, with an increase in contact time, Na(I), K(I), Cs(I), La(III), Y(III), Ru(III), Mo(VI), and Pd(II) showed very weak or almost no adsorption towards (DtBuCH18C6 + TBP)/SiO₂-P. Their distribution coefficients (K_d) at contact time of 300 min were always below 3.98 cm³/g except 38.78 cm³/g for Ba(II). Such a low value in the distribution coefficient (K_d) was due to the weak complexation of these metals with DtBuCH18C6. The main reason resulted from the lack of affinity of the hard-atom oxygen contained in DtBuCH18C6 molecule for metals. On the other hand, the chemical properties of all lanthanides in aqueous solution are quite similar due to the lanthanide contraction. Because La(III) and

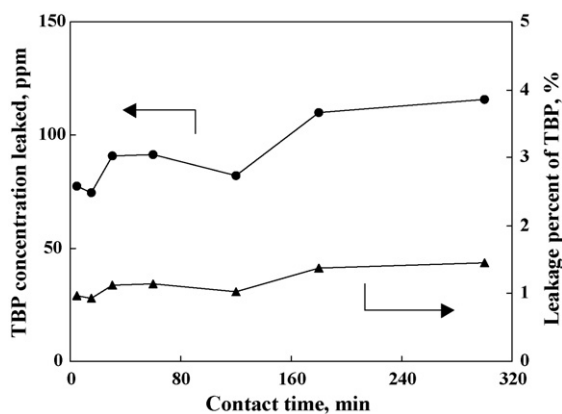


Fig. 5. Leakage of TBP from (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₄ with a change in contact time. Experimental conditions consisted with those of showing in Fig. 4.

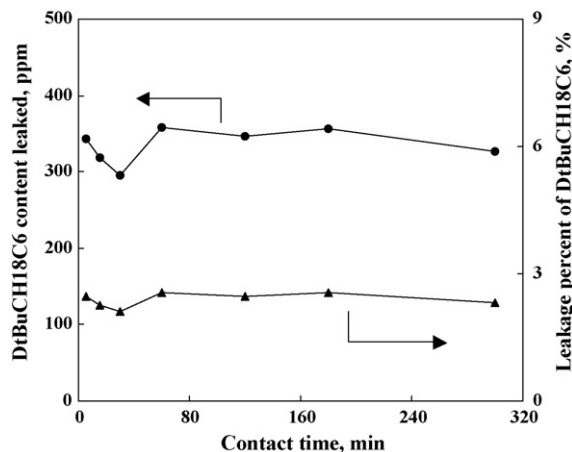


Fig. 6. Leakage of DtBuCH18C6 from (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₄ with a change in contact time. Experimental conditions consisted with those of showing in Fig. 4.

Y(III) showed no adsorption, so, it is predicted that in 2.0 M HNO₃, all of the RE(III) elements have no adsorption towards (DtBuCH18C6 + TBP)/SiO₂-P. Similarly, for the actinide elements, their ionic radii decrease with increasing atomic number, indicative of decreased shielding by f electrons of the outer valence electrons nuclear charge. This makes the actinide contraction very similar to the lanthanide contraction, i.e., all of minor actinide MA(III) elements have very weak or almost no adsorption towards (DtBuCH18C6 + TBP)/SiO₂-P. So, RE(III) and the long-lived MA(III) contained in HLLW solution will probably show no adverse impact on the effective elimination of Sr(II).

Contrary to the elements tested above, the adsorption of Sr(II) onto (DtBuCH18C6 + TBP)/SiO₂-P increased rapidly with an increase in contact time and did not seem to reach adsorption equilibrium, even though the contact time was up to 300 min. The distribution coefficient (K_d) of Sr(II) was 48.74 cm³/g at 5 min, 120.9 cm³/g at 60 min, and 317.0 cm³/g at 300 min. This revealed that Sr(II), one of the main heat generators, had slow adsorption kinetics onto (DtBuCH18C6 + TBP)/SiO₂-P. It might result from the slow complexation of Sr(II) and DtBuCH18C6. On the other hand, the apparent shape and character of the dynamic adsorption curve of Sr(II) consisted with those of the chemical adsorption of metal ions. This implied that in 2.0 M HNO₃ solution, the adsorption of Sr(II) onto (DtBuCH18C6 + TBP)/SiO₂-P belonged to the chemical adsorption, i.e., the chemical complexation of Sr(II) and (DtBuCH18C6 + TBP)/SiO₂-P was the rate-controlling step, which was the slow kinetics process. The difference in the adsorption of the tested metals reflected that (DtBuCH18C6 + TBP)/SiO₂-P polymeric adsorbent had excellent adsorption ability and high selectivity for Sr(II) over all of the tested elements except Ba(II).

In addition, Cs(I) showed no adsorption. This makes the complete separation of Sr(II) from Cs(I)-containing HLLW solution possible. So, it is predicted that in 2.0 M HNO₃, two heat generators Cs(I) and Sr(II) can be partitioned mutually

through (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite. Only Ba(II) had the adverse impact. The resulting conclusion consisted with that of DtBuCH18C6/SiO₂-P, which was not modified with TBP.

Fig. 5 shows the leakage of TBP from (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₃. It was found that with an increase in contact time, the concentration of TBP leaked in aqueous phase increased gradually. The value of TBP leakage was 77.43 ppm at 5 min, 91.47 ppm at 60 min, and 115.6 ppm at 300 min. The corresponding percentage of TBP leakage was 0.97% at 5 min, 1.14% at 60 min, and 1.45% at 300 min. Such a low value in the quantity of TBP leaked reflected that in 2.0 M HNO₃, the macroporous silica-based (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite was a stable adsorbent at the tested experimental conditions.

Fig. 6 shows the effect of contact time on the leakage of DtBuCH18C6 from (DtBuCH18C6 + TBP)/SiO₂-P. Obviously, with a continuous increase in contact time, the change in the concentration of DtBuCH18C6 leaked was insignificant. The leakage of DtBuCH18C6 was 343.8 ppm at 5 min, 357.7 ppm at 60 min, and 326.1 ppm at 300 min. The corresponding percentage of DtBuCH18C6 leaked was 2.45% at 5 min, 2.55% at 60 min, and 2.32% at 300 min. The average concentration and percentage of DtBuCH18C6 leaked were 334.7 ppm and 2.39%, respectively.

In previous studies [25], we investigated the leakage behavior of DtBuCH18C6 from DtBuCH18C6/SiO₂-P, which was not modified by TBP. It was found that in the same adsorption conditions, for example, the same phase ratio of 0.25 g/5 cm⁵, HNO₃ concentration of 2.0 M, temperature of 298 K, and metal concentration of 5 × 10⁻³ M, the concentration of DtBuCH18C6 leaked in aqueous phase was 989.9 ppm at 5 min, 793.0 ppm at 60 min, and 658.4 ppm at 360 min. The corresponding percentage of DtBuCH18C6 leaked was 5.94% at 5 min, 4.75% at 60 min, and 3.95% at 360 min. The average concentration and percentage in contact time of 360 min was 797.3 ppm and 4.78%.

In comparison with the quantities of DtBuCH18C6 leaked from its silica-based impregnated polymeric composites with and without modification by TBP, it is clear that in 2.0 M HNO₃, the amount of DtBuCH18C6 leaked from (DtBuCH18C6 + TBP)/SiO₂-P was much lower than that from DtBuCH18C6/SiO₂-P. So, an introduction of TBP as a molecular modifier into the pores of SiO₂-P particles was effective for the significant reduction of DtBuCH18C6 leakage into aqueous solution. This might result from the association reaction between DtBuCH18C6 and TBP. Possible associated species, DtBuCH18C6·TBP, formed through hydrogen bonding in pores of SiO₂-P particles might be the main reason why the leakage of DtBuCH18C6 decreased significantly. The possible association is illustrated in Fig. 7.

The significant reduction of DtBuCH18C6 leakage through molecular modification with TBP makes application of the silica-based (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite in the cycle separation of Sr(II) from HLLW promising. However, the structure and the complex reaction between TBP and DtBuCH18C6 have not been reported yet.

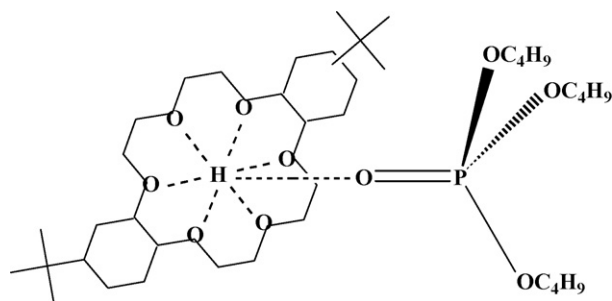


Fig. 7. Possibly associated species of DtBuCH18C6 and TBP through hydrogen bonding.

3.2. Dependence of (DtBuCH18C6 + TBP)/SiO₂-P adsorption on HNO₃ concentration

DtBuCH18C6 is a neutral chelating agent having six hard-atom oxygens, which has high affinity for hydrogen. This makes the effect of HNO₃ concentration on the complex of metals with DtBuCH18C6 strong. In reprocessing of nuclear spent fuel, the acidity in HLLW is usually around 3.0 M HNO₃.

To investigate the adsorption and leakage behavior of (DtBuCH18C6 + TBP)/SiO₂-P, the effect of HNO₃ concentration in a range of 0.1–5.0 M on the adsorption of Sr(II) and other simulated elements Cs(I), Ba(II), Ru(III), Mo(VI), Pd(II), Y(III), Na(I), La(III), and K(I) onto (DtBuCH18C6 + TBP)/SiO₂-P was studied at metal concentration of 5 × 10⁻³ M, phase ratio of 25 g/5 cm⁵, and contact time of 300 min at 298 K. The quantities of phosphorus and TOC leaked from the (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite were measured by ICP-OES and TOC-VCPN analysis. The contents of DtBuCH18C6 and TBP leaked were then calculated. The results are illustrated in Figs. 8–10, respectively.

Fig. 8 shows the adsorption properties of the (DtBuCH18C6 + TBP)/SiO₂-P adsorbent for the tested fission and non-fission products in a wide HNO₃ concentration range of 0.1–5.0 M. It was found that with an increase in the HNO₃ concentration, the adsorption of Sr(II) towards (DtBuCH18C6 + TBP)/SiO₂-P

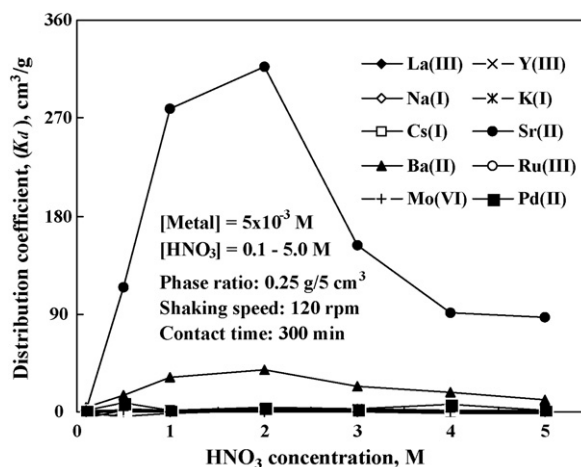


Fig. 8. Adsorption of (DtBuCH18C6 + TBP)/SiO₂-P for Sr(II) and other typically simulated elements in a wide HNO₃ concentration range of 0.1–5.0 M at 298 K. [Metal] = 5 × 10⁻³ M, phase ratio: 0.25 g/5 cm³, contact time: 300 min.

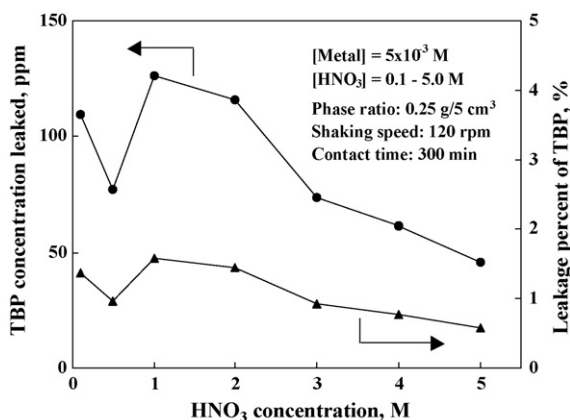


Fig. 9. TBP leakage from (DtBuCH18C6 + TBP)/SiO₂-P in the HNO₃ concentration range of 0.1–5.0 M. Experimental conditions consisted with those of showing in Fig. 8.

quickly increased from 0.1 to 1.0 M HNO₃, slowly increased to 2.0 M HNO₃, and then decreased. The distribution coefficient (K_d) of Sr(II) was 1.60 cm³/g in 0.1 M HNO₃, 279.2 cm³/g in 1.0 M HNO₃, 317.0 cm³/g in 2.0 M HNO₃, and 87.51 cm³/g in 5.0 M HNO₃. The other metals always showed very weak or almost no adsorption and their distribution coefficients (K_d) were below 3.0 cm³/g except for Ba(II) having K_d of 38.77 cm³/g. So, in 2.0 M HNO₃ solution. The silica-based (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite had high adsorption ability and excellent selectivity for Sr(II) over all of the tested elements. This makes the separation of Sr(II) from an acidic HLLW solution containing alkali metals, alkaline earths, fission products Pd(II), Mo(VI), Ru(III), MA(III), and RE(III) by (DtBuCH18C6 + TBP)/SiO₂-P feasible.

Fig. 9 shows the leakage of TBP from (DtBuCH18C6 + TBP)/SiO₂-P in HNO₃ solution in a range of 0.1–5.0 M. As can be seen, with an increase in HNO₃ concentration, the concentration of TBP leaked in aqueous phase increased obviously from 0.1 to 1.0 M and then decreased quickly. The quantity of TBP leaked was 109.7 ppm in 0.1 M HNO₃, 115.6 ppm in 2.0 M

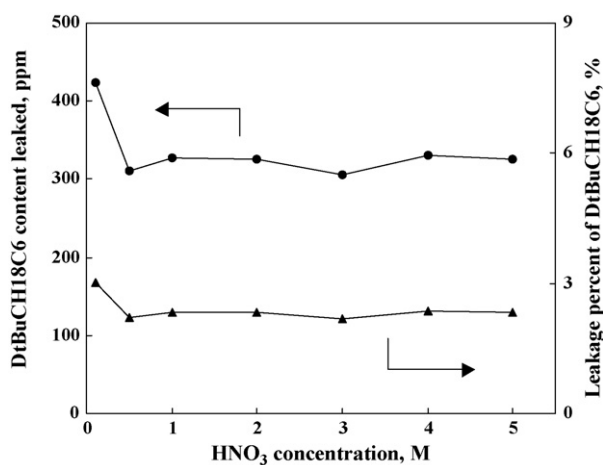


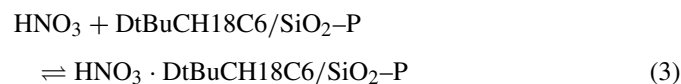
Fig. 10. DtBuCH18C6 Leakage from (DtBuCH18C6 + TBP)/SiO₂-P in the HNO₃ concentration range of 0.1–5.0 M. Experimental conditions consisted with those of showing in Fig. 8.

HNO₃, and 45.81 ppm in 5.0 M HNO₃. The change trend in corresponding percentage of TBP leaked was similar to one the change in the TBP concentration leaked. The value was 1.37% in 0.1 M HNO₃, 1.44% in 2.0 M HNO₃, and 0.57% in 5.0 M HNO₃. The increase in the TBP content in the HNO₃ concentration range of 0.1–1.0 M was due to the solubility of TBP in aqueous phase. It is well known that TBP is a hydrophilic compound containing P=O functional group, which has high affinity for aqueous solution, so, in low HNO₃ concentration solution, TBP molecule can easily interact with the polar water molecule, i.e., TBP showed high solubility because of its affinity for aqueous solution. The subsequent decrease in the TBP concentration leaked in excess of 1.0 M HNO₃ was due to the association reaction of TBP and HNO₃ molecule of high concentration through intermolecular interaction. Their association was described as follows:



The formation of the associated species, HNO₃·nTBP, made the physical distribution of TBP in aqueous phase significantly lower. This resulted in an obvious decrease in the leakage of TBP. In Purex process and its modified process, 30% TBP in hydrocarbon diluent was usually used as an organic phase to extract U(VI) and Pu(VI) from 3.0 M HNO₃. It was reported a series of the associated formations of TBP with HNO₃ such as HNO₃·TBP, HNO₃·2TBP, HNO₃·3TBP, and HNO₃·4TBP have been demonstrated [26–30]. So, the obvious decrease in the concentration of TBP leaked from 1.0 to 5.0 M HNO₃ was ascribed to the effective association of TBP with HNO₃ through hydrogen bonding.

Fig. 10 shows the leakage behavior of DtBuCH18C6 from (DtBuCH18C6 + TBP)/SiO₂-P with an increase in the HNO₃ concentration at 298 K. It was clear that in the tested acidity range, the leakage of DtBuCH18C6 basically kept constant except in 0.1 M HNO₃. The average quantity of DtBuCH18C6 leaked was 422.7 ppm in 0.1 M HNO₃ and 321.3 ppm in HNO₃ concentration range of 0.5–5.0 M. The high leakage of DtBuCH18C6 in 0.1 M HNO₃ resulted from the high solubility of (DtBuCH18C6 + TBP)/SiO₂-P because of its good affinity towards aqueous solution. The low leakage of DtBuCH18C6 in the range of 0.5–5.0 M HNO₃ might be due to two formations of the associated species DtBuCH18C6·TBP as shown in Fig. 7 and HNO₃·DtBuCH18C6/SiO₂-P through intermolecular interaction as described follows:



On the other hand, Cs(I), another heat generator, showed almost no adsorption within the whole HNO₃ concentration range studied. This made the mutual partitioning of Sr(II) and Cs(I) promising, i.e., after the separation of Sr(II) from 2.0 M HNO₃ by (DtBuCH18C6 + TBP)/SiO₂-P, Cs(I) contained in effluent can be partitioned from 4.0 M HNO₃ by another novel silica-based 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) impregnated polymeric composite (Calix[4]arene-R14/SiO₂-P) as depicted in Fig. 11, which

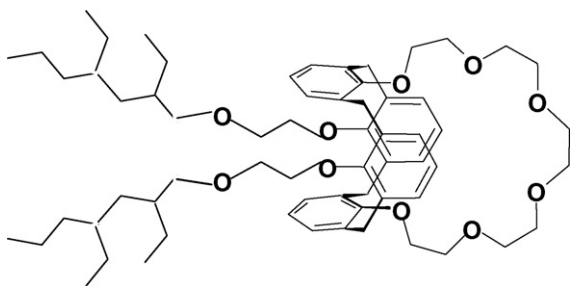


Fig. 11. Molecular structure of 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14).

Table 2
DtBuCH18C6 leakage from DtBuCH18C6/SiO₂-P in the HNO₃ concentration range of 0.1–5.0 M

HNO ₃ concentration (M)	DtBuCH18C6 concentration leaked (ppm)	DtBuCH18C6 percentage leaked (%)
0.001	821.0	4.9
0.01	914.6	5.5
0.1	796.5	4.8
1.0	612.3	3.7
2.0	658.4	4.0
3.0	713.7	4.3

Other conditions consisted with those of showing in Fig. 8.

was developed recently in our laboratory [31]. Regarding the chromatographic partitioning of Sr(II) and Cs(I) from a simulated HLLW solution by column operation is planned to be performed in next fiscal year.

To evaluate the leakage of DtBuCH18C6 from DtBuCH18C6 impregnated polymeric composites with and without molecular modification by TBP, the physical distribution of DtBuCH18C6/SiO₂-P in aqueous solution was investigated in the HNO₃ concentration range of 0.001–3.0 M. The other experimental conditions consisted with those of showing in Fig. 8. The results are shown in Table 2.

Obviously, the quantity of DtBuCH18C6 leaked from DtBuCH18C6/SiO₂-P was in a range of 612.3–914.6 ppm with an average value of 752.8 ppm, which was higher than that of 321.3 ppm leaked from (DtBuCH18C6 + TBP)/SiO₂-P modified by TBP.

Based on the results shown in Fig. 10 and Table 2, it is demonstrated that the introduction of TBP as a molecular modifier into the pores of the SiO₂-P particles can reduce significantly the leakage of DtBuCH18C6. The association of DtBuCH18C6 and TBP through intermolecular interaction, i.e., hydrogen bonding, is the main reason. This is of great benefit to the extension of the used life-time of (DtBuCH18C6 + TBP)/SiO₂-P in recycle operation. It makes the Sr(II) separation from a genuine HLLW by extraction chromatography promising.

4. Conclusions

DtBuCH18C6 is an effective chelating agent for highly selective elimination of Sr(II), one of the main heat generators in HLLW. To reduce significantly its leakage, a

novel improved silica-based impregnated polymeric composite (DtBuCH18C6 + TBP)/SiO₂-P, was synthesized using TBP as a molecular modifier.

The adsorption of 10 typically simulated fission and non-fission products Na(I), K(I), Cs(I), Ba(II), Ru(III), Mo(VI), Sr(II), Pd(II), La(III), and Y(III) onto (DtBuCH18C6 + TBP)/SiO₂-P was investigated. It was done through the examination of the effects of contact time and HNO₃ concentration in the range of 0.1 M to 5.0 M (DtBuCH18C6 + TBP)/SiO₂-P in 2.0 M HNO₃ showed high adsorption ability and excellent selectivity for Sr(II) over all of the tested elements. Furthermore, the bleeding of DtBuCH18C6 from (DtBuCH18C6 + TBP)/SiO₂-P was much lower than that from DtBuCH18C6/SiO₂-P without molecular modification with TBP. The significant reduction of DtBuCH18C6 leakage from its silica-based adsorbent modified by TBP was achieved.

The results obtained in present work demonstrated that in 2.0 M HNO₃, the macroporous silica-based (DtBuCH18C6 + TBP)/SiO₂-P polymeric composite is promising for the application in partitioning of Sr(II) from HLLW in MAREC process.

Acknowledgments

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