Synthesis of a Macroporous Silica-Based Derivative of Pyridine Material and Its Application in Separation of Palladium

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A novel macroporous silica-based 2,6-bis(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine (BDBTP) material, BDBTP/SiO_2-P, was prepared through impregnation and immobilization of BDBTP and octanol into the pores of the SiO_2-P particles. The adsorption of 10 typical fission and nonfission elements contained in highly active liquid waste (HLW) onto BDBTP/SiO_2-P was investigated by examining the effect of contact time and the HNO_3 concentration in the range of 0.1–5.0 M. Pd(II), a weak Lewis acid and an electron-pair acceptor, was strongly complexed with nitrogen, a weak Lewis base and an electron-pair donor. BDBTP/SiO_2-P showed excellent adsorption ability and high selectivity for Pd(II) over all the tested metals. The separation of Pd(II) from a simulated HLW was performed by BDBTP/SiO_2-P packed column. Pd(II) was effectively eluted with 0.2 M thiourea and separated from the others. It demonstrated that in HNO_3, application of the macroporous silica-based BDBTP/SiO_2-P material in partitioning and recovery of Pd(II) from HLW is promising. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 3074–3083, 2010

Keywords: synthesis, macroporous silica-based composite, separation, palladium, highly active liquid waste

Introduction

In current reprocessing of nuclear spent fuel, either the Purex process or its modified version by using 30% tri-*n*-butyl phosphate/kerosene as an extraction system is effective for partitioning and recovery of uranium and plutonium. As a result, a lot of the fission products (FPs) such as the long-lived minor actinides (MAs), heat emitting nuclides Cs and Sr, rare earths (REs), noble metals, Mo, Tc, Zr, etc. are contained in highly active liquid waste (HLW).[1] For the purpose of environment protection, elimination of these radionuclides as well as effective treatment and disposal of HLW are required. Much attention has been focused on the separation of MAs due to partitioning and transmutation (P/T) strategy.[2,3] However, effective separation and recovery of the long-lived Pd from HLW has not been investigated.

As one of the main FPs, Pd has both stable and radioactive isotopes generated by the fission process of uranium or plutonium or by β-decay of adjacent species produced from fission reaction. Pd-107 with a half life of 6.5×10^6 years is

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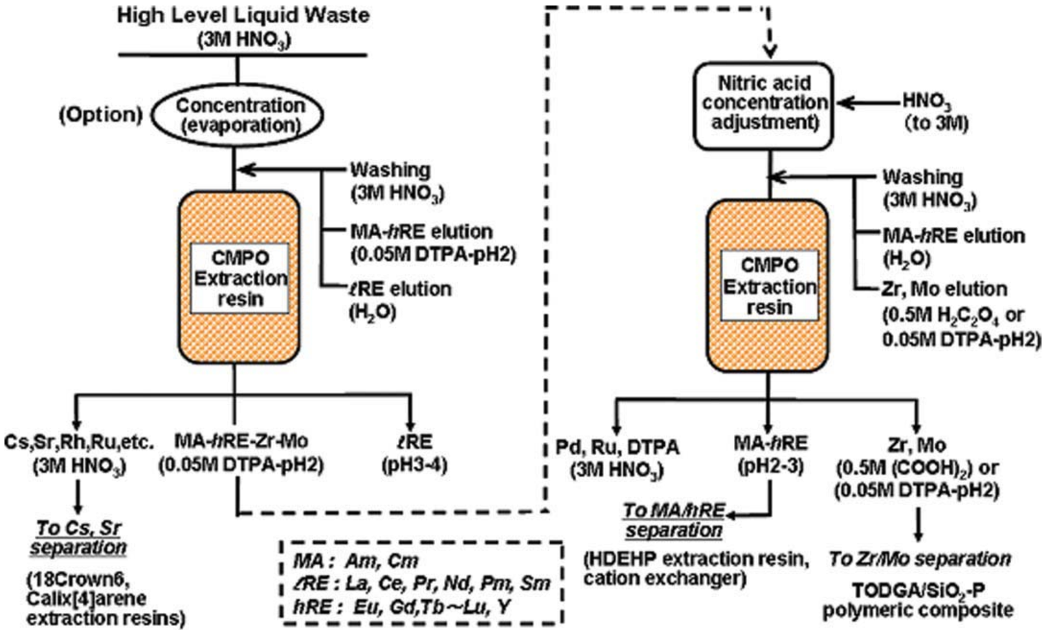

Figure 1. Flowsheet of MAREC process developed for minor actinides and some specific fission products partitioning from HLW by extraction chromatography.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a soft β-emitter of 0.035 MeV energy. The quantity of Pd produced in nuclear spent fuel is significant and approximate to 1–2 kg/ton. The portion of Pd-107 in the typical fission generated Pd is about 17.5%. The removal of Pd can likely make the vitrification as a final disposal method of HLW easier. Hence, for the purpose of significantly reducing the long-term adverse impact of Pd-107 on environment, the effective elimination of Pd-107 from HLW is valuable.

Liquid–liquid solvent extraction is one of the effective conventional separation techniques. For the purpose of treatment and disposal of HLW, a variety of extraction processes have been developed to separate radionuclides utilizing some selective extractants such as bis(2,4,4-trime-thylpentyl)dithiophosphinic acid, octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphoshine oxide, trialkyl phosphine oxide, and *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane-1,5-diamide.[1,4,5] Because of the formation of the third phase, generation of the large quantity of secondary wastes resulted from the hydrolytic and radiolytic degradation of organic extractants and diluents occurred. If extraction chromatography is used, the radionuclides would be concentrated to a minimal volume thereby facilitating their storage or disposal.

In extraction chromatography, an inert support is impregnated with an organic extractant, either alone or in combination with a suitable diluent, to produce a solid sorbent capable of selectively removing certain metal ions from aqueous solution.[6,7] It provides a simple and effective means by which the separation and preconcentration of a variety of radionuclides can be accomplished.[8,9] In effect, the extraction chromatography combines the selectivity of solvent extraction with the simplicity and multistage character of column chromatographic system. However, no sufficient attention has been paid to this aspect with the exception of some comparatively simple concentration of solution used to the purpose of sample analysis in laboratory. Therefore, as an alternative separation method, utilizing the extraction chromatography in HLW partitioning is meaningful.

Based on the SETFICS process and some investigations,[10–12] an advanced partitioning technology entitled *M*inor *A*ctinides *R*ecovery from HLW by *E*xtraction *C*hromatography (MAREC) process as shown in Figure 1 have been developed.[13–16] The long-lived MAs such as Am(III) and Cm(III) were separated using two columns packed with a macroporous silica-based CMPO polymeric composite, $CMPO/SiO_2$-P. The resultant MA-containing effluent was separated to (1) Pd–Ru, (2) MA–*h*RE, and (3) Zr–Mo, respectively, by using H_2O and 0.05 M diethylenetriaminepentaacetic acid (DTPA)-pH 2.0 or 0.5 M $H_2C_2O_4$ as eluents. Heat emitting nuclides Sr(II) and Cs(I), Mo(VI), Zr(IV), and the other FPs were partitioned by a novel macroporous silica-based 4,4′,(5′)-di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), TODGA, or supermolecular recognition agent 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) impregnated polymeric composite, $DtBuCH18C6/SiO_2$-P, $TODGA/SiO_2$-P, or (Calix[4]arene-$R14/SiO_2$-P).[17–23]

2,6-Bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (R-BTP) as shown in Figure 2 is a neutral multicoordinate ligand containing soft-atom nitrogen. It had excellent extraction selectivity for trivalent MA(III) such as Am(III) and Cm(III).[24–28] The preliminary results showed that Am(III) was separated from 0.01 M HNO_3-1 M $NaNO_3$ medium containing Ce(III), Nd(III), Eu(III), Gd(III), and Y(III) by extraction chromatography.[29] In addition, according to the Lewis theory of acid–

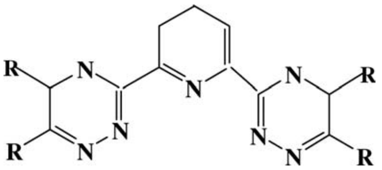

Figure 2. Molecular structure of 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine.

base reactions, nitrogen inside R-BTP molecule has excellent affinity for Pd(II), that is, it can be strongly complexed by R-BTP. It makes application of R-BTP in partitioning of Pd(II) possible. However, regarding application of R-BTP extractant or related solid adsorbent in the separation of Pd(II) from HLW has not been reported so far.

To seek the possibility of Pd(II) elimination from HLW, a novel macroporous silica-based 2,6-bis(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine (BDBTP) polymeric material, BDBTP/SiO_2-P, was synthesized. It was achieved by impregnation and immobilization of BDBTP and 1-octanol molecules into the pores of ~50 μm SiO_2-P particles via molecular modification. The adsorption of some typical fission and non-FPs Sr(II), Ba(II), Cs(I), Na(I), K(I), Pd(II), La(III), Y(III), Ru(III), and Mo(VI) onto BDBTP/SiO_2-P was investigated at 298 K. It was performed through examination of the effects of contact time and the HNO_3 concentration in the range of 0.1–5.0 M. The chromatographic separation of Pd(II) from a 2.0 M HNO_3 solution containing ~5.0 mM of the tested metals by the BDBTP/SiO_2-P material packed column was investigated using 2.0 M HNO_3 and 0.2 M thiourea-0.1 M HNO_3 as eluents. The possibility and feasibility of applying the macroporous silica-based BDBTP/SiO_2-P material in partitioning of Pd(II) from HLW was demonstrated.

Experimental

Reagents

Alkali metal nitrates M^INO_3 (M^I = Na, K, and Cs), alkaline earths nitrates $M^{II}(NO_3)_2$ (M^{II} = Sr and Ba), $RE(NO_3)_3\cdot 6H_2O$ (RE = La and Y), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ used were of analytical grade. Palladium nitrate solution with 4.5 wt % of Pd(II) was provided by Tanaka Noble Metal Co., Japan. Ruthenium (III) nitrosyl nitrate solution with 1.5 wt % of Ru(III) was provided by the Stream Chemicals, USA. Both La(III) and Y(III) were used as the representatives of all of the REs to understand their adsorption behavior because of the similarity in chemical properties. The concentrations of all the tested elements in HNO_3 medium were around 5.0×10^{-3} M (M = mol/dm^3). The HNO_3 solutions of different concentrations were prepared temporarily.

A neutral chelating agent having nitrogen donors, BDBTP as showing in Figure 3 was synthesized.[25,30] The preparation procedure was described as follows: (1) Synthesis of 2,6-pyridinedicarboxamide dihydrazone by the reaction of 2,6-pyridine with hydrazine hydrate, (2) Synthesis of α-diketone by the reduction with sodium and then the oxidation with copper acetate, and (3) Synthesis of BDBTP by the reaction of 2,6-pyridinedicarboxamide dihydrazone with α-diketone. The resultant BDBTP was characterized by elementary analysis, ^1H NMR, MS, TG-DSC, and high pressure liquid chromatography. Its purity was determined to be greater than 98.5%. A modifier 1-octanol with purity higher than 99% was an available commercial product. It was used to modify BDBTP through intermolecular interaction force. 0.2 M Thiourea-0.1 M HNO_3 was used to elute Pd(II) in the loading and elution cycle. Methanol, dichloromethane, and the other inorganic/organic reagents were of analytical grade and were used without further purification.

The macroporous silica-based SiO_2-P particles and novel silica-based chelating material, BDBTP/SiO_2-P, were prepared in our laboratory.[31,32] A symbol P in SiO_2-P shows styrene–divinylbenzene copolymer, which was prepared by means of a polymerization reaction taking place inside the macroporous SiO_2 substrate.

Synthesis of BDBTP/SiO_2-P polymeric material

The affinity of copolymer contained inside the SiO_2-P particles toward BDBTP is weak. Before the synthesis of BDBTP/SiO_2-P polymeric material, the SiO_2-P particles were treated actively by methanol and acetone. The method of treatment by methanol was described as follows: a weighted quantity of the SiO_2-P particles were mixed with about 100 cm^3 of methanol into 300 cm^3 of conical flask, shaken mechanically at 120 rpm for 60 min. After separation, it was dried in a vacuum drying oven at 318 K for 24 h. The same procedure was repeated for several times.

The synthesis of the BDBTP/SiO_2-P composite was described as follows: the weighted quantity of BDBTP and the amount of 1-ocatnol calculated were dissolved completely with 80 cm^3 of dichloromethane in a 300 cm^3 of glass conical flask, then, a given quantity of the SiO_2-P particles was added under shaking. The mixture was stirred mechanically using an EYELA N-1000 Model rotary evaporator (Tokyo Rikakikai Co., Japan) for 90 min, and then it was moved into a silicon-oil bath controlled using an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co., Japan) and stirred continuously for 180 min at 323 K. The purpose was to impregnate the BDBTP and 1-ocatnol molecules into the pores of the SiO_2-P particles through physical evaporation and immobilization. Following

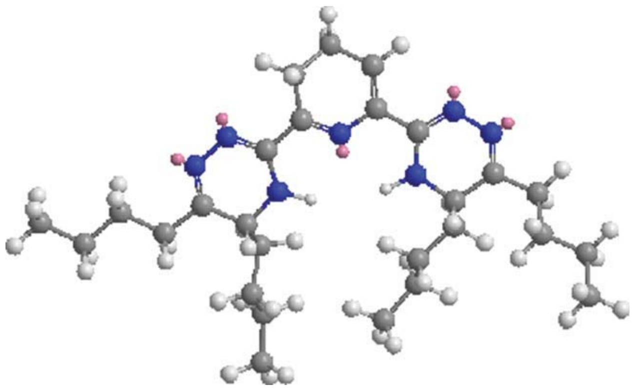

Figure 3. Molecular structure of 2,6-bis(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine (BDBTP).

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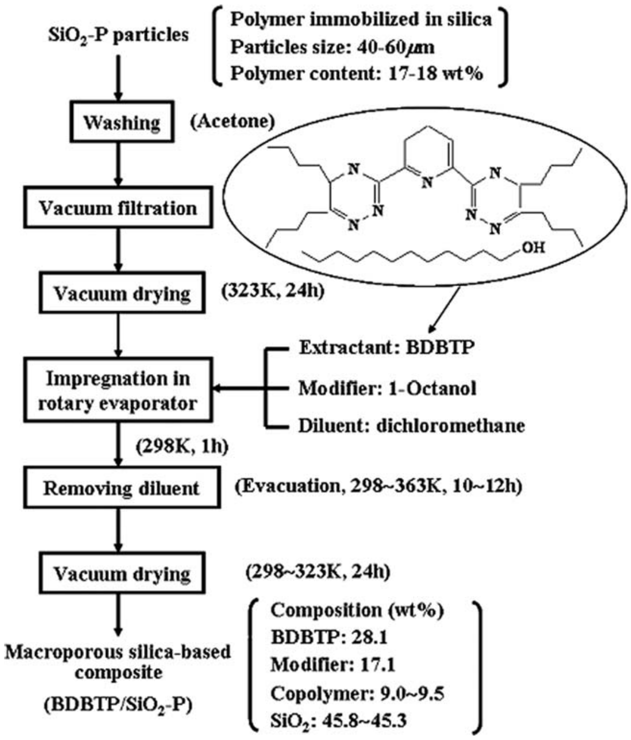


Figure 4. Synthesis of the novel silica-based BDBTP/SiO_2-P polymeric composite.

drying it in a vacuum drying oven at 323 K for overnight, a deep red macroporous silica-based polymeric composite, BDBTP/SiO_2-P, was obtained. It was characterized by elementary analysis TG-DSC and FTTR. The synthesis schematic diagram and some photos of BDBTP/SiO_2-P are shown in Figures 4 and 5, respectively. The physical and chemical parameters are listed in Table 1.

Adsorption of the tested metals onto BDBTP/SiO_2-P

The static-state adsorption of all the tested elements onto BDBTP/SiO_2-P was performed at 298 K, which was controlled using a TAITEC MM-10 Model thermostated water bath shaker. A 5 cm^3 of HNO_3 solution containing $\sim 5.0 \times 10^{-3}$ M of Sr(II), Ba(II), Cs(I), Na(I), K(I), Pd(II), La(III), Y(III), Ru(III), and Mo(VI) as an aqueous phase and the amount of BDBTP/SiO_2-P weighed as a solid phase were mixed into a 50 cm^3 ground glass-stopped flask. It was then shaken mechanically at 120 rpm at a given contact time. The HNO_3 concentration in aqueous phase varied in the range of 0.1–5.0 M. After the phase separation through a membrane filter with the pores of ~ 0.45 μm, the concentrations of the tested elements in aqueous phase were measured using a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, USA) with the exception of the content of Cs(I), Na(I), and K(I) that was analyzed using a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian, USA). The distribution coefficients (K_d) of the tested elements toward the functional composite BDBTP/SiO_2-P were evaluated as follows:

$$K_\mathrm{d} = \frac{C_\mathrm{o} - C_\mathrm{e}}{C_\mathrm{e}} \times \frac{V}{W}\ (\mathrm{cm}^3/\mathrm{g}) \tag{1}$$

where C_o and C_e show the initial and equilibrium contents of the tested metals in aqueous phase, respectively. W and V denote the weight of BDBTP/SiO_2-P and the volume of aqueous phase used in the experiments.

Chromatography partitioning of Pd(II)

The separation of Pd(II) from a HNO_3 solution containing the tested metals was performed by BDBTP/SiO_2-P packed column at 298 K. Before the partitioning, the given quantity of BDBTP/SiO_2-P polymeric composite was equilibrated using 2.0 M HNO_3 solution. It was then packed into a Pyrex glass column with a dimension of 10 mm in inner diameter and 300 mm in length under 0.25–0.35 MPa of N_2 gas pressure. The density of the extraction resin in the column was ~ 0.62 g/cm^3. No significant pressure drop was found through the column due to the monodisperse and rigid silica-based support, which is different from the conventional polymer-based one. A constant temperature, 298 K, in the loading and elution cycles was controlled by the circulation of the thermostated water through an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co., Japan). The flow rate in column was kept at 1.0 cm^3/min using a NPG-20UL Model pressure gage (Nihon Seimitsu Kagaku Co., Japan) and a PDB-FT 4602 Model pressure limiter [Jing–Wei Friendship (Beijing) Technical development Co., China]. The concentrations of HNO_3 and the tested metals in feed solution were

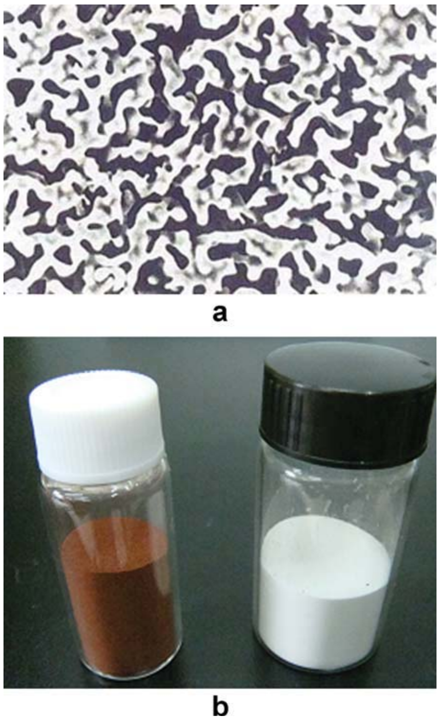
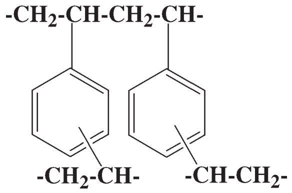


Figure 5. Photos of the macroporous SiO_2 particles support and silica-based BDBTP/SiO_2-P composite.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Parameters of the Novel Silica-Based BDBTP Impregnated Polymeric Composite Modified with 1-Ocatnol

Macroporous Silica-Based Polymeric Composite	$BDBTP/SiO_2$-P
Chelating functional group	2,6-bis(5,6-dibutyl-1, 2,4-triazine-3-yl)pyridine
Pore fraction	0.69
Specific surface area	3.66 m^2/g
Integrated pore volume	1.1 cm^3/g
Mean pore size	0.6 μm
Bead diameter	40–60 μm
Molecular modifier	1-Ocatnol
Copolymer inside SiO_2-P support	Macroporous SiO_2 particles modified by following inert copolymer-containing compound 
Appearance	Deep red
Affinity for water or acidic solution	Good

2.0 M and 5.0 mM. The schematic diagram of the column operation for partitioning of Pd(II) from a simulated HLW is illustrated in Figure 6.

As a 2.0 M HNO_3 solution containing Sr(II), Ba(II), Cs(I), Na(I), K(I), Pd(II), La(III), Y(III), Ru(III), and Mo(VI) was supplied to the $BDBTP/SiO_2$-P packed column, the given volumes of 2.0 M HNO_3 and 0.2 M Thiourea-0.1 M HNO_3 as eluents were subsequently pumped downflow through the adsorption column. Effluent fraction of 5 cm^3 aliquots was collected using an EYELA DC-1500 Model autofractional collector (Tokyo Rikakikai Co., Japan). The concentrations of the tested metals in effluent were analyzed by the ICP-OES or AAS as mentioned above.

Results and Discussion

Dependence of the tested elements adsorption on contact time

There are seven nitrogen atoms inside BDBTP molecule. According to the Lewis theory of acid–base reactions, bases donate pairs of electrons, whereas acids accept them. A Lewis acid is therefore any ion or molecule, such as the H^+ and metal ions, that can accept a pair of nonbonding valence electrons. In other words, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance that can donate a pair of nonbonding electrons. A Lewis base is therefore an electron-pair donor. From this point, BDBTP is considered to be an electron-pair donor, that is, a Lewis base. Because nitrogen atom is a so-called soft-atom, BDBTP acts as a soft Lewis base. Meanwhile, Pd(II) is an electron-pair acceptor, that is, a Lewis acid due to unsaturated p orbit. Based on the electronic structure of Pd(II), it is, therefore, considered to be a soft-acid. So, a stable complexation can occur when Pd^{2+} ion acting as a Lewis acid picks up the pairs of electrons from neighboring nitrogen atoms inside BDBTP molecule.

To understand the complexation of BDBTP, the adsorption of some typical fission and non-FPs Sr(II), Ba(II), Cs(I), Na(I), K(I), Pd(II), La(III), Y(III), Ru(III), and Mo(VI) onto $BDBTP/SiO_2$-P with a change in contact time was investigated in 2.0 M HNO_3 at 298 K. It was performed at phase ratio of 0.25 g/5 cm^3, metal concentration of 5.0×10^{-3} M, and shaking speed of 120 rpm. The results are shown in Figure 7.

Figure 7 shows the dependence of the adsorption of the tested metals onto the $BDBTP/SiO_2$-P polymeric composite

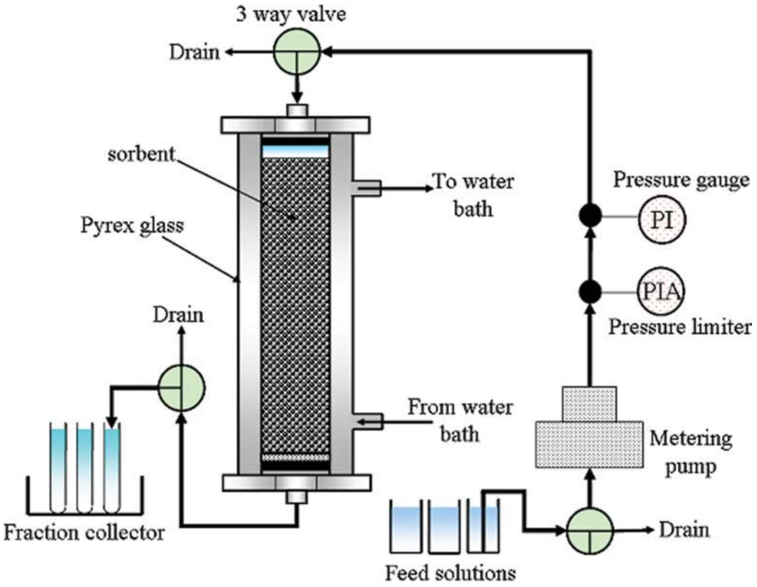


Figure 6. Schematic diagram of experimental apparatus for Pd(II) partitioning from HLW by extraction chromatography.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

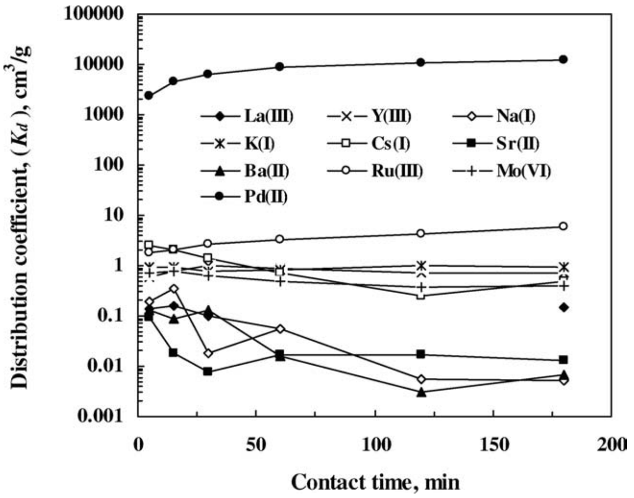


Figure 7. Dependence of the tested metals adsorption onto the BDBTP/SiO$_2$-P composite on contact time in 2.0 M HNO$_3$ at 298 K.

on contact time in 2.0 M HNO$_3$ at 298 K. With an increase in contact time, the tested Sr(II), Ba(II), Cs(I), Na(I), K(I), La(III), Y(III), Ru(III), and Mo(VI) showed weak or almost no adsorption onto the BDBTP/SiO$_2$-P polymeric composite. The distribution coefficient (K_d) at contact time of 180 min was always below 0.96 cm^3/g for the above metals Sr(II), Ba(II), Cs(I), Na(I), K(I), La(III), Y(III), and Mo(VI) with the exception of 5.74 cm^3/g for Ru(III). Such a low value in the distribution coefficient resulted from the weak complexation of these metals with nitrogen atom inside BDBTP molecule.

On the other hand, it is known that the chemical properties of all of lanthanides in aqueous solution are quite similar due to the lanthanide contraction. So, the negligible adsorption of La(III) and Y(III) predicts that in 2.0 M HNO$_3$, all of the RE(III) elements might have negligible adsorption onto BDBTP/SiO$_2$-P. According to the Lewis theory of acid–base reactions, the trivalent rare earth ions are the hard-acid substance being capable of effective recognizing and accepting a pair of nonbonding valence electrons from electron-pair donor. The lack of affinity of the soft-base nitrogen inside BDBTP molecule for the hard-acid REs(III) ions might be the main reason, that is, no complexation of REs(III) with BDBTP resulted from their unmatched acid–base properties. As a result, almost all of REs(III) contained in HLW solution might have no adverse impact on the elimination of Pd(II).

Opposite to the tested metals mentioned above, the amount of Pd(II) adsorbed onto the BDBTP/SiO$_2$-P polymeric composite quickly increased with increasing contact time and did not seem to reach the adsorption equilibrium, even though the contact time was up to 200 min. The distribution coefficient (K_d) of Pd(II) in 2.0 M HNO$_3$ was 2310.2 cm^3/g at 5 min, 6236.4 cm^3/g at 30 min, 10,705 cm^3/g at 120 min, and 11,822 cm^3/g at 180 min. This revealed that in 2.0 M HNO$_3$, Pd(II), one of the long-lived radionuclides contained in HLW, had fast adsorption kinetics onto the BDBTP/SiO$_2$-P composite. In addition, the apparent shape and character of the dynamic adsorption curve of Pd(II) agreed with that of the chemical adsorption of metal ion. So, the adsorption mechanism of Pd(II) onto the BDBTP/SiO$_2$-P composite in HNO$_3$ solution was considered to be the chemical adsorption, that is, the chemical complexation of Pd(II) with BDBTP might be the rate-controlling step.

Based on the above discussion, the difference in the adsorption of the tested metal ions exhibited that in 2.0 M HNO$_3$, the novel macroporous silica-based BDBTP/SiO$_2$-P polymeric composite had excellent adsorption ability and high selectivity for Pd(II) over all of the tested elements. The tested metals, namely, Sr(II), Ba(II), Cs(I), Na(I), K(I), La(III), Y(III), Ru(III), and Mo(VI) have no adverse impact on the adsorption of Pd(II) onto BDBTP/SiO$_2$-P. It is of great benefit to the elimination of Pd(II) from an acidic HLW using the novel BDBTP/SiO$_2$-P composite through extraction chromatography.

Dependence of the tested elements adsorption on the HNO$_3$ concentration

Based on the special molecular structure of BDBTP, nitrogen atom inside BDBTP has high affinity for hydrogen to form the stable ammonium with HNO$_3$. So, the concentration of HNO$_3$ exhibits obvious effect on the complex formation of the tested metals with BDBTP. It is known that in reprocessing of nuclear spent fuel, the HLW produced is a HNO$_3$ medium usually with concentration around 3.0 M. Thus, in the adsorption process, the complexation of Pd(II) with BDBTP and the protonation of BDBTP with HNO$_3$ are two competiting reactions.

To investigate the adsorption property of BDBTP/SiO$_2$-P, the effect of HNO$_3$ concentration in a range of 0.1–5.0 M on the adsorption of Pd(II) and the other typical elements Sr(II), Ba(II), Cs(I), Na(I), K(I), La(III), Y(III), Ru(III), and Mo(VI) onto BDBTP/SiO$_2$-P was studied. It was performed at metal concentration of 5.0×10^{-3} M, phase ratio of 25 g/ 5 cm^5, and contact time of 120 min at 298 K. The corresponding results are illustrated in Figure 8.

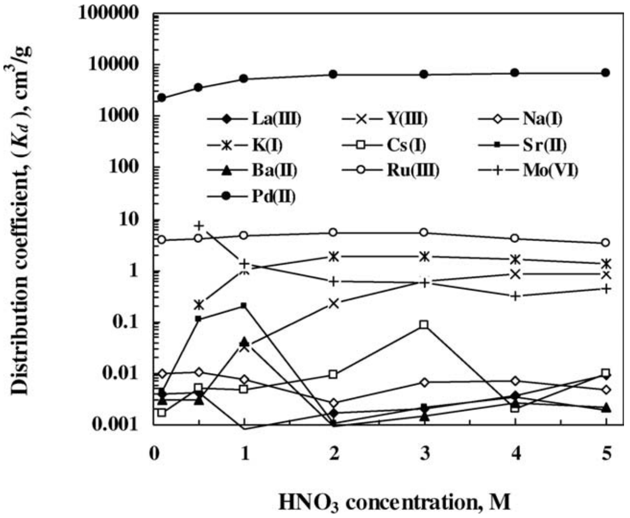


Figure 8. Dependence of the tested metals adsorption onto the BDBTP/SiO$_2$-P composite on the HNO$_3$ concentration in a range of 0.3–5.0 M at 298 K.

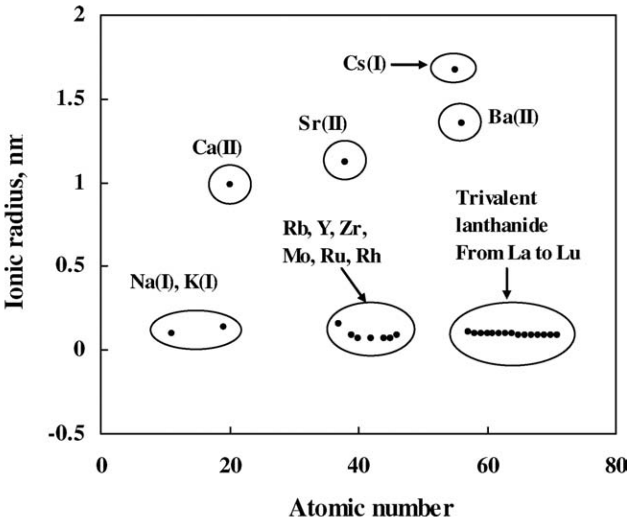


Figure 9. Distribution of elements showing no adverse impact on the adsorption of Pd(II) onto BDBTP/SiO_2-P in HNO_3 concentration range tested.

Figure 8 shows the adsorption property of the BDBTP/SiO_2-P composite for the tested fission and non-FPs in the HNO_3 concentration range of 0.1–5.0 M. As can be seen, with increasing the HNO_3 concentration, the adsorption of Pd(II) onto BDBTP/SiO_2-P increased quickly from 0.1 to 2.0 M HNO_3 and then basically kept constant. The distribution coefficient (K_d) of Pd(II) was 2228.0 cm^3/g in 0.1 M HNO_3, 5077.8 cm^3/g in 1.0 M HNO_3, 6506.0 cm^3/g in 3.0 M HNO_3, and 6668.4 cm^3/g in 5.0 M HNO_3. The other metals always showed weak or almost no adsorption and their distribution coefficients (K_d) were below 6.0 cm^3/g. BDBTP/SiO_2-P polymeric composite had high adsorption ability and excellent selectivity for Pd(II) over all of the tested elements in the tested HNO_3 concentration range. The optimum adsorption acidity of Pd(II) in the experimental conditions was therefore determined to 2.0 M HNO_3.

It was found that the change in the distribution coefficients (K_d) of La(III) and Y(III) onto the novel macroporous silica-based BDBTP/SiO_2-P polymeric composite with an increase in the HNO_3 concentration were insignificant. In other words, almost no adsorption of BDBTP/SiO_2-P for La(III) and Y(III) was demonstrated. In addition, no adsorption of Sr(II), Ba(II), Cs(I), Na(I), and K(I) onto BDBTP/SiO_2-P means that in the tested HNO_3 concentration range, the elements in the IA and IIA in the Periodic Table of Elements might be no adsorption onto BDBTP/SiO_2-P. This makes it possible that more than 26 of elements such as those metals in IA and IIA as well as Ru(III), Rh(III), Zr(IV), Mo(VI), and 16 species of REs(III) might show no adverse impact on the adsorption and separation of Pd(II) by BDBTP/SiO_2-P. The relevant distribution of elements is illustrated in Figure 9. It is of great benefit to the effective elimination of Pd(II) from the complex HLW solution.

On the other hand, Pd(II), a weak electron-pair acceptor, usually exists in HNO_3 medium in the form of $Pd(H_2O)_2(NO_3)_2$ as shown in Figure 10, whereas the chelating agent BDBTP, a weak electron-pair donor, exists in the form of ammonium nitrate, $[BDBTPH]^{\oplus}NO_3^{\ominus}$. It can be formed by the reaction of BDBTP with HNO_3 according to the following equation:

$$HNO_3 + BDBTP \rightleftharpoons [BDBTPH]^{\oplus}NO_3^{\ominus} \qquad (2)$$

It is, therefore, clear that in the adsorption of Pd(II) onto BDBTP/SiO_2-P in HNO_3 medium, the complexation of Pd(II) with BDBTP/SiO_2-P as well as the association of BDBTP/SiO_2-P with HNO_3 molecule were two competitive reactions. The quick increase of distribution coefficient (K_d) of Pd(II) in the HNO_3 concentration range of 0.1–2.0 M was ascribed to the complexation of BDBTP/SiO_2-P with Pd(II), which was dominant, whereas the protonation of BDBTP was insignificant. In excess of 2.0 M HNO_3, the association of BDBTP/SiO_2-P with HNO_3 increased. It resulted in a decrease in the available concentration of BDBTP inside BDBTP/SiO_2-P being capable of complexing Pd(II). So, the increase in the distribution coefficient (K_d) of Pd(II) in the HNO_3 concentration range of 2.0–5.0 M HNO_3 was very slow and almost constant. It indicated that in high HNO_3 concentration, the complexation of BDBTP/SiO_2-P for Pd(II) and the association of BDBTP/SiO_2-P with HNO_3 were nip and tuck.

Based on the adsorption behavior of BDBTP/SiO_2-P, if assume that the composition of the complex formation of BDBTP/SiO_2-P with Pd(II) is Pd(**NO_3**)**$_2$·2BDBTP**/SiO_2-P as shown in Figure 11, then, the adsorption mechanism of Pd(II) onto the novel BDBTP/SiO_2-P composite was proposed as follows:1. In 0.1–2.0 M HNO_3, the adsorption of Pd(II) onto BDBTP/SiO_2-P was dominant.

$$Pd^{2+} + 2NO_3 + 2BDBTP/SiO_2\text{–}P \rightleftharpoons Pd(NO_3)_2{\bullet}2BDBTP/SiO_2\text{–}P \qquad (3)$$

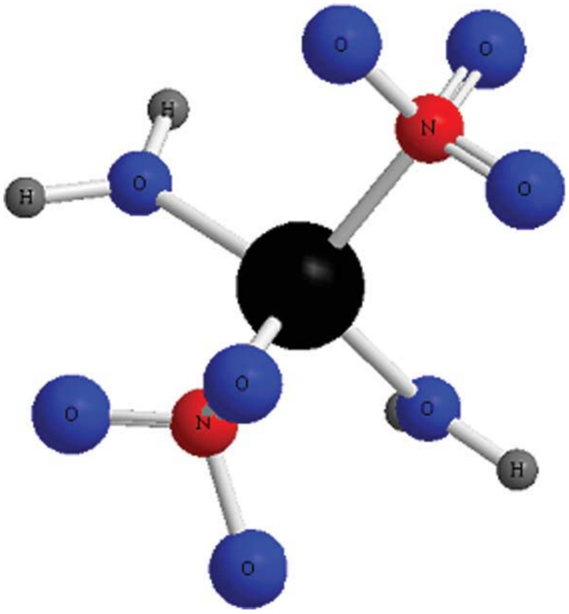


Figure 10. Structure of hydrous ion $[Pd(NO_3)_2(H_2O)_2]^{2+}$ in HNO_3 medium.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

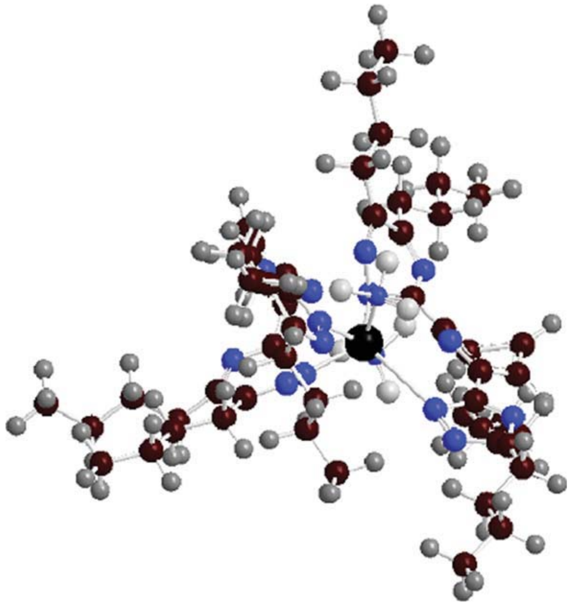


Figure 11. Structure of the complex formation of Pd(II) with BDBTP.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2 In excess of 2.0 M HNO_3, the adsorption of BDBTP/SiO_2-P for Pd(II) and HNO_3 was nip and tuck. It could be represented by the combination of Eqs. 3 and 4.

$$HHO_3 + BDBTP/SiO_2\text{-}P \rightleftharpoons [BDBTPH/SiO_2\text{-}P]^{\oplus}NO_3^{\ominus} \quad (4)$$

BDBTP is a multidentate ligand containing nitrogen atom, regarding the composition and structure of the complex formation of Pd(II) with BDBTP have not been reported. The relevant investigations are being carried out.

Chromatographic partitioning of Pd(II)

The separation of Pd(II) from a 2.0 M HNO_3 was performed using the BDBTP/SiO_2-P polymeric composite packed column at 298 K. To effectively adsorb the tested elements, the silica-based materials used were pre-equilibrated fully by 2.0 M HNO_3 before experiment. The concentrations of the tested Sr(II), Ba(II), Na(I), K(I), Pd(II), La(III), Y(III), Cs(I), Ru(III), and Mo(VI) in feed solution were $\sim 5.0 \times 10^{-3}$ M. The column dimensions selected were 10 mm in inner diameter and 300 mm in length. The flow rate was controlled to 1.0 cm^3/min. The partitioning results using 2.0 M HNO_3 and 0.2 M thiourea-0.1 M HNO_3 as eluents are illustrated in Figure 12.

As feed solution was supplied to the adsorption column, the tested elements Sr(II), Ba(II), Na(I), K(I), La(III), Y(III), Cs(I), Mo(VI), and the majority of Ru(III) showed no adsorption and quickly leaked out the column along with 2.0 M HNO_3. Such an easy elution of these elements in the column operation resulted from the weak complexation with BDBTP. Subsequently, with a successive supplement of 0.2 M thiourea-0.1 M HNO_3 to the column, Pd(II) adsorbed strongly by BDBTP/SiO_2-P was eluted and flowed into effluent along with a little of Ru(III). The elution band observed was narrow with almost no elution tailing in the elution curve, reflecting effective desorption and rapid elution kinetics of Pd(II) from the loaded BDBTP/SiO_2-P. Namely, Pd(II) could be effectively complexed with C=S functional group of thiourea molecule.[33,34] According to the Lewis theory of acid–base reactions, S atom is a soft–Lewis base, that is, a soft–electron-pair donor, which is similar to N atom. Because S is a softer base than that of N, thiourea shows stronger complexation with Pd(II) ion, a soft–Lewis acid, than that of BDBTP. Hence, the satisfactory elution of Pd(II) was ascribed to effective substitution of BDBTP in Pd(II) complex inside BDBTP/SiO_2-P with thiourea. Assuming the composition of the complex between Pd(II) and thiourea is $[Pd(NH_2CSNH_2)_4](NO_3)_2$,[35] the elution of Pd(II) with 0.2 M thiourea-0.1 M HNO_3 from the loaded BDBTP/SiO_2-P composite was proposed as follows:

$$\begin{aligned} &Pd(NO_3)_2{\cdot}2BDBTP/SiO_2\text{-} + 4NH_2CSNH_2 \rightleftharpoons \\ &\qquad [Pd(NH_2CSNH_2)_4](NO_3)_2 + 2BDBTP/SiO_2\text{-}P \end{aligned} \quad (5)$$

Y(III) is a special rare earth. It was eluted off and flowed into effluent along with La(III), 2.0 M HNO_3, and the other tested metals. It reflected that all of REs(III) showed no adsorption onto BDBTP/SiO_2-P and had no adverse impact on the elution of Pd(II).

Based on the adsorption and elution behavior of the tested metals, it is demonstrated that in 2.0 M HNO_3, application of the novel macroporous silica-based BDBTP/SiO_2-P composite in partitioning of a long-lived Pd(II) from HLW in the MAREC process is promising by extraction chromatography. It is of great benefit to avoid a long-termed adverse impact of radionuclides on the environment. The purpose of environment protection is therefore achieved.

The resistant property of the BDBTP/SiO_2-P materials against γ-irradiation in HNO_3 solution is being carried out.

Concluding Remarks

Pd-107 with a half life of 6.5×10^6 years is one of the radionuclides contained in an acidic HLW. It has long-termed

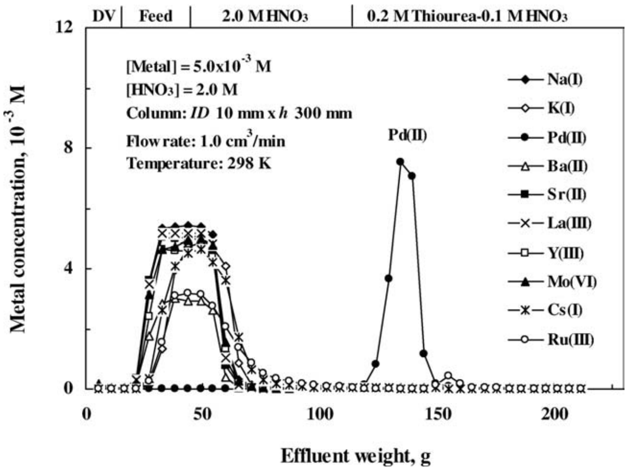


Figure 12. Chromatographic partitioning of Pd(II) from 2.0 M HNO_3 by BDBTP/SiO_2-P packed column at 298 K.

potential harmful to the environment. Effective partitioning of Pd(II) has always been one of the most challenging works. To seek a new pathway to separate Pd(II) from the Pd–Ru group in the MAREC process, a novel macroporous silica-based BDBTP impregnated functional material, BDBTP/SiO_2-P, was prepared by molecular modification of BDBTP with 1-octanol.

The adsorption behavior of some typical metals Sr(II), Ba(II), La(III), Y(III), Ru(III), Cs(I), Na(I), K(I), Pd(II), and Mo(VI) onto the BDBTP/SiO_2-P material was investigated at 298 K. The effects of contact time and the HNO_3 concentration in a range of 0.1–5.0 M were examined. It was found that the distribution coefficient of Pd(II) in the tested HNO_3 concentration range was much higher than those of the tested metals. The novel BDBTP/SiO_2-P material showed excellent adsorption ability and high selectivity for Pd(II) over all of the tested elements. The optimum HNO_3 concentration in the adsorption of Pd(II) onto BDBTP/SiO_2-P was determined to be 2.0 M. It resulted from the strong complexation of Pd(II), a weak electron-pair acceptor, with nitrogen atom, a weak electron-pair donor, inside BDBTP molecule based on the Lewis theory of acid–base reaction. Based on the batch experiments, the separation of Pd(II) from a simulated HLW solution was performed by BDBTP/SiO_2-P packed column using 2.0 M HNO_3 and 0.2 M thiourea-0.1 M HNO_3 as eluents. The tested Sr(II), Ba(II), Cs(I), Na(I), K(I), La(III), Y(III), Mo(VI), and the majority of Ru(III) showed no adsorption and broke through the column readily along with 2.0 M HNO_3. Pd(II) was effectively eluted with thiourea due to the strong complexation.

The experimental results demonstrated that the novel macroporous silica-based BDBTP/SiO_2-P is a promising material to apply in partitioning of Pd(II) from an acidic HLW in the MAREC process.

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