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Preparation of a Macroporous Silica–Pyridine Multidentate Material and Its Adsorption Behavior for Some Typical Elements

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*A new macroporous silica-based-polymer (SiO_2-P) soft ligand composite material, 2,6-bis(5,6-di(*iso*-butyl)-1,2,4-triazine-3-yl)pyridine (BDIBTP/SiO_2-P), was synthesized by impregnation and immobilization of BDIBTP and 1-octanol molecules into the pores of the SiO_2-P particles. The impact of some typical alkali metal and alkaline earths Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II) containing in highly active liquid waste (HLW) on the adsorption of Pd(II) onto BDIBTP/SiO_2-P was studied. It was performed by examining the effects of contact time and the HNO_3 concentration in the range of 0.3–7.0 M. BDIBTP/SiO_2-P showed strong adsorption ability and high selectivity for Pd(II) over all the tested metals. The chromatographic partitioning of Pd(II) from a simulated HLW solution was conducted by BDIBTP/SiO_2-P packed column. Pd(II) was effectively eluted with 0.2 M thiourea–0.1 M HNO_3. The others showed no adverse impact on separation of Pd(II). The results are beneficial to partitioning of minor actinides and Pd(II) together from HLW by BDIBTP/SiO_2-P in the MPS process developed.* © 2012 American Institute of Chemical Engineers *AIChE J,* 58: 3517–3525, 2012

Keywords: absorption, separation techniques, materials, chromatography

Introduction

The long-lived minor actinides (MAs), heat-emitting nuclides Cs and Sr, rare earths (REs), noble metals, and the others are those metals contained in highly active liquid waste (HLW).[1,2] They are important fission products (FPs) generated in reprocessing of nuclear spent fuel. It is known that many radionuclides have potential risk and long-termed harm to the vitrified HLW in final geological disposal. As a result, it is reported that it can cause a serious radiation hazard to health and environment. In these nuclides, the representative metals such as Cs, Sr, and some long-lived nuclides MAs (Am and Cm), I, and Tc are specially paid attention. To minimize the long-termed radiological risk and facilitate the management, the most of attentions are being focused on effective separation and recovery of these metals from HLW. Up to now, it has been one of the most challenging works in chemical engineering. However, no attention was paid to the partitioning and recovery of the long-lived nuclide Pd, one of the precious metals contained in HLW.

Pd locates in d-block in the periodic table of the elements. It is one of the FPs in HLW. The radioactive isotope, ^{107}Pd with a half-life of 6.5×10^6 years, is a soft β-emitter of 0.035 MeV energy. The quantity of Pd in nuclear spent fuel is reported to be approximate to 1–2 kg/ton. The portion of ^{107}Pd in the typical fission-generated Pd is about 17.5%. Because the medium of HLW produced is a HNO_3 solution, Pd exists in the form of $Pd(NO_3)_2$. It was said that the removal of Pd likely makes the vitrification of HLW easier, which is of great beneficial to safe treatment and disposal of HLW. Therefore, the effective elimination of Pd from HLW to a great extent is considerably meaningful.

One of the main separation techniques used currently in partitioning of HLW is liquid–liquid solvent extraction. Based on some highly specific chelating agents such as octyl(phenyl)-*N*,*N*-di-isobutylcarbamoylmethylphosphine oxide (CMPO) and *N*,*N*,*N*′,*N*′-tetra-octyl-3-oxapentane-1,5-diamide (TODGA), it seems to effective in partitioning of trivalent MAs(III) such as Am(III) and Cm(III) by CMPO- or TODGA-containing extraction processes.[3-7] At the same time, some disadvantages such as the formation of the third phase and generation of the large quantity of secondary wastes resulted from the hydrolytic and radiolytic degradation of organic extractants and diluents occurred. This makes it possible that as an alternative method, using the extraction chromatography in HLW partitioning is promising. Moreover, the quantity of Pd(II) in HLW is not so high.

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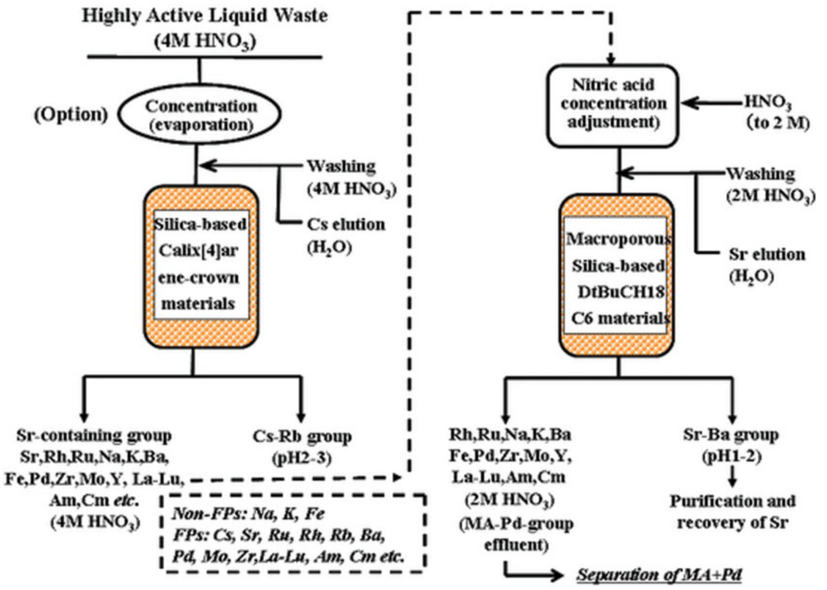

Figure 1. SPEC process for strontium/cesium partitioning from HLW by extraction chromatography using two novel macroporous silica-based supramolecular recognition materials.

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Considering the character of solvent extraction and the amount of Pd(II), if extraction chromatography with a stationary phase is used, the radionuclides would be concentrated to a minimal volume thereby facilitating their storage or disposal. Furthermore, extraction chromatography provides a simple and effective means by which the separation and/or preconcentration of a variety of radionuclides can be accomplished.[8-10] It combines the high selectivity of solvent extraction with the simplicity and multistage character of column operation system. Therefore, chromatographic separation of them from HLW is possible and feasible. Developing a new material is an effective pathway for achieving this purpose.

We have recently developed the advanced partitioning technology called SPEC (Strontium/cesium Partitioning from HLW by Extraction Chromatography) process as shown in Figure 1 to separate heat-emitting nuclides Cs(I) and Sr(II) from HLW using two novel macroporous silica-based-polymer (SiO_2-P) supramolecular recognition materials.[11] It was synthesized by impregnating and immobilizing the supramolecular recognition agent, 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) or 4,4′,(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), into the macroporous silica-based-polymer (SiO_2-P) particles support with a mean diameter of 50 μm.[12,13] Two adsorption columns packed with (Calix[4]arene-R14+M)/SiO_2-P and (DtBuCH18C6+M)/SiO_2-P were used for the separation of the elements by means of selective adsorption and elution procedures. In the first column packed with (Calix[4]arene-R14+M)/SiO_2-P, the elements was effectively separated into the following two groups: (1) Na(I), K(I), Sr(II), Ba(II), Pd(II), Zr(IV), RE(III) (La-Lu and Y), Rh(III), Ru(III), MA(III), and Mo(VI) (Sr-containing group), and (2) Cs(I)-Rb(I) (Cs-group) by eluting with 4.0 M HNO_3 and water, respectively. In the second column packed with (DtBu CH18C6+M)/SiO_2-P, the Sr-containing group was separated into the following two groups: (1) Na(I), K(I), Rh(III), Ru(III), RE(III) (La-Lu and Y), MA(III), Pd(II), Zr(IV), and Mo(VI) (MA-Pd-group), and (2) Sr(II)-Ba(II) (Sr-group) by eluting with 2.0 M HNO_3 and water, respectively. The partitioning of Cs(I) and Sr(II) from HLW by extraction chromatography was achieved.[14-16] Meanwhile, the long-lived MA(III) and Pd(II) flowed into the MA-Pd-group effluent along with all of REs(III), alkali metals, alkaline earths, and the others.

Some derivatives of monopyridine and bipyridine compounds such as 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (dialkyl-BTP) and 6,6’-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2’-bipyridine (dialkyl-BTBP) as shown in Figure 2 with more than seven N atoms are multidentate soft ligands.[17–23] They are a kind of weak Lewis base and electron-pair donor. It exhibited better extraction ability and high selectivity for trivalent Am(III) and Cm(III),[24-26] a Lewis acid and an electron-pair acceptor, while had weak or almost no extraction for trivalent RE(III). This makes the partitioning of MA(III)/

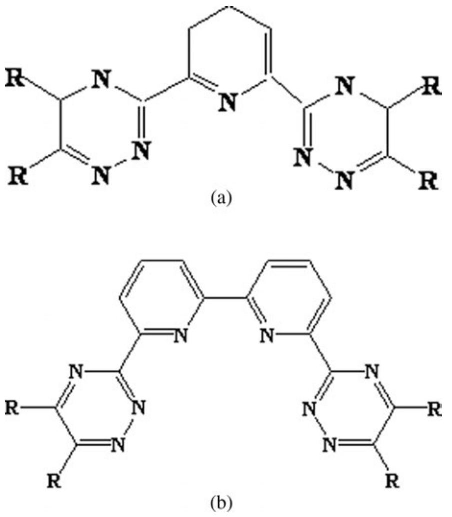

Figure 2. Molecular structures of monopyridine and bipyridine compounds.

(a) Molecular structure of 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (dialkyl-BTP) and (b) 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (dialkyl-BTBP).

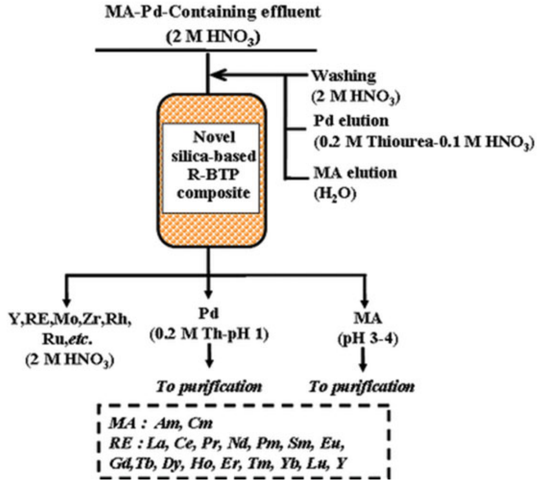

Figure 3. MPS: A concept process of MA(III) and Pd(II) Separation from HLW by extraction chromatography using the novel macroporous silica-based soft-ligand materials.

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RE(III) easier. In addition to MA(III), we recently found that the derivative of monopyridine and bipyridine compounds seemed to have an excellent complexing ability for Pd(II). It can be explained by combination of the structures of Pd(II) with pyridine according to the classical Lewis theory of acid and base reactions.

Based on the derivative of monopyridines and bipyridines and some investigations carried out, the advanced MPS (MA(III) and Pd(II) Separation by extraction chromatography) process as shown in Figure 3 has been developed in this work. It was performed by the column operation using a kind of the macroporous silica-based derivative of monopyridines or bipyridines impregnated materials, dialkyl-BTP/SiO_2-P or dialkyl-BTBP/SiO_2-P. All of REs(III) including Y(III) and from La(III) to Lu(III), some alkali metal, alkaline earths, and the other FPs flowed into effluent (noted as nonadsorption group) along with HNO_3 solution due to no adsorption. The long-lived MA(III) and Pd(II) were separated by 0.2 M thiourea–0.1 M HNO_3 and water as eluents.[27-29] However, the adsorption and elution behavior of Pd(II) with the new macroporous silica–pyridine materials have not been understood yet. Almost no attention is paid to separation of Pd(II) by dialkyl-BTP/SiO_2-P or dialkyl-BTBP/SiO_2-P. Furthermore, the effect of some typical fission and non-FPs contained in HLW on the Pd(II) adsorption has also not been reported. Finding the optimum macroporous silica–pyridine material for separation of Pd(II) is necessary.

To understand the adsorption behavior of Pd(II), a novel macroporous silica-based 2,6-bis(5,6-di(*iso*-butyl)-1,2,4-triazine-3-yl)pyridine (BDIBTP) composite material, BDIBTP/SiO_2-P, was synthesized. It was prepared by impregnation and immobilization of BDIBTP into the pores of the macroporous SiO_2-P particles. Based on the Lewis theory of acid and base reactions, the adsorption of some typical alkali metal and alkaline earths Cs(I), Na(I), K(I), Rb(I), Sr(II), Ba(II), and Pd(II) onto the BDIBTP/SiO_2-P materials was investigated. It was carried out by examination of the effects of contact time and the concentration of HNO_3 in the range of 0.3–7.0 M. The complexing property and the adsorption mechanism of Pd(II) onto BDIBTP/SiO_2-P were discussed. The chromatographic partitioning of Pd(II) from a HNO_3 solution containing some typical fission and non-FPs such as alkali metal, alkaline earths, La(III), Y(III), Mo(VI), Zr(IV), Ru(III), and Rh(III) by BDIBTP/SiO_2-P packed column was conducted. It was operated using 1.0 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 material BDIBTP/SiO_2-P in partitioning of MA(III) and Pd(II) together from HLW were evaluated.

Experimental

Reagents

Alkali metal nitrates M^INO_3 (M^I = Na, K, Cs, and Rb), alkaline earths nitrates $M^{II}(NO_3)_2$ (M^{II} = Sr and Ba), $RE(NO_3)_3\bullet 6H_2O$ (RE = La and Y), $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$, and $ZrO(NO_3)_2\bullet 2H_2O$ used were of analytical grade. Ruthenium (III) nitrosyl nitrate solution with 1.5 wt % Ru(III) was provided by the Alfa Aesar, USA. Palladium nitrate solution with 4.5 wt % Pd(II) was provided by the Tanaka Noble Metal, Japan. Both La(III) and Y(III) were used as the representatives of all rare earths REs(III) so as to understand their adsorption behavior because of lanthanide contraction, which results in their similarity in chemical properties. Bivalent Pd(II) is a weak Lewis acid and an electron-pair acceptor. It can be strongly complexed by nitrogen-containing chelating agent, a weak Lewis base and an electron-pair donor. It is attributed to the effective match of the Lewis acid–base properties between Pd(II) and soft-atom nitrogen. Therefore, Pd(II) was selected as an representative of precious metals. The concentrations of all the tested metals were around 5.0×10^{-3} M (M = mol/dm^3). The HNO_3 solutions of different concentrations used in the experiment were prepared temporarily.

A multidentate soft ligand, BDIBTP, was prepared quantitatively.[30] A synthesis technical route is shown in Figure 4. The purity of BDIBTP, a khaki yellow product, was determined to be more than 98.5% through high-performance liquid chromatography. Methanol, dichloromethane, and the other inorganic/organic reagents were of analytical grade and were used without further purification.

The macroporous SiO_2-P particles and a novel silica-based multidentate composite material, BDIBTP/SiO_2-P, were synthesized. It was conducted through impregnating and immobilizing BDIBTP and 1-octanol molecules into the pores of the macroporous SiO_2-P particles. 1-Octanol with —OH group was used to modify BDIBTP by intermolecular interaction force as shown in Figure 5. A symbol P in SiO_2-P denotes styrene–divinylbenzene copolymer, which was prepared by means of a polymerization reaction inside the macroporous SiO_2 substrate. The schematic diagram of synthesis of the BDIBTP/SiO_2-P material is shown in Figure 6.

Adsorption of the tested metals onto BDIBTP/SiO_2-P

The adsorption behavior of the tested metals onto BDIBTP/SiO_2-P was performed at 298 K, which was controlled using a TAITEC MM-10 Model thermostated water bath shaker. All of the experimental data were repeated three times under the same conditions. As a HNO_3 solution containing about 5.0 mM of Sr(II), Ba(II), Cs(I), Na(I), K(I), Rb(I), and Pd(II) as an aqueous phase and the amount of BDIBTP/SiO_2-P weighed as a solid phase were mixed into a 50 cm^3 of ground glass-stopped flask, it was then shaken mechanically at 120 rpm for a designed contact time. The

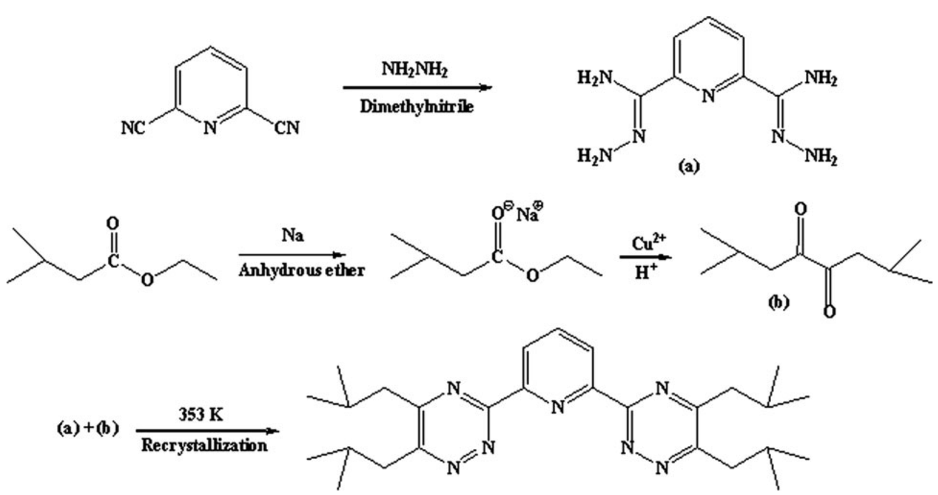

Figure 4. Technical route of synthesis of 2,6-bis(5,6-di(*iso*-butyl)-1,2,4-triazine-3-yl)pyridine (BDIBTP).

ratio of aqueous phase to solid one was 5 cm^3 to 0.25 g. The HNO_3 concentration in aqueous phase was varied in the range of 0.3–7.0 M. Following the phase separation by a membrane filter with the pores of $\sim 0.45\ \mu m$, the concentrations of the tested metals in aqueous phase were determined using a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, USA) with the exception of the contents of Cs(I), Na(I), Rb(I), and K(I) that were analyzed using a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian, USA). The distribution coefficients (K_d) of the tested elements onto the functional material BDIBTP/SiO_2-P were evaluated as follows

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

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

Chromatography partitioning of Pd(II)

The chromatographic separation of Pd(II) from a HNO_3 solution containing some typical fission and non-FPs was performed using BDIBTP/SiO_2-P packed column. Its dimension designed was 10 mm in inner diameter and 300 mm in length. It was packed under 0.25–0.35 MPa of N_2 gas pressure. Then, it was equilibrated using 2.0 M HNO_3. No significant pressure drop was found through the whole adsorption column because of the monodisperse and rigid silica-based support[0], which is usually different from the conventional polymer-based one. The operation temperature, 298 K, in the loading and elution cycles, was controlled using an EYELA NTT-1200 Model water jacket. The feed solution was composed of 5.0 mM of Sr(II), Ba(II), Cs(I), Na(I), K(I), Rb(I), and Pd(II) as well as the other typical FPs such as Mo(VI), Zr(IV), Ru(III), Rh(III), La(III), and Y(III). The flow rate in column operation process was 1.0 cm^3/min, which was controlled using a NPG-20UL Model pressure gage (Nihon Seimitsu Kagaku, Japan) and a PDB-FT 4602 Model pressure limiter (Jing-Wei Friendship (Beijing) Technical Development, China). The schematic diagram of partitioning of Pd(II) from a simulated HLW is illustrated in Figure 7.

When a 2.0 M HNO_3 solution containing the tested metals was supplied to the BDIBTP/SiO_2-P packed column, the designed 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. A total of 5 cm^3 aliquots of effluent fraction were collected one by one using an EYELA DC-1500 Model autofractional collector (Tokyo Rikakikai, Japan). The concentrations of the tested metals in effluent

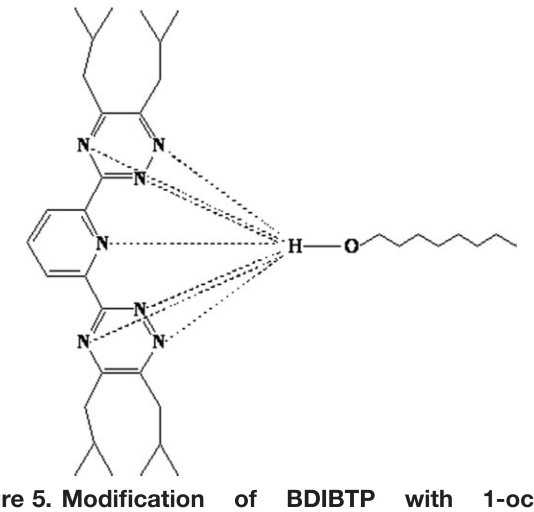

Figure 5. Modification of BDIBTP with 1-octanol through molecular interaction force.

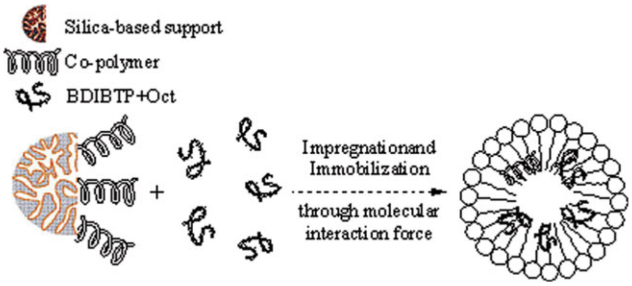

Figure 6. Synthesis schematic diagram of the novel macroporous silica-based materials BDIBTP/SiO_2-P.

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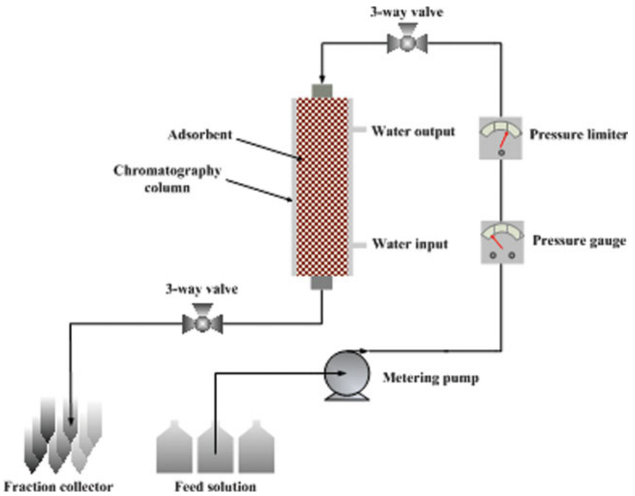

Figure 7. Experimental apparatus of the column operation separation by extraction chromatography.

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were then analyzed using the ICP-OES or AAS mentioned above.

Results and Discussion

Dependence of the tested elements adsorption on contact time

Theoretically, bivalent Pd(II) and the tested metals in IA and IIA groups may have different adsorption kinetics onto the BDIBTP/SiO_2-P materials because of the different valent electronic structures. It implies that the contact time may have obvious impact on the adsorption behavior of BDIBTP/SiO_2-P for these metals in HNO_3 solution.

To evaluate the complexation of the macroporous silica-based BDIBTP impregnated materials, the adsorption of some typical metals such as Na(I), K(I), Cs(I), Rb(I), Sr(II), Ba(II), and Pd(II) onto BDIBTP/SiO_2-P with a change in contact time in 2.0 M HNO_3 was investigated at 298 K. The relevant adsorption results are shown in Figure 8.

Figure 8 shows the dependence of the adsorption kinetics of the tested elements onto the BDI BTP/SiO_2-P functional material on contact time in 2.0 M HNO_3 at 298 K. As can be seen, with an increase in contact time, the tested alkali metals and alkaline earths had weak or almost no adsorption onto BDIBTP/SiO_2-P. The distribution coefficients (K_d) of Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II) at contact time of 240 min were always below 1.8 cm^3/g, which resulted from the weak complexation of these metals with nitrogen atom inside BDIBTP molecule. It showed that in 2.0 M HNO_3 solution, the adsorption of all of alkali metals and alkaline earths onto BDIBTP/SiO_2-P might be negligible. As a result, almost all of metals in IA and IIA groups contained in HLW might have no adverse impact on the adsorption of BDIBTP/SiO_2-P.

Contrast with the tested metals mentioned above, it was found that the adsorption of Pd(II) onto the BDIBTP/SiO_2-P materials was strong. The adsorption curve of Pd(II) increased quickly with increasing contact time and basically reached the adsorption equilibrium at 180 min. The distribution coefficient (K_d) of Pd(II) in 2.0 M HNO_3 was 54.78 cm^3/g at 5 min, 101.3 cm^3/g at 30 min, 837.0 cm^3/g at 120 min, 1582 cm^3/g at 180 min, and 1600 cm^3/g at 240 min. It reflected that in 2.0 M HNO_3, Pd(II) had fast adsorption kinetics onto BDIBTP/SiO_2-P material. In addition, the apparent shape and character of the dynamic adsorption curve of Pd(II) were similar to that of the typical chemical adsorption of metal ions.[31,32] The adsorption mechanism of Pd(II) onto BDIBTP/SiO_2-P in HNO_3 solution was considered to be the chemical adsorption, i.e., the chemical complexation of Pd(II) with BDIBTP might be the rate-controlling step. Therefore, the strong adsorption of Pd(II) onto the BDIBTP/SiO_2-P materials was attributed to the effective complexation of Pd(II) with nitrogen inside BDIBTP.

The different adsorption behavior of BDIBTP/SiO_2-P for metals was related to their Lewis acid–base properties. In terms of the classical Lewis theory of acid–base reactions, the multinitrogen BDIBTP is an electron-pair donor, a Lewis base. Because nitrogen atom is a so-called soft atom, BDIBTP acts as a soft Lewis base. Meanwhile, the selected metal either Cs(I), Na(I), K(I), Rb(I), Sr(II), Ba(II), or Pd(II) is an electron-pair acceptor, a Lewis acid, due to unsaturated s- or p-orbit. Based on the difference of the valent electronic structures of the tested elements, the softness and hardness of the Lewis acid of these metals are, therefore, different. It is considered to be the soft Lewis acid for Pd(II) and the hard Lewis acid for Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II). As a result, a stable complexation probably occurs when Pd(II) acting as a soft Lewis acid picks up the pairs of electrons from neighboring soft-atom nitrogen in BDIBTP, whereas an extremely unstable complexation might take place between the soft-Lewis base BDIBTP and hard-Lewis acid Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II). Therefore, almost no complexation of the tested metals in IA and IIA groups with BDIBTP/SiO_2-P resulted from the unmatched Lewis acid–base properties of them. Namely, only Pd(II) could be effectively complexed with BDIBTP/SiO_2-P and formed to the stable complex, which made the chemical adsorption of Pd(II) stronger.

According to the discussion above, the difference in the adsorption of the tested metal ions exhibited that in 2.0 M HNO_3, BDIBTP/SiO_2-P showed excellent adsorption ability and high selectivity for Pd(II) over all of the tested elements.

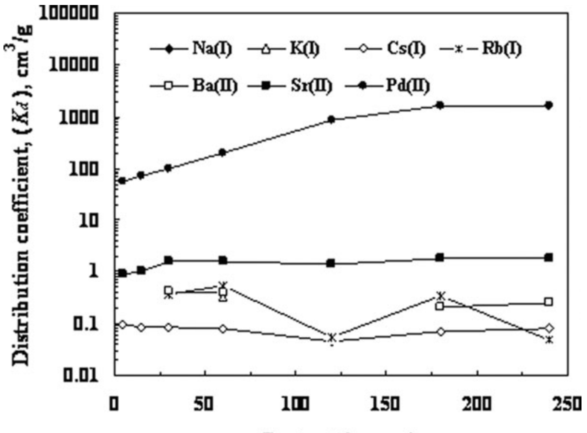

Figure 8. Dependence of the tested metals adsorption onto BDIBTP/SiO_2-P on contact time in 2.0 M HNO_3 at 298 K.

[Metal]: 5 mM, phase ratio: 0.25 g/5 cm^3, and shaking speed: 120 rpm.

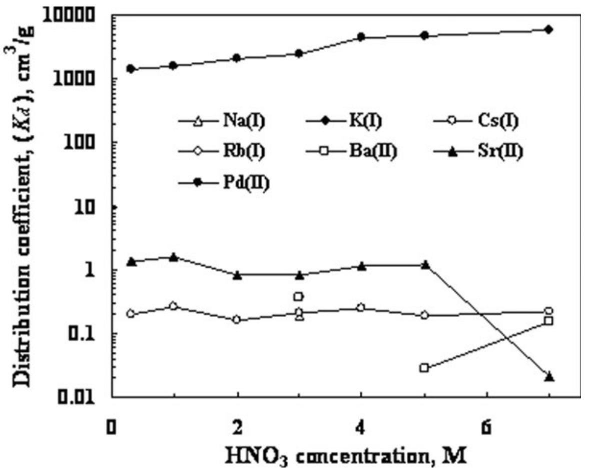

Figure 9. Dependence of the tested metals adsorption onto BDIBTP/SiO_2-P on the HNO_3 concentration in the range of 0.3–7.0 M at 298 K.

[Metal]: 5 mM, phase ratio: 0.25 g/5 cm^3, shaking speed: 120 rpm, and contact time: 240 min.

Dependence of the tested elements adsorption on the HNO_3 concentration

Nitrogen in the BDIBTP molecular has high affinity for hydrogen ion by forming the stable ammonium salt through the acid–base neutralization reactions. It is known that in reprocessing of nuclear spent fuel, the HLW generated in Purex or its modified process is a HNO_3 medium around 3.0 M. The concentration of HNO_3 probably has effect on the chemical complexation of the tested metals with BDIBTP in BDIBTP/SiO_2-P. This makes it possible that in the adsorption process, the complexation of the tested metals with BDIBTP/SiO_2-P and the protonation of BDIBTP/SiO_2-P with HNO_3 are two competitive reactions.

To understand the adsorption of BDIBTP/SiO_2-P, the effect of the concentration of HNO_3 in the range of 0.3–7.0 M on the adsorption of the tested metals Cs(I), Na(I), K(I), Rb(I), Sr(II), Ba(II), and Pd(II) onto the BDIBTP/SiO_2-P materials was investigated at 298 K. The relevant results are shown in Figure 9.

Figure 9 shows the chemical adsorption of BDIBTP/SiO_2-P for the tested fission and non-FPs with a change in the HNO_3 concentration. It is clear that with increasing the concentration of HNO_3, the adsorption of Pd(II) onto BDIBTP/SiO_2-P increased from 0.3 M HNO_3 to 4.0 M HNO_3 and then slowly increased to 7.0 M HNO_3. The distribution coefficient (K_d) of Pd(II) was always more than 1.374×10^3 cm^3/g, whereas the others showed weak or almost no adsorption and their distribution coefficients (K_d) were below 1.625 cm^3/g. Such a great difference in the distribution coefficient (K_d) reflected that in the tested concentration range of HNO_3, the novel silica-based materials BDIBTP/SiO_2-P had very strong adsorption ability and excellent selectivity for Pd(II) over all of the tested elements. Considering some advantages in experimental operation at low HNO_3 concentration, the possible adsorption acidity of Pd(II) onto BDIBTP/SiO_2-P was determined to be in the range of 0.3–2.0 M HNO_3.

In comparison with Pd(II), the change in the distribution coefficients (K_d) of Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II) onto BDIBTP/SiO_2-P with an increase in the HNO_3 concentration was insignificant. It means that in the tested HNO_3 concentration solution, the elements in IA and IIA groups in the periodic table of elements had almost no adsorption onto BDIBTP/SiO_2-P. Combination of strong extraction of BDIBTP for MA(III) with almost no extraction for RE(III), 16 species of REs(III) including Y(III) and from La(III) to Lu(III) might have no adverse impact on the adsorption of Pd(II) and MA(III) onto BDIBTP/SiO_2-P. It is beneficial to separation of Pd(II) and MA(III) together from HLW.

On the other hand, bivalent Pd(II) usually exists in the form of hydrous $Pd(H_2O)_2(NO_3)_2$ in HNO_3 medium, whereas the multinitrogen compound BDIBTP exists in the form of ammonium nitrate, $[BDIBTPH]^{\oplus}NO_3^{\ominus}$. It was formed through the protonation of BDIBTP with HNO_3 by means of the following equation

$$HNO_3 + BDIBTP \rightleftharpoons [BDIBTPH]^{\oplus}NO_3^{\ominus} \tag{2}$$

Similarly, the multidentate material BDIBTP/SiO_2-P was also capable of being protonated and formed to $[BDIBTPH/SiO_2\text{-}P]^{\oplus}NO_3^{\ominus}$.

It is clear that in theoretical, the chemical adsorption of Pd(II) onto BDIBTP/SiO_2-P as well as the association of BDIBTP/SiO_2-P with HNO_3 should be two competitive reactions. However, it was found that in Figure 9, the adsorption of BDIBTP/SiO_2-P for Pd(II) always increased with increasing the HNO_3 concentration, whereas the decrease in the distribution coefficient (K_d) of Pd(II) at high HNO_3 concentration did not seem to appear. It indicated that in the whole HNO_3 concentration range tested, the chemical adsorption of Pd(II) onto the BDIBTP/SiO_2-P materials was dominant. The increase in the distribution coefficient (K_d) of Pd(II) in the concentration range of 0.3–7.0 M HNO_3 was attributed to effective complexation of BDIBTP inside BDIBTP/SiO_2-P with Pd(II).

To further know the adsorption mechanism, the effect of the concentration of HNO_3 in the range of 7.0–11.0M on the adsorption of Pd(II) onto BDIBTP/SiO_2-P was studied at the same experimental conditions. It was found that in excess of 9.0 M HNO_3, the adsorption of Pd(II) onto BDIBTP/SiO_2-P decreased, reflecting that the protonation of BDIBTP/SiO_2-P with HNO_3 was dominant. It resulted in a decrease in the available concentration of BDIBTP inside BDIBTP/SiO_2-P being capable of complexing Pd(II).

Based on the adsorption behavior of BDIBTP/SiO_2-P, if the composition of the complex formation of BDIBTP/SiO_2-P and Pd(II) is assumed to be $[Pd(BDIBTP/SiO_2\text{-}P)_2](NO_3)_2$,[33] then the adsorption mechanism of Pd(II) onto the novel materials BDIBTP/SiO_2-P was proposed as follows:

1. In the HNO_3 concentration range of 0.3–9.0 M, the adsorption of Pd(II) onto the BDIBTP/SiO_2-P materials was dominant. The adsorption equation was described as follows

$$Pd^{2+} + 2NO_3^- + 2BDIBTP/SiO_2\text{-}P \rightleftharpoons [Pd(BDIBTP/SiO_2\text{-}P)_2](NO_3)_2 \tag{3}$$

2. In excess of 9.0 M HNO_3, the protonation of BDIBTP/SiO_2-P with HNO_3 was dominant. It could be represented by Eq. 4.

$$HNO_3 + BDIBTP/SiO_2\text{-}P \rightleftharpoons [BDIBTPH/SiO_2\text{-}P]^{\oplus}NO_3^{\ominus} \tag{4}$$

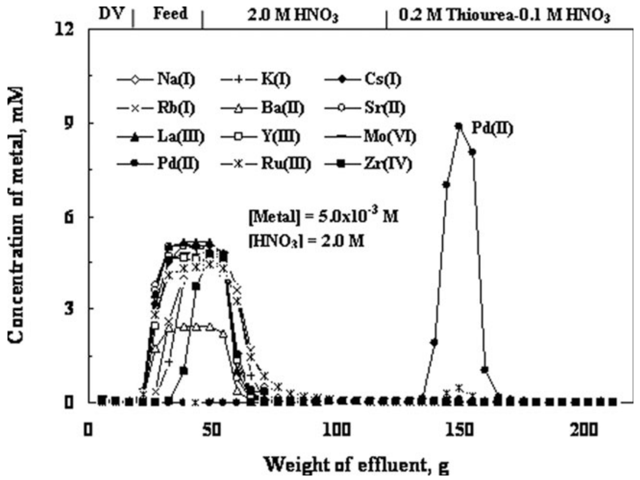

Figure 10. Chromatographic partitioning of Pd(II) from 2.0 M HNO_3 by BDIBTP/SiO_2-P packed column at 298 K.

Column: ID 10 mm × *h* 300 mm and flow rate: 1.0 cm^3/min.

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

Chromatographic partitioning of Pd(II)

The separation of Pd(II) from a simulated HLW solution of 2.0 M HNO_3 was performed using the BDIBTP/SiO_2-P materials packed column at 298 K. Before the column operation BDIBTP/SiO_2-P was pre-equilibrated by 2.0 M HNO_3. The concentrations of the tested metals in feed solution were about 5.0×10^{-3} M. The flow rate in the loading and elution cycles was controlled to 1.0 cm^3/min using the pressure gage and pressure limiter. After the sample was collected, the mass balance of the tested metals in the separation operation was calculated. 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 10.

In the previous studies,[27] the adsorption behavior of some typical FPs such as La(III), Y(III), Zr(IV), Mo(VI), Ru(III), Pd(II), and Rh(III) onto BDIBTP/SiO_2-P was examined. La(III) and Y(III) were used as the representatives of all of rare earths REs(III) because of the lanthanide contraction, which results in their similarity in chemical properties. It was found that in the tested HNO_3 concentration range of 0.3–7.0 M, the tested metals showed weak or almost no adsorption toward BDIBTP/SiO_2-P. Namely, La(III), Y(III), Zr(IV), Mo(VI), Ru(III), and Rh(III) might have no adverse impact on the separation of Pd(II).

Combining the current and previous experimental results, it is clear that almost more than 26 elements such as those metals in IA and IIA in the periodic table of the elements as well as Ru(III), Rh(III), Zr(IV), Mo(VI), and 16 species of REs(III) including Y(III) and from La(III) to Lu(III) likely show no adverse impact on the adsorption and separation of Pd(II) by the novel materials BDIBTP/SiO_2-P. It is of great beneficial to the effective elimination of Pd(II) from a complicated HLW solution.

To confirm the results mentioned above, a 2.0 M HNO_3 solution containing 13 elements such as Cs(I), Na(I), K(I), Rb(I), Sr(II), Ba(II), Pd(II), La(III), Y(III), Ru(III), Rh(III), Zr(IV), and Mo(VI) was used as feed solution. La(III) and Y(III) were used as the representatives of all rare earths REs(III) to understand their adsorption behavior because of lanthanide contraction.

As can be seen, with the supplement of feed solution to the adsorption column, 12 species of the tested elements Cs(I), Na(I), K(I), Rb(I), Sr(II), Ba(II), La(III), Y(III), Zr(IV), Mo(VI), Rh(III), and the majority of Ru(III) showed no adsorption onto BDIBTP/SiO_2-P and quickly leaked out the column along with 2.0 M HNO_3. No adsorption behavior of these tested metals in the column separation operation was similar to those of in the batch experiments. It ascribed to the weak complexation of BDIBTP, a soft Lewis base, with these metals. Meanwhile, Pd(II) was strongly adsorbed onto BDIBTP/SiO_2-P and did not appear in effluent.

In terms of no adsorption behavior of La(III) and Y(III), it is predicted that in 2.0 HNO_3 solution, 16 species of trivalent REs(III) such as Y(III) and from La(III) to Lu(III) contained in HLW have no adsorption ability onto BDIBTP/SiO_2-P and can flow into effluent along with La(III), Y(III), and 2.0 M HNO_3. The conclusion of REs(III) showing no adverse impact on the separation of Pd(II) by BDIBTP/SiO_2-P packed column was verified.

Then, with a successive supplement of 0.2 M thiourea–0.1 M HNO_3 to the column, Pd(II) was efficiently eluted and flowed into effluent along with a little of Ru(III). The elution band appeared in elution curve of Pd(II) was narrow, sharp, and showed short elution tailing, which meant that Pd(II) was desorbed completely from the loaded BDIBTP/SiO_2-P materials. Such an excellent elution of Pd(II) in column operation reflected that the macroporous silica-based molecular recognition material had fast elution kinetics for Pd(II). It was considered to be the quick decomposition of the complex of Pd(II) and BDIBTP/SiO_2-P with a rapid decrease in the NO_3^- concentration in the resin bed. Namely, Pd(II) could be effectively complexed with C=S functional group in thiourea molecule.[34,35] According to the Lewis theory of acid–base reactions, S atom in C=S group is a soft-Lewis base, i.e., a soft-electron-pair donor, which is similar to N atom in BDIBTP. Because the base property of S is more softer than that of N, thiourea shows more stronger complexation with Pd(II) than that of BDIBTP. Therefore, the satisfactory elution of Pd(II) was attributed to the effective substitution of the complex of Pd(II) with thiourea for the complex of Pd(II) with BDIBTP inside BDIBTP/SiO_2-P. The corresponding adsorption and elution mechanism of Pd(II) in the loading and elution cycles is shown in Figure 11. The elution of Pd(II) with 0.2 M thiourea–0.1 M HNO_3 from the loaded BDIBTP/SiO_2-P composite materials was proposed as follows

$$\begin{aligned} \mathrm{Pd(NO_3)_2 \bullet 2BDIBTP/SiO_2\text{-}P + 4NH_2CSNH_2} \rightleftharpoons \\ \mathrm{[Pd(NH_2CSNH_2)_4](NO_3)_2 + 2BDIBTP/SiO_2\text{-}P} \end{aligned} \qquad (5)$$

According to the mass balance, the recovery percent of the tested metals was calculated to be 98.2% for Pd(II) and in the range of 98.6–102.3% for the others. A satisfactory partitioning and recovery of Pd(II) from the tested metals were achieved.

Based on the results of the column operation, it was found that in 2.0 M HNO_3, almost 26 of the typical fission and non-FPs had no adsorption onto BDIBTP/SiO_2-P with an exception of a little of Ru(III). The relationship between

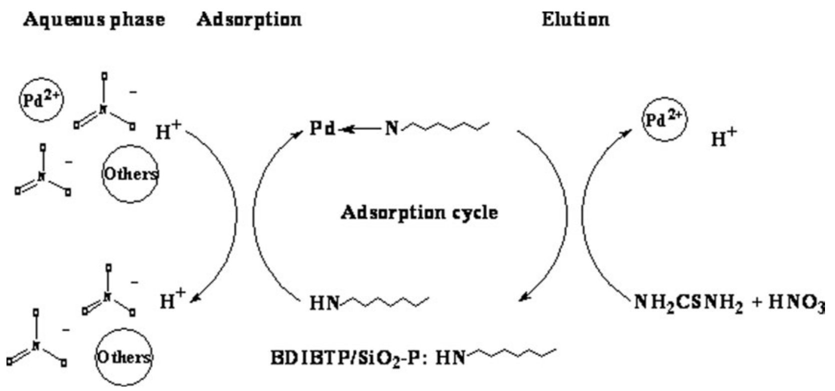

Figure 11. Adsorption and elution mechanism of Pd(II) in chromatographic partitioning.

ionic radius, atomic number, and the distribution coefficients (K_d) of 26 elements in 2.0 M HNO_3 in three dimensions is presented in Figure 12. This reveals that in HNO_3 medium, application of the BDIBTP/SiO_2-P materials in effective partitioning of Pd(II), a long-lived nuclide, from HLW by extraction chromatography is promising. Considering the chemical complexation of BDIBTP with MAs(III) such as Am(III) and Cm(III), it is feasible to simultaneously separate the long-lived MA(III) and Pd(II) from HLW by the MPS process developed.

The resistant behavior of the BDIBTP/SiO_2-P materials against HNO_3 was studied at 298 K. The preliminary results showed that in the temperature range of 288–303 K, BDIHTP/SiO_2-P had better resistance in 1.0 M HNO_3. The relevant investigations are being carried out.

Concluding Remarks

In separation of Cs(I) and Sr(II) from HLW in the SPEC process developed, the long-lived MA(III) and Pd(II) showed no adsorption onto (Calix[4]arene-R14+M)/SiO_2-P and flowed into MA-Pd-group effluent along with all of REs(III), alkali metals, alkaline earths, and the others. To partition MA(III) and Pd(II) together, a macroporous silica-based BDIBTP impregnated molecular recognition material, BDIBTP/SiO_2-P, was prepared.

The effect of some typical alkali metal and alkaline earths Cs(I), Na(I), K(I), Rb(I), Sr(II), and Ba(II) on the Pd(II) adsorption onto the BDIBTP/SiO_2-P material was investigated. It was evaluated by examining the effects of contact time and the HNO_3 concentration in a range of 0.3–7.0 M. BDIBTP/SiO_2-P showed excellent adsorption ability and high selectivity for Pd(II) over all the tested elements. The optimum HNO_3 concentration in the adsorption of Pd(II) was determined to be in the range of 0.3–2.0 M. Considering the adsorption of La(III), Y(III), Ru(III), Zr(IV), and Mo(VI) onto BDIBTP/SiO_2-P conducted previously, the chromatographic separation of Pd(II) from 2.0 M HNO_3 was performed using BDIBTP/SiO_2-P packed column. More than 26 of fission and non-FPs such as alkali metal, alkaline earths, 16 species of REs(III), Ru(III), Zr(IV), and Mo(VI) showed no adverse impact on the Pd(II) adsorption onto BDIBTP/SiO_2-P. Pd(II) was effectively eluted with 0.2 M thiourea–0.1 M HNO_3. The adsorption and partitioning of Pd(II) under BDIBTP/SiO_2-P as an adsorbent were understood.

Considering the complexing ability of MA(III) with BDIBTP, the results demonstrated that the macroporous silica-based material BDIBTP/SiO_2-P is promising to apply in partitioning of MA(III) and Pd(II) together in the MPS process.

Acknowledgments

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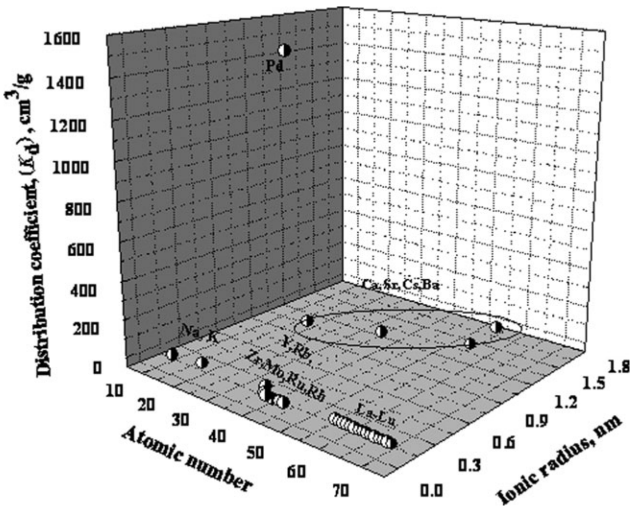

Figure 12. Relationship between ionic radius, atomic number, and the distribution coefficients (K_d) of 26 elements in three dimensions.

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