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Synthesis of a Novel Silica-Based Macroporous Polymer Containing TODGA Chelating Agent and Its Application in the Chromatographic Separation of Mo(VI) and Zr(IV) from Diethylenetriaminepentaacetic Acid

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Abstract: A novel silica-based N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) chelating polymeric material (TODGA/SiO_2-P) was synthesized by impregnating TODGA into ~50 μm of spherical SiO_2-P particles for separating Mo(VI) and Zr(IV) from a HNO_3 solution containing 0.05 M diethylenetriaminepentacetic acid (DTPA) in minor actinides recovery by extraction chromatography (MAREC) process. The adsorption of TODGA/SiO_2-P for Mo(VI) and Zr(IV) was investigated by examining the influence of HNO_3 and DTPA concentrations. It was found that HNO_3 concentration from 0.3 M to 9 M either with or without 0.05 M DTPA had a strong effect on the adsorption of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P. In the absence of 0.05 M DTPA, both the adsorption of Mo(VI) and Zr(IV) decreased with an increase in the concentration of HNO_3 from 0.3 M to 3 M and then gradually increased. In the presence of 0.05 M DTPA, Zr(IV) showed scarcely any adsorption towards TODGA/SiO_2-P below 2 M HNO_3 and was gradually adsorbed from 2 M to 3 M HNO_3 while Mo(VI) showed almost no

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adsorption. In excess of 3 M HNO_3, the adsorption curve of Mo(VI) or Zr(IV) fully overlapped with that of the absence of 0.05 M DTPA. This resulted from the dissociation of Mo(VI) or Zr(IV) from its complex with DTPA because of full protonation of DTPA in high HNO_3 concentration and the strong complexation taking place simultaneously with TODGA/SiO_2-P. In terms of the batch experiments, the separation of Mo(VI) and Zr(IV) from a 3 M HNO_3 solution containing 0.05 M DTPA was performed by employing the TODGA/SiO_2-P packed column at 50°C. Molybdenum(VI) was found to leak out of the column along with 3 M HNO_3. Zirconium(IV) adsorbed by TODGA/SiO_2-P was effectively eluted by 0.5 M $H_2C_2O_4$. The recovery was 101.6% for Mo(VI) and 94.8% for Zr(IV).

Keywords: N,N,N′,N′-Tetraoctyl-3-oxapentane-1,5-diamide, macroporous silica-based polymeric composite, adsorption, chromatographic separation, MAREC process

INTRODUCTION

It is well known that a variety of extraction processes such as TRUEX, UNEX, SETFICS, TRPO, TODGA, UNEX and others using various organic chelating agents such as octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), and 2,6-bis(5,6-dialkyl-1,2,4,-triazine-3-yl)pyridine (R-BTP), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) etc., are quite effective for the separation of long-lived radioisotopes from high level liquid waste (HLLW) in the reprocessing process (1–4). However, the investigations carried out currently focused mainly on the separation of actinides and lanthanides by liquid-liquid solvent extraction (5–7). Sufficient attention on the separation of fission products (FPs) such as Mo and Zr contained in acidic HLLW by extraction chromatographic resin is lacking.

A new partitioning process named MAREC (Minor Actinides Recovery from HLLW by Extraction Chromatography) process using a more novel silica-based CMPO extraction resin (CMPO/SiO_2-P) has been proposed and developed recently by the title authors for separating Am(III) and Cm(III) from a 3 M HNO_3 solution (8, 9). These studies are carried out based on a separation flow sheet as illustrated in Fig. 1. Two columns packed with CMPO/SiO_2-P extraction resin are utilized for the chromatographic separation of the elements through selective adsorption and elution procedures. In the first column, the elements can be effectively separated into the following three groups depending on their different adsorption and elution behavior which result from the complexation ability of the metal ions with CMPO and diethylenetriaminepentaacetic acid (DTPA): 1) nonadsorptive FP elements such as Cs, Sr, Rh, and Ru; 2) minor actinides (MA), heavy rare earths (*h*RE) (Eu-Lu and Y), Zr, Mo, and Pd; and 3) light rare earths (*l*RE). The MA-containing effluent is applied to the second column where the elements are separated to 1) Pd, 2) MA-*h*RE, and 3) Zr-Mo, respectively, by using H_2O and 0.05 M

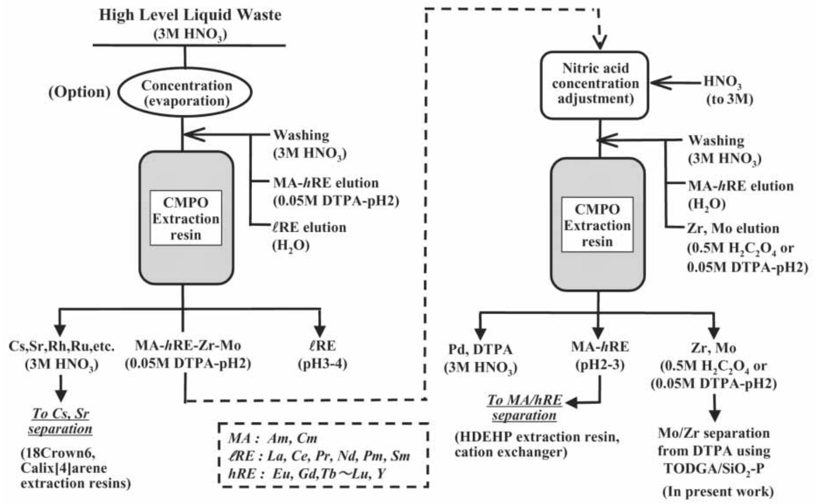

Figure 1. Flowsheet of MAREC process for the partitioning of minor actinides from an acidic HLLW by extraction chromatography.

DTPA-pH 2.0 or 0.5 M $H_2C_2O_4$ as eluents (10, 11). In terms of this process, the preliminary investigations such as the elimination of Sr(II) by a silica-based 4,4′,(5′)-di(tert-butylcyclohexano)-18-crown-6 (DtBuCH18C6) polymeric composite and the resistance properties of some adsorbents mainly used in MAREC process against HNO_3, heat, and γ-irradiation were performed (12–16). Moreover, the resultant Zr-Mo solution containing 0.05 M DTPA or 0.5 M $H_2C_2O_4$ provides a possibility for the separation of Mo(VI) and Zr(IV) from each other.

Molybdenum (Mo) is one of the main fission products and shears about 0.6–0.7 wt% of the total quantity of FPs produced in the reprocessing process of nuclear spent fuel from the fast breed reactor (FBR). It is reported that Mo hampers the vitrification of HLLW in final disposal process because of low solubility of Mo oxides in molten glass materials. Moreover, most of the Mo produced in the reprocessing process is the stable isotope, except Mo-99, which has a short half-life of 2.75 days. From the viewpoint of reduction significant of the quantity of high radioactive liquid and solid waste and geologic disposal of HLLW, the removal of Mo from HLLW is quite necessary in technique. On the other hand, in the MAREC process we developed, requires the elimination of Mo from Zr solution containing 0.05 M DTPA or 0.5 M $H_2C_2O_4$ to a great extent.

N,N,N′,N′-Tetraoctyl-3-oxapentane-1,5-diamide (TODGA) is a hard-donor complexant containing O-atom. It could effectively separate actinides(III) and lanthanides(III) from HLLW based on the different coordination ability of TODGA and these metals (17–21). Consideration of a difference in affinity of the O atom contained in the TODGA molecule with Mo(VI) and Zr(IV), may make the separation of Mo(VI) and Zr(IV) feasible. To verify this hypothesis and separate Mo(VI) and Zr(IV) from their mixture obtained in the second column in the MAREC process, we have developed and synthesized a novel silica-based macroporous TODGA extraction resin (TODGA/SiO_2-P) by impregnating TODGA into the pores of polymeric SiO_2-P particles. In present works, the adsorption properties of this new extraction resin for Mo(VI) and Zr(IV) were investigated in a wide HNO_3 concentration range of 0.3–9 M with and without containing 0.05 M DTPA. On the basis of the batch experiments, the separation of Mo(VI) and Zr(IV) from a 3 M HNO_3 solution containing 0.05 M DTPA was performed by the TODGA/SiO_2-P resin packed column.

EXPERIMENTAL

Materials

The $ZrO(NO_3)_2 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were of analytical grade. The concentrations of Mo(VI) and Zr(IV) used were 5.01×10^{-3} M and 3.36×10^{-3} M in batch experiments as well as 7.57×10^{-3} M and 5.12×10^{-3} M in column experiments, respectively. A hard-donor chelating agent N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), with a purity greater than 99%, was an available commercial product and was purchased from the Kanto Chemical Co. Inc., Japan. Diethylenetriaminepentaacetic acid (DTPA) employed as a chelating eluent was purchased from Tokyo Kasei Kogyo Co. Ltd., Japan, and its purity was greater than 98%. To avoid a precipitate of Zr(IV), HNO_3 concentration in each sample used was above 0.3 M. The various solutions of Mo(VI) and Zr(IV) with a given HNO_3 concentration, 0.01–0.45 M DTPA, 0.5 M $H_2C_2O_4$, and Mo(VI)-Zr(IV)-3 M HNO_3-0.05 M DTPA feed solution were prepared temporarily.

The silica-based TODGA extraction resin (TODGA/SiO_2-P) used was synthesized in our laboratory utilizing an advanced impregnation technique developed recently, i.e., by impregnating TODGA molecule into the pores of SiO_2-P particles, which was prepared in advance by an immobilization reaction of inert copolymer inside macroporous SiO_2. The immobilization procedure was caused by a polymerization reaction between the SiO_2 particles and some selected organic monomers, initiators, and solvent such as m/p-divinylbenzene, α,α-azobisisobutyronitrile, 1,1-azobiscyclohexane-1-carbonitrile, m/p-formylstyrene, methylbenzoate, and diotylphthatate as described previously (12, 22). The P contained in the SiO_2-P particles refers to the resultant inert styrene-divinylbenzene copolymer.

Oxalic acid, methanol, dichloromethane, and other reagents used in the experiments were of analytical grade and were used without further purification.

Synthesis of Silica-Based TODGA/SiO_2-P

Prior to synthesis of TODGA/SiO_2-P the macroporous SiO_2-P particles used were washed fully by methanol three times at room temperature. A 10 g amount of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide dissolved in 200 mL of dichloromethane and 20 g of SiO_2-P particles were mixed into a 500 mL flask and stirred mechanistically for 90 min at room temperature. Subsequently, the mixture was moved into a silicon-oil bath controlled by an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co. Ltd., Japan) and stirred further for about 180 min at around 50°C to impregnate and immobilize N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide molecule into the pores of SiO_2-P particles. After drying in a vacuum drying oven at 50°C for 24 h, the polymeric adsorption material TODGA/SiO_2-P was obtained. It was characterized using a TGA-50 Model thermogravimetric analyzer (Shimadzu, Japan), a DSC-50 Model differential scanning calorimeter (Shimadzu, Japan), and a FlashEA-1112 CHNS-O Model elementary analyzer (Thermofinnigan, Italy), respectively. The composition (wt%) of resulting TODGA/SiO_2-P polymeric composite was determined as 33.3 wt% TODGA, 11.4 wt% organic copolymer, and 55.3 wt% SiO_2-substrate, respectively. The schematic diagram of synthesizing TODGA/SiO_2-P polymeric adsorbent was illustrated in Fig. 2.

Adsorption of Mo(VI) and Zr(IV) Towards TODGA/SiO_2-P

All of the batch experiments were performed at the phase ratio of 0.25 g/5 mL and shaking speed of 120 rpm. A weighed amount of dry TODGA/SiO_2-P extraction resin as a solid phase was mixed with 5 mL of HNO_3 solution containing 5.01×10^{-3} M Mo(VI) and 3.36×10^{-3} M Zr(IV) in the absence or presence of DTPA as a solid phase into a 50 mL ground glass-stopped flask and shaken mechanically using a MM-10 Model thermostated water bath shaker (TAITEC, Japan) for 180 min. The concentrations of HNO_3 and DTPA were from 0.3 M to 9 M and from 0.01 M to 0.45 M, respectively. The shaking speed was 120 rpm. After the phase separation, the concentrations of Mo(VI) and Zr(IV) in aqueous phase were determined with an SPS 5000 Model ICP-AES (Atomic Emission Spectrometer, Seiko, Japan). The distribution coefficients (K_d) of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P

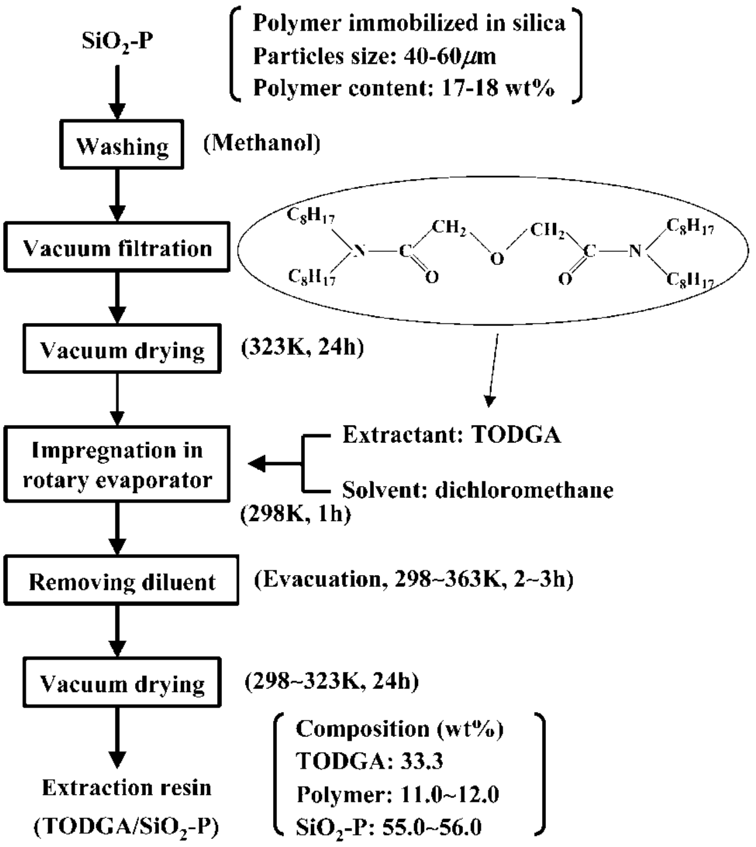

Figure 2. Synthesis of macroporous TODGA/SiO_2-P polymeric adsorption material.

extraction resin were calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \text{ (mL/g)} \qquad (1)$$

where C_o and C_e denote the concentrations of Mo(VI) and Zr(IV) in aqueous phase initially and at a later time, respectively. W and V represent the weight of dry TODGA/SiO_2-P extraction resin and the volume of the aqueous phase used in the experiments.

Chromatographic Separation of Mo(VI) and Zr(IV)

A weighed quantity of TODGA/SiO_2-P extraction resin equilibrated fully with 3 M HNO_3 before experiments was packed into a glass column with

10 mm in inner diameter and 220 mm in length. A constant temperature used in the loading and elution cycle was maintained at 50°C by circulating the thermostated water through an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co. Ltd., Japan). The flow rate was controlled to 1 mL/min. After the feed solution containing 7.57×10^{-3} M Mo(VI), 5.12×10^{-3} M Zr(IV), 0.05 M DTPA, and 3 M HNO_3 passed through the column, the given volumes of 3 M HNO_3, 0.1 M HNO_3, distilled water, and 0.5 M $H_2C_2O_4$ as eluents were subsequently pumped down-flow through the adsorption column. 10 mL aliquots of effluent fractions were collected by a DC-1500 Model Auto-Fractional Collector (Eyela, Japan). The concentrations of Mo(VI) and Zr(IV) in effluent were analyzed by ICP-AES mentioned previously.

RESULTS AND DISCUSSION

Adsorption Equilibrium of Mo(VI) and Zr(IV) Towards TODGA/SiO_2-P

The effect of contact time on the adsorption of TODGA/SiO_2-P extraction resin for Mo(VI) and Zr(IV) in 3 M HNO_3 with and without containing 0.05 M DTPA was studied at a phase ratio of 0.25 g/5 mL at 25°C. The concentrations of Mo(VI) and Zr(IV) in the aqueous phase were 5.01×10^{-3} M and 3.36×10^{-3} M, respectively. The results were shown in Fig. 3. Evidently, with an increase in contact time, the adsorption of Zr(IV) towards TODGA/SiO_2-P increased rapidly initially and reached the equilibrium quickly after 100 min. Despite the distribution coefficient of Zr(IV) in 3 M HNO_3–0.05 M DTPA was slightly lower than that in 3 M HNO_3, the distribution coefficients of Zr(IV) onto TODGA/SiO_2-P both in the absence and presence of 0.05 M DTPA always showed considerably higher and were over 1.2×10^4 mL/g. Such a high value in the distribution coefficient was due to the strong complexation of TODGA/SiO_2-P resin for Zr(IV). The influence of 0.05 M DTPA on the adsorption of Zr(IV) seemed not very significant. Contrary to the high adsorption of Zr(IV), Mo(VI) showed almost no adsorption towards TODGA/SiO_2-P in 3 M HNO_3 both with and without 0.05 M DTPA, and the distribution coefficient of Mo(VI) was always below 4 mL/g. This low value in the distribution coefficient indicated that in 3 M HNO_3, the complex ability of TODGA/SiO_2-P for Mo(VI) in both cases was very weak. Such a poor ability in the forming complex resulted in Mo(VI) almost uncomplexing with TODGA/SiO_2-P resin. Based on an obvious difference in the adsorption ability of TODGA/SiO_2-P for Mo(VI) and Zr(IV) in 3 M HNO_3, it was promising to separate Mo(VI) and Zr(IV) each from 0.05 M DTPA.

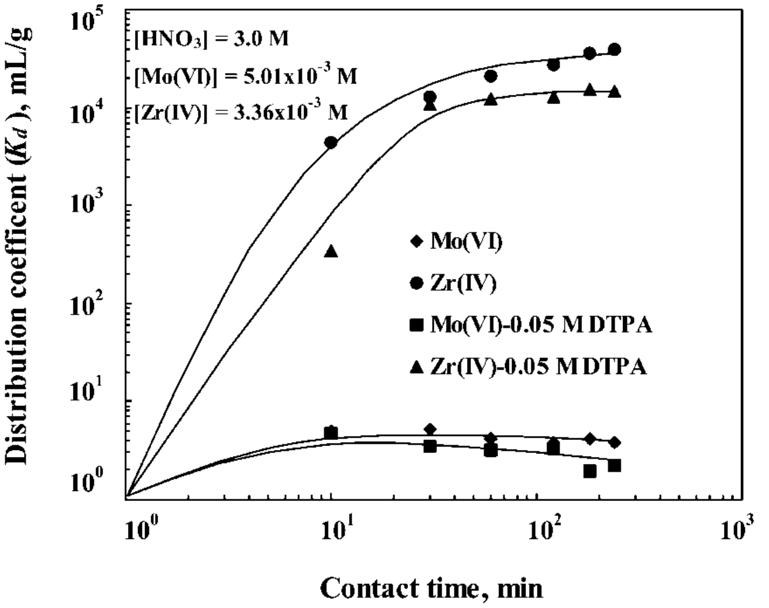

Figure 3. Adsorption of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P resin with a change in contact time. [HNO_3] = 3.0 M, the phase ratio = 0.25 g/5 mL.

Effect of HNO_3 Concentration on the Adsorption of Mo(VI) and Zr(IV)

The influence of HNO_3 concentration at the range of 0.3 M to 9.0 M on the adsorption of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P resin was investigated at the constant phase ratio, the concentrations of Mo(VI) and Zr(IV) and contact time were 0.20 g/5 mL, 5.01×10^{-3} M, 3.36×10^{-3} M, and 180 min, respectively. The results are shown in Figs. 4 and 5, respectively. As can be seen from Fig. 4, in the absence of 0.05 M DTPA, the distribution coefficient (K_d) of Mo(VI) noticeably lowered with an increase in the HNO_3 concentration from 0.3 M to 3 M and then slowly increased from 3.0 M to 9 M. However, in the presence of 0.05 M DTPA, the adsorption of Mo(VI) onto TODGA/SiO_2-P resin was always quite weak before 3 M HNO_3, i.e., Mo(VI) showed almost no adsorption onto TODGA/SiO_2-P resin, which resulted from the complexation of Mo(VI) with DTPA. Then, the adsorption of TODGA/SiO_2-P resin for Mo(VI) gradually increased. In the whole adsorption process, a valuable phenomenon was that both the adsorption curves of Mo(VI) towards TODGA/SiO_2-P resin overlapped fully in both cases. Such an overlapping in the adsorption curves reflected that 3 M HNO_3 was an interconversion acidity for the complex formation and

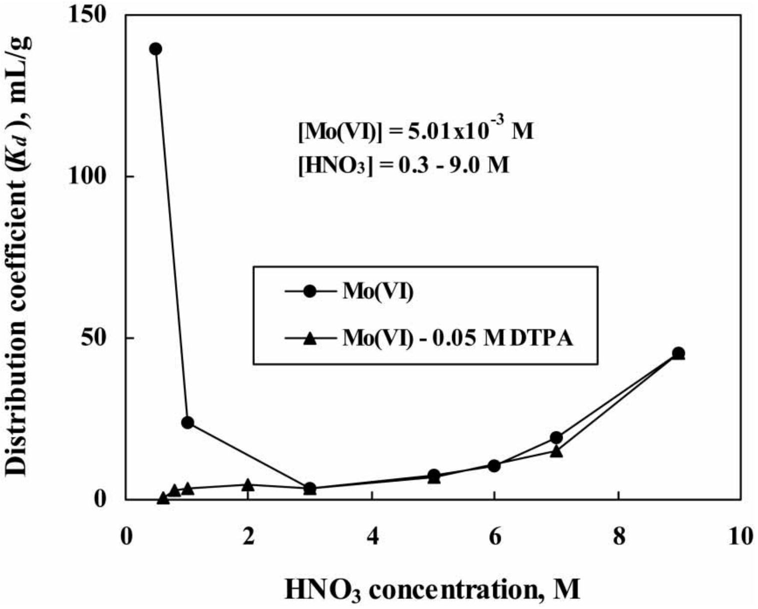

Figure 4. Effect of HNO_3 concentration on the adsorption of Mo(VI) towards TODGA/SiO_2-P resin. The phase ratio = 0.20 g/5 mL, [HNO_3] = 0.3–9 M, [DTPA] = 0.05 M.

dissociation of Mo(VI) and DTPA, i.e., the complex of Mo(VI) and DTPA was formed below 3 M HNO_3 and dissociated completely in more than 3 M HNO_3. The dissociation of Mo(VI) ion from its complex with DTPA in excess of 3 M HNO_3 resulted from the full protonation of DTPA. So, in the presence of 0.05 M DTPA, Mo(VI) could be complexed and adsorbed gradually by TODGA/SiO_2-P resin after 3 M HNO_3.

However, the detailed composition of the complex of Mo(VI) and DTPA has not been reported because of the quite complicated species of Mo(VI) in acidic solution (23–27). According to previous investigations, if one assumes that the composition of the complex of Mo(VI) and DTPA is $HMoO_3 \cdot H_4DTPA$, then the possible interconversion equilibrium of the complex of Mo(VI) and DTPA is described as follows:

$$HMoO_3 \cdot H_4DTPA + H^+ \underset{<3\ M\ HNO_3}{\overset{\geq 3\ M\ HNO_3}{\rightleftharpoons}} HMoO_3^+ + H_5DTPA \qquad (2)$$

The complex composition of Mo(VI) and TODGA also has not been reported. For the complexation and adsorption of Mo(VI) towards TODGA/SiO_2-P, assuming that the complex composition of Mo(VI) and TODGA was $HMoO_3(NO_3) \cdot 2TODGA$, then the corresponding adsorption

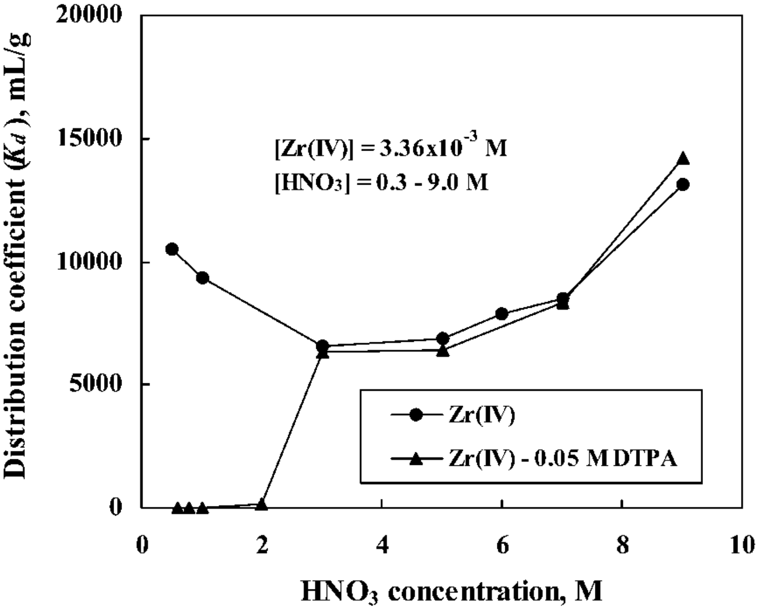

Figure 5. Effect of HNO_3 concentration on the adsorption of Zr(IV) onto TODGA/SiO_2-P. $[HNO_3] = 0.3$–$9\,M$, $[DTPA] = 0.05\,M$, the phase ratio $= 0.20\,g/5\,mL$.

equilibrium is presented as follows:

$$HMoO_3^+ + NO_3^- + 2TODGA/SiO_2\text{-}P \xrightleftharpoons{\geq 3\ M\ HNO_3} HMoO_3(NO_3) \cdot 2TODGA/SiO_2\text{-}P \tag{3}$$

Figure 5 shows the distribution coefficient (K_d) of Zr(IV) towards TODGA/SiO_2-P resin in a wide HNO_3 concentration range of 0.3 M to 9 M. It was clear that in the absence of 0.05 M DTPA, the change trend in the adsorption of Zr(IV) onto TODGA/SiO_2-P was quite similar to that of Mo(VI), although the distribution coefficient (K_d) of Zr(IV) was obviously higher that of Mo(VI). However, in the presence of 0.05 M DTPA, the Zr(IV) adsorption behavior was different from that of Mo(VI). The Zr(IV) showed no adsorption onto TODGA/SiO_2-P resin before 2 M HNO_3, which resulted from the strong complexation of Zr(IV) with DTPA, part adsorption in the range of 2 M to 3 M HNO_3. In excess of 3 M HNO_3, Zr(IV) dissociated completely from its complex with DTPA, was strongly complexed, and was adsorbed by TODGA/SiO_2-P extraction resin. Moreover, the adsorption curves of TODGA/SiO_2-P resin for Zr(IV) both in the absence and presence of 0.05 M DTPA overlapped, which was quite similar to that of Mo(VI). Such an overlapping in the adsorption curves of Zr(IV) also can be ascribed to the full protonation of DTPA in high HNO_3 concentration. The possible interconversion equilibrium of Zr(IV) with DTPA was expressed as follows:

$$\begin{aligned} &ZrO \cdot H_3DTPA\,(\text{or } Zr(NO_3)_2 \cdot H_3DTPA) + 2H^+ \\ &\quad \underset{<2\text{ M } HNO_3}{\overset{\geq 3\text{ M } HNO_3}{\rightleftharpoons}} \mathit{hboxZrO}^{2+}(\text{or } Zr(NO_3)_2^{2+}) + H_5DTPA \end{aligned} \tag{4}$$

If one assumes that the complex composition of Zr(IV) and TODGA is $ZrO(NO_3)_2$ (or $Zr(NO_3)_4) \cdot 2$TODGA, then, the adsorption equilibrium of Zr(IV) towards TODGA/SiO_2-P is described as follows:

$$\begin{aligned} &ZrO^{2+}(\text{or } Zr(NO_3)_2{}^{2+}) + 2NO_3^- + 2\text{TODGA/SiO}_2\text{-P} \\ &\quad \overset{\geq 2\text{ M } HNO_3}{\rightleftharpoons} ZrO(NO_3)_2(\text{or } Zr(NO_3)_4) \cdot 2\text{TODGA/SiO}_2\text{-P} \end{aligned} \tag{5}$$

Unfortunately, the detailed compositions and structures of the complex of Zr(IV) with TODGA and DTPA have not been reported so far.

Figures 4 and 5 clearly showed the adsorption of Zr(IV) and Mo(VI) onto TODGA/SiO_2-P resin strongly relied on the HNO_3 concentration, which significantly affected the formation and dissociation of the complexes of Mo(VI) with DTPA and TODGA/SiO_2-P as well as Zr(IV) with DTPA and TODGA/SiO_2-P, respectively. Because of the protonation of DTPA, the complexes of Mo(VI) or Zr(IV) with DTPA and TODGA/SiO_2-P were interconvertible at 3 M HNO_3.

Effect of DTPA Concentration on the Adsorption of Mo(VI) and Zr(IV)

The previous results showed that DTPA as a chelating agent had an obvious impact for the adsorption of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P resin based on its complexation and protonation in HNO_3 solution. To understand the effect of DTPA concentration, the adsorption of TODGA/SiO_2-P for a 3 M HNO_3 solution containing 5.01×10^{-3} M Mo(VI) and 3.36×10^{-3} M Zr(IV) was investigated at the DTPA concentration of 0.01 M to 0.45 M and a phase ratio of 0.20 g/5 mL, respectively. The results were shown in Fig. 6. With an increase in the DTPA concentration, the distribution coefficient (K_d) of Zr(IV) towards TODGA/SiO_2-P evidently decreased from 0.04 M to 0.2 M DTPA and then rapidly decreased in excess of 0.2 M DTPA. Such a decrease in the distribution coefficient resulted from the strongly complex reaction between DTPA and Zr(IV), which was produced by its dissociation of the complex with TODGA/SiO_2-P resin. The complexation of DTPA and Zr(IV) in experiment conditions was dominant in comparison with the protonation of DTPA and the complexation of TODGA/SiO_2-P and Zr(IV). So, in excess of 0.2 M, DTPA could still complex with Zr(IV) in 3 M HNO_3

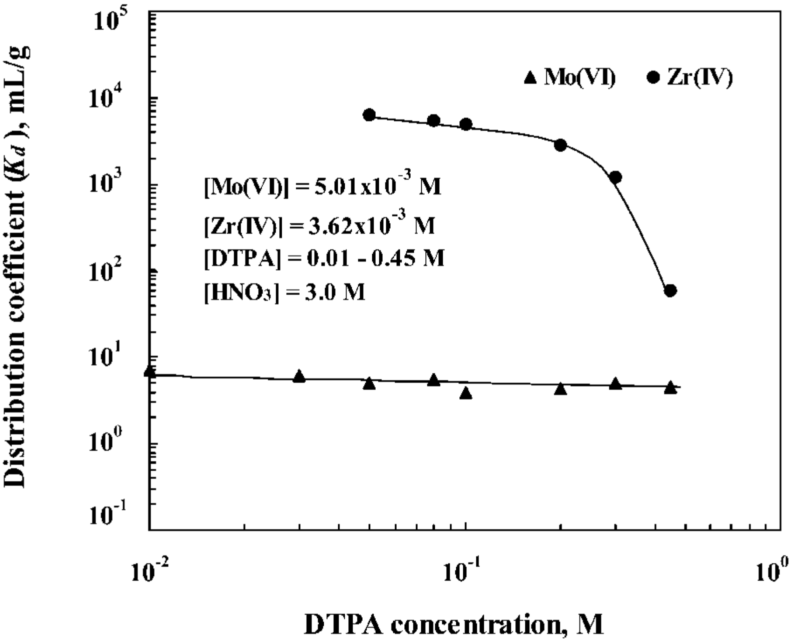

Figure 6. Effect of DTPA concentration on the adsorption of Mo(VI) and Zr(IV) towards TODGA/SiO$_2$-P. [HNO$_3$] = 3.0 M, [DTPA] = 0.01–0.45 M, the phase ratio of 0.20 g/5 mL.

even if it was a weakly acidic chelating agent. The distribution coefficient of Zr(IV) was 6.36 × 10^3 mL/g for 0.05 M DTPA and 58.0 mL/g for 0.45 M DTPA, respectively. The low distribution coefficient of Zr(IV) in high DTPA concentration reflected that Zr(IV) could be dissociated from its complex with TODGA/SiO$_2$-P by the competitive reaction with DTPA, i.e., with an increase in the DTPA concentration, the complex of Zr(IV) and TODGA/SiO$_2$-P could convert gradually to the complex of Zr(IV) and DTPA. The adsorption of TODGA/SiO$_2$-P for Zr(IV), therefore, decreased.

The distribution coefficient (K_d) of Mo(VI) onto TODGA/SiO$_2$-P resin was always quite low and below 6 mL/g in the whole concentration range of 0.01–0.45 M DTPA. Such a low value showed that when Mo(VI) existed in the 3 M HNO$_3$ solution there was almost no adsorption onto TODGA/SiO$_2$-P resin.

Chromatographic Separation of Mo(VI) and Zr(IV) from 0.05 M DTPA

According to the batch experimental results, the separation of Mo(VI) and Zr(IV) from a 0.05 M DTPA solution, which was obtained in the second adsorption column in the MAREC process, was performed by a TODGA/SiO_2-P resin packed column at 50°C. To ensure effective adsorption of Zr(IV) towards TODGA/SiO_2-P resin, prior to the experiment the concentration of HNO_3 in feed solution was conditioned to 3.0 M by addition of the concentrated HNO_3. Such an acidification process was necessary for the dissociation of all of free Zr(IV) ions from the Zr(IV)-DTPA complex completely based on a full protonation reaction of DTPA and proton. The Mo(VI) and Zr(IV) concentrations in feed solution were 7.57×10^{-3} M Mo(VI) and 5.12×10^{-3} M Zr(IV). The column dimension was 10 mm in inner diameter and 220 mm in length. The flow rate was 1 mL/min. The separation results achieved by employing 3 M HNO_3 and 0.5 M DTPA-pH 0.73 as eluents are illustrated in Fig. 7.

As can be seen, with a supplement of washing solution, Mo(VI) showed no adsorption and quickly leaked out the column completely along with 3 M HNO_3. Such an effortless elution resulted from the considerably weak complexation of TODGA/SiO_2-P for Mo(VI). Contrary to Mo(VI), the Zr(IV) dissociated from Zr(IV)-DTPA complex in 3 M HNO_3 was strongly complexed and firmly adsorbed by TODGA/SiO_2-P resin and did not leak out of the column along with Mo(VI). However, only a portion of Zr(IV)

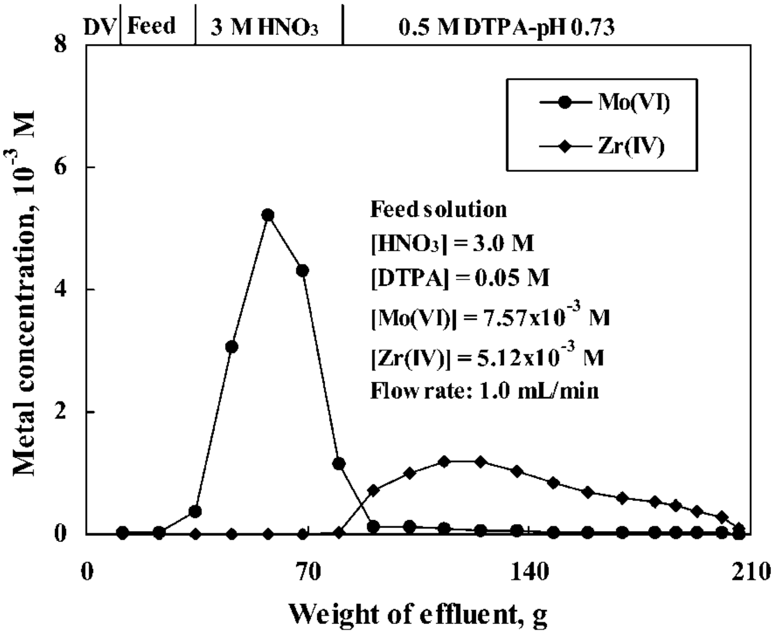

Figure 7. Column separation of Mo(VI) and Zr(IV) from a 3.0 M HNO_3 solution containing 0.05 M DTPA by TODGA/SiO_2-P packed column employing 0.5 M DTPA-pH 0.73 as an eluent at 50°C. Column dimension: Φ 10 mm × *h* 220 mm, flow rate: 1 mL/min.

was desorbed from the loaded TODGA/SiO_2-P resin by eluting with 0.5 M DTPA-pH 0.73. The recovery rate was 99.98% for Mo(VI) and 40.5% for Zr(IV). Previous studies showed that the Zr(IV) loaded in CMPO/SiO_2-P extraction resin was effectively eluted out and recovered by employing 0.05 M DTPA-pH 2.0 as an eluent (11). Such a noticeable difference in the elution efficiency of Zr(IV) indicated that the kinetics exchange reaction of substituting the complex of Zr(IV) and DTPA for the complex of Zr(IV) and TODGA/SiO_2-P resin was probably a slow process.

In addition to DTPA, 0.5 M $H_2C_2O_4$ as a chelating agent, was also found to be capable of efficiently eluting Zr(IV) from the loaded CMPO/SiO_2-P resin in MAREC process (14).

To investigate the possibility of applying 0.5 M $H_2C_2O_4$ in the separation of Mo(VI) and Zr(IV), especially to improve the elution effect of Zr(IV), a similar separation experiment of Zr(IV) and Mo(VI) from 3 M HNO_3–0.05 M DTPA was performed at 50°C and the results were shown in Fig. 8.

Obviously, Mo(VI) showed no adsorption towards TODGA/SiO_2-P resin and leaked out of the column along with 3 M HNO_3, which was quite identical with results illustrated in Fig. 7. Its recovery rate was 101.6%. Following eluting the loaded TODGA/SiO_2-P with 0.1 M HNO_3 and distilled water, 0.5 M $H_2C_2O_4$ aqueous solution was employed to elute Zr(IV), which was

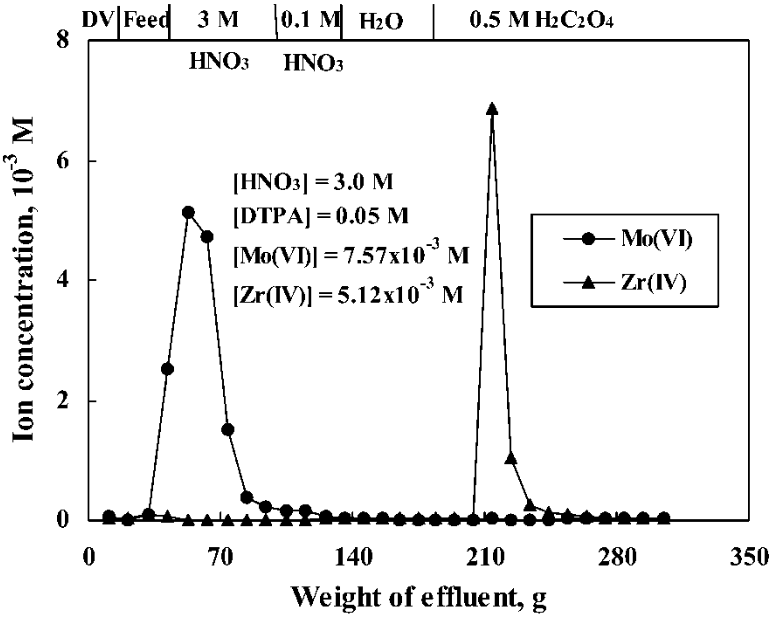

Figure 8. Separation of Mo(VI) and Zr(IV) from 0.05 M DTPA-3.0 M HNO_3 using 0.5 M $H_2C_2O_4$ as an eluent at 50°C. Column dimension: Φ 10 mm × *h* 220 mm, flow rate: 1 mL/min.

firmly adsorbed by TODGA/SiO_2-P resin. With an increase in 0.5 M $H_2C_2O_4$, it was found that the Zr(IV) concentration in the effluent increased rapidly and then decreased, showing that Zr(IV) was efficiently eluted. Such an obvious change was due to the effective complexation of Zr(IV) with 0.5 M $H_2C_2O_4$, i.e., substituting the complex of Zr(IV) and $H_2C_2O_4$ for the complex of Zr(IV) and TODGA/SiO_2-P was a fast process of the kinetics exchange. The percentage recovered was calculated to be 94.8%. This results showed that the separation of Mo(VI) and Zr(IV) from a 3 M HNO_3 solution containing 0.05 M DTPA by TODGA/SiO_2-P resin packed column was technically feasible.

CONCLUSIONS

The adsorption behavior of Mo(VI) and Zr(IV) towards TODGA/SiO_2-P extraction resin was investigated by examining the effect of contact time and the concentrations of HNO_3 and DTPA. It was found that the adsorption of Mo(VI) and Zr(IV) strongly depended on the change in the HNO_3 concentration from 0.3 M to 9 M. 3 M HNO_3 was a critical acidity for the complex formation and dissociation of Mo(VI) with DTPA and TODGA/SiO_2-P as well as Zr(IV) with DTPA and TODGA/SiO_2-P. The adsorption of TODGA/SiO_2-P for Zr(IV) in 3 M HNO_3 either with or without 0.05 M DTPA was higher than that of Mo(VI), while Mo(VI) showed almost no adsorption towards TODGA/SiO_2-P.

Based on batch experiments, the separation of Mo(VI) and Zr(IV) from a 3 M HNO_3–0.05 M DTPA solution was performed by the TODGA/SiO_2-P resin packed column utilizing 3 M HNO_3, 0.1 M HNO_3, distilled water, and 0.5 M $H_2C_2O_4$ aqueous solution as eluents at 50°C. It was found that Mo(VI) and Zr(IV) were effectively eluted out by 3 M HNO_3 and 0.5 M $H_2C_2O_4$, respectively. The recovery was 101.6% for Mo(VI) and 94.8% for Zr(IV), respectively. Such a result reflected that Mo(VI) and Zr(IV) could be separated from each other by a HNO_3 solution containing 0.05 M DTPA using the method of extraction chromatography.

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