Influences of Pore and Particle Sizes of CMPO/SiO₂-P Adsorbent on Extraction Chromatography Process

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Abstract

Extraction chromatography is promising technology for trivalent minor actinides recovery from spent nuclear fuel. In this study, CMPO-impregnated adsorbents with various pore and particle sizes of SiO₂ particles were prepared, and influences of those properties on the adsorption/elution performances were investigated by batch-wise adsorption experiments and column experiments. Only surface of the particle contributed to adsorption when the pore size is too small. In this system, adsorption/elution kinetics was favorable, whereas adsorption capacity was poor. Broadening in the pore size was revealed to enhance diffusion of mobile phase into the particle, and then elution rate was also improved. Since too large pore size might lead weak mechanical strength, refinement in the pore size considering practical operation condition might be required. Large particle showed fine adsorption performance through batch-wise experiments, but formation of channeling or voids inside the packed bed were observed in the column operation. The voids lead poor breakthrough and elution performances. The particle size had to be smaller than 200 μm for the extraction chromatography system though large particle is desirable in the respects of remote handling and adsorption performance.

Keywords: extraction chromatography, adsorbent, CMPO, pore size, particle size

1. Introduction

Partitioning and transmutation of trans uranium (TRU) elements in the high level liquid waste (HLLW) generated in the reprocessing of the spent nuclear fuel is one of matters of public concern, and it is expected to reduce the volume and the potential hazard of the vitrified final waste [1]. However, partitioning of the TRU elements involves difficulty in chemical separation between minor actinides (MA(III): Am(III) and Cm(III)) and other fission products (FPs) such as lanthanides, Mo and Zr, etc. Solvent extraction processes such as DIAMEX-SANEX process [2], TALSPEAK process [3], TRUEX process [4], SETFICS process [5] have been developed for MA(III) recovery. Those processes require diluent for organic extractants, and large amount of secondary waste is suspected to be generated. As an alternative to the solvent extraction, the extraction chromatography technology is promising [6] and Japan Atomic Energy Agency has been conducting fundamental studies for the implementation [7–11].

In the extraction chromatography, porous silica particles with diameter of 50 μm and pore size of 50 nm coated by styrene-divinyl benzene co-polymer (referred as SiO₂-P) which holds an extractant in it are used as the adsorbent, and they are packed in a column. Elements are separated through adsorption/elution reactions inside the packed column. This technology requires much less organic compounds than those used in the solvent extraction, thus it is expected to reduce not only the amount of the secondary waste but also the scale of instruments.

MA(III) recovery flow-sheet utilizing adsorbent involving n-octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide (CMPO) has been developed by our group, and performance of an engineering scale column system [7–9] and validity of the flow-sheet for the genuine HLLW [10,11] were demonstrated. In order to enhance operability of the adsor-
bents in the engineering scale system by remote handling and to reduce pressure drop by the packed column, sizes of the particle and of the pore are desirable to be increased. The particle and pore sizes influence on dense of the packing and the specific surface area of the adsorbent, therefore sizing up of those parameters are apprehended to reduce the performances of the adsorbent and the packed column. Influences of them on the performance of adsorbents and column are important information to design the practical system. Although influence of pore and particle size on separation process are generally investigated for liquid chromatography with high pressure\textsuperscript{12,13} or supercritical fluid chromatography for separation of large size organics\textsuperscript{14,15}, those for the extraction chromatography for separation metallic cations with relatively low pressure have not been investigated so far. In this study, CMPO/SiO\textsubscript{2}-P adsorbents with various pore and particle sizes were prepared, and batch-wise adsorption experiments and column operation experiments were carried out to evaluate adsorption/elution performances.

2. Experimental

2.1 Preparation of adsorbents

The porous silica particles with various average pore and particle sizes as shown in the Table 1 were prepared by sol-gel method. Styrene-divinyl benzene co-polymer coating on those particles and impregnation of CMPO into the polymer were carried out according to an article\textsuperscript{16}. Degree of the cross linkage of the polymer was 15%. Weight ratio of the polymer was about 24 wt\%, and weight ratio of the impregnated CMPO in the adsorbents are also shown in Table 1.

2.2 Batch-wise adsorption

Distribution coefficients at various acidity, adsorption isotherm and adsorption rate were evaluated through batch-wise adsorption experiments. 0.2 g of the adsorbents were mixed with 4 mL of the feed solution containing Nd(III) or Y(III). Then, they were shaken for a certain period in the water bath whose temperature was controlled at 323 K. Concentrations of the cations in the supernatant solution were measured by UV-vis absorption spectroscopy. Acidity of the feed solution, concentration of the cations and shaking time were parametrically changed depending on the characteristics to be evaluated. Experimental conditions are shown in Table 2.

2.3 Column operation

The breakthrough and elution curves were obtained by column experiments. Experimental setup is shown in Fig. 1. The setup consists of a column with water jacket, water circulating system, a pressure gage, a pump and tanks. The adsorbents were packed into a glass column with 10 mm ID×100 mm length (the bed volume: 7.85 cm\textsuperscript{3}), and temperature inside the column was controlled at 323 K by the circulating water.

In order to obtain the breakthrough curve of the column, a feed solution containing Nd(III) was fed into the column. The feed solution, wash solution and eluent were sequentially fed into the column to obtain the elution curves. The effluent was fractionally collected at downstream of the column by the fraction collector, and concentrations of the cations in the effluents were measured by UV-vis absorption spectroscopy. Experimental conditions for the breakthrough curves and elution curves are shown in Table 3 and 4, respectively.

3. Results and Discussion

3.1 Influence of pore size

3.1.1 Batch-wise adsorption

The distribution coefficient $K_d$ (dm\textsuperscript{3}/g) was calculated by the following equation,

$$K_d = \frac{C_0 - C_s}{C_s} \times \frac{V}{W}$$

where $C_0$ and $C_s$ are concentrations of cations in the solution before and after the adsorption, respectively, $V$ is volume of
occupied in the pore, and that must obstruct the diffusion of the mobile phase into the pore. Effect of the diffusion on the adsorption/elution performance will be discussed also by the column separation experiments in the following section. The larger pore size is suspected to result in weak mechanical strength of the particle. The pore size and porosity should be decided based on requirement in the strength of the particle from design of the practical system.

The distribution coefficient $K_d$ of Y(III) simply increased with increasing the acidity of the feed solution, while those of Nd(III) took local maximums at $[\text{HNO}_3]=1 \text{ mol/dm}^3$. The similar phenomena were also observed in the solvent extraction system, and the lighter lanthanide systems showed the larger drop in the $K_d$ at high acidity region $^{18}$. The decrease in the $K_d$ was explained by that extraction sites in CMPO molecule are occupied with NO$_3^-$ $^{18}$. Another article also reported that CMPO is consumed not only by Ln(III) extraction but also by HNO$_3$ extraction at high acidic region $^{19}$. Consequently, the different behavior of the $K_d$ between Nd(III) and Y(III) can be attributed to extraction competition between Ln(III) and NO$_3^-$ by CMPO. The $K_d$ of Ln(III) at high acidic region are possible to be increased by mixing TBP into CMPO owing to interaction between TBP and HNO$_3$ $^{20}$.

Adsorption isotherms of Nd(III) on CMPO/SiO$_2$-P adsorbent are shown in Fig. 4. Solid lines in the figures are fitted curves according to the Langmuir formula expressed by following equation,

$$W = \frac{aW_sC}{1+aC}$$ (2)

the solution, $w$ is weight of the adsorbent. $K_d$ of Y(III) and Nd(III) at various acidity are shown in Fig. 2 and 3, respectively. $K_d$ of Y(III) and Nd(III) increased with increasing the pore diameter. The larger pore is expected to contribute the better diffusion of the mobile phase inside the particle. The better diffusion may enhance formation of complex of cations with CMPO impregnated. Favorable diffusion condition of the mobile phase inside the particle must be the most important characteristics to achieve excellent adsorption/desorption performance. The adsorbent with the smallest pore showed far less adsorption than the other adsorbents. According to crystal structure of CMPO $^{17}$, molecular size of CMPO was roughly estimated to be 1–2 nm. Since 2 or 3 CMPO molecules are required to form a complex with a lanthanide ion, thickness of the polymer coating on the surface of the silica should be larger than the smallest pore size (i.e. 3 nm) for keeping CMPO molecules enough to extract a lanthanide ion. It is possible to consider that the polymer and the extractant occupied in the pore, and that must obstruct the diffusion of the mobile phase into the pore. Effect of the diffusion on the adsorption/elution performance will be discussed also by the column separation experiments in the following section. The larger pore size is suspected to result in weak mechanical strength of the particle. The pore size and porosity should be decided based on requirement in the strength of the particle from design of the practical system.

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Adsorption isotherms of Nd(III) on CMPO/SiO$_2$-P adsorbent are shown in Fig. 4. Solid lines in the figures are fitted curves according to the Langmuir formula expressed by following equation,

$$W = \frac{aW_sC}{1+aC}$$ (2)
influenced on the adsorption rate, rate-controlling factor of this system must be not the diffusion inside the particle but the extraction reaction.

3.1.2 Column operation

Breakthrough curves obtained for Q50-50 and Q200-50 are shown in Fig. 6 and 7, respectively. The flow velocity seems to be independent on the breakthrough behavior for Q50-50, however slope of the curve got gentler as increase in the flow velocity for Q200-50. There were not distinct influence of the flow velocity on the breakthrough curves for adsorbents Q3-50 and 10-50 also. Those results suggest that diffusion of the mobile phase inside the pore is slow even for the larger pore size and that several adsorption sites inside the particle with smaller pore size might not be used in the column operation. Diffusion of the mobile phase inside the

![Figure 5](image5.png)

**Figure 5** shows adsorption rates of Nd(III) on the CMPO/SiO$_2$-P adsorbents. The adsorption equilibrium was achieved after 10 minutes shaking for all the adsorbents. Adsorption rate is dominated by molecular diffusions in boundary layer, diffusion inside the particle and extraction by CMPO. Those experiments were carried out at the same temperature, therefore motilities in the boundary layer can be considered as the same between the adsorbents. Since pore size did not

![Figure 6](image6.png)

**Figure 6** Adsorption isotherms of Nd(III) on CMPO/SiO$_2$-P adsorbents. 

$[\text{Nd(III)}]=10 \text{ mM}$
particle in the column operation is not enough to achieve the same adsorption capacity with those evaluated by the batch-wise operation. Since the flow velocity is desirable to be increased to achieve large throughput, the flow velocity inside the packed column is necessary to be optimized for effective utilization of the adsorption sites. Flow velocity of $3 \text{ cm}^3/\text{min}$ might be appropriate to achieve both the efficient use in the adsorption sites and the large throughput.

Breakthrough curves of particles with various pore sizes for the flow rate of $3 \text{ cm}^3/\text{min}$ are shown in Fig. 8. The breakthrough points of adsorbent reasonably agreed with the static adsorption capacity evaluated in the bath-wise adsorption experiments. The slopes of those curves were slightly different between the adsorbents. Shaper slope for the Q10-50 is considered to be the less diffusion of the mobile phase inside the particle than that of Q50-50. The utilization efficiency in the adsorption sites might increase with increasing the pore size.

The elution curves of Nd(III) for the adsorbents with various pore sizes are shown in Fig. 9. The elution from the bed of Q3-50 was clearly faster than those of other adsorbents. Only the surface of adsorbent Q3-50 is considered to contribute to adsorption/desorption reactions. Loaded Nd(III) was eluted at $V=8–12 \text{ BV}$ for the adsorbents except for Q3-50,
and elution profile shifted to left side with increasing the pore size. It is reasonable to consider that diffusion of the eluent inside the particle was enhanced with increasing the pore size and then the diffusion speeded up the elution. Recovery ratios of Nd(III) from the packed columns are shown in Table 6. Recovery ratio from Q3-50 was lower than those from other adsorbents, and almost all Nd(III) were recovered from Q10-50, Q50-50 and Q200-50. Since the pore of Q3-50 must be occupied by the polymer and extractant as discussed above, some part of Nd(III) adsorbed on the surface possibly diffused inside the pore before the elution operation. Diffusion of the loaded Nd(III) into core of the particle and less diffusion of eluent inside the particle might be one of the reasons for the low recovery ratio. In the respects of the elution behavior and of the absorption capacity, the adsorbent with the largest pore size was preferable. However, flow velocity has to be optimized according to balance between required throughput and performance of the column.

3.2 Influence of particle size
3.2.1 Batch-wise adsorption

Distribution coefficient $K_d$ of Y(III) and Nd(III) on CMPO/SiO$_2$-P with various particle size are shown in Fig. 10 and 11, respectively. $K_d$ of Y(III) increased with increase in the acidity and particle size. Profile of $K_d$ for Nd(III) was the same with that in Fig. 3, and $K_d$ took local maximum at [HNO$_3$]=1 mol/dm$^3$. Those dependences of $K_d$ on the acidity can be explained by the same manner with the discussion in Section 3.1.1. The $K_d$ of Nd(III) also increased with increase in the particle size. On general, porous particle with the smaller particle size has the larger surface area per unit weight. If the number of adsorption sites is proportional to the surface area, the smaller particle should show the larger $K_d$. However, those results seem to show opposite tendency. Some area inside the pore might not contribute to the adsorption. Consequently, it is reasonable to consider that some part of CMPO impreg-
3.2.2 Column Operation

For the packed bed of Q50-200 and Q50-300, voids inside the bed were observed as shown in Fig. 14. Formation of channeling inside the bed is also suspected. Specific techniques for making uniform bed with those adsorbents should be developed. Breakthrough curves obtained for adsorbents of Q50-300 with various flow rates are shown in Fig. 15. Slopes of those curves are gentler than those obtained for Q50-50 as shown in Fig. 6, and distinct dependence on the flow velocity on the slope was not confirmed. These results imply that the voids and/or the channeling possibly obstruct the uniform and quick adsorption and that influences of the flow rate on the breakthrough behavior must be smaller than those from the voids or channeling.

The breakthrough curves of Nd(III) for the adsorbents with various particle sizes at flow rate of 3 cm$^3$/min are shown in Fig. 16. The curve of Q50-200 had gentle rise and
the fastest breakthrough, and it did not reach at $C/C_0 = 1$ even at $V > 20$ BV. The curve of Q50-300 had the slowest breakthrough, but it also showed slow adsorption and did not come at the 100% breakthrough. Since the voids in the bed move slightly between the particles by the flow, the distribution of the voids can affect the breakthrough points and adsorption equilibrium behavior.

4. Conclusion

In order to optimize operability of the adsorbents in the extraction chromatography system and to enhance the performance of the adsorbent, CMPO/SiO$_2$-P adsorbents with various pore and particle sizes were prepared, and characteristics of the adsorbents were evaluated through distribution coefficient, adsorption isotherm, adsorption rate, and breakthrough/elution behavior. Adsorption capacity was dominated not by the structure of the adsorbent but by amount of the extractant impregnated. The adsorbent with the largest pore size were revealed to show quick elution with short tail. Enlargement in the pore size must be one of the most effective improvements of the adsorbents to enhance the adsorption/elution performance. The appropriate pore size and porosity might be designed with consideration of operation conditions since those properties influence on the strength of the particle and large pressure on the column possibly damages the adsorbent mechanically. Adsorbent with particle size of more than 200 $\mu$m formed channeling or voids inside the bed. They are suspected to lead slow adsorption/elution behavior, and smaller adsorbents must be desirable in the respect of performance of the column. If larger particles are required for the engineering scale system, specific technique to eliminate the channeling and the voids should be developed.
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