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Optimizing composition of TODGA/SiO₂-P adsorbent for extraction chromatography process

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Abstract

As a part of developing extraction chromatography technology for minor actinides (MA(III); Am and Cm) recovery from spent fast reactor fuels, improvement on the TODGA/SiO₂-P adsorbent to enhance its desorption efficiency was carried out. Batchwise adsorption/elution experiments showed that optimizations in amount of the extractant impregnated in the support of the SiO₂-P which is the porous silica coated with polymer and degree of the cross linkage of polymer succeeded in finding the optimum values. Inactive column separation experiments with the simulated high level liquid waste and the optimized adsorbent revealed that decontamination factors of fission products can also be improved as well as the recovery yields.

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Keywords: Extraction chromatography, minor actinides, TODGA, porous support, degree of cross linkage

1. Introduction

Japan Atomic Energy Agency has been developing extraction chromatography technology for minor actinides (MA(III); Am and Cm) recovery from spent fast reactor fuels [1]. For the technology, the adsorbent is prepared by impregnating an extractant into the support of porous silica particle coated with styrene-divinylbenzene polymer (referred as SiO₂-P) [2]. The candidate flow-sheet using TODGA and iso-Hex BTP were selected for

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MA and lanthanides (Ln) recovery and MA/Ln separation, respectively [3]. Column separation experiments with the genuine high level liquid waste for demonstrating the flow-sheet has revealed that recovery yield of MA from the TODGA/SiO₂-P adsorbent should be improved, especially, in its desorption kinetics [4].

Adsorption/desorption properties of actinides are characterized by reversible complexation with the extractant impregnated and by diffusions of the mobile phase inside the particle and of the adsorbed cations on the stationary phase. The TODGA extraction is fast and reversible [3,5], therefore enhancement of the diffusions inside particle must be improved. From the point of view, amount of extractant and degree of the cross linkage of styrene-divinylbenzene polymer are quite important chemical factors. They are considered to affect the diffusions. In this study, those two parameters were optimized to give a better desorption efficiency with maintaining its adsorption capacity.

2. Experimental

2.1. Preparation of adsorbents

The adsorbents were prepared in a same manner of the article [3]. Porous silica particles with diameter of 50 μm coated by styrene–divinylbenzene polymer (SiO₂-P) were used as the support of extractants. Degree of cross linkage of the polymer was parametrically changed for 10, 15 and 20% by controlling the ratio of divinylbenzene to styrene when polymerization. Amount of extractants impregnated were also parametrically changed for 10, 20 and 33.3 wt% of adsorbents. The reference values of degree of the cross linkage and the concentration of extractant impregnated in our previous study were 15% and 33.3wt%, respectively. Tri-*n*-octylphosphine oxide (TOPO), *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and *N,N,N,N*'-tetra-*n*-octyl-diglycolamide (TODGA) were used as the extractants. TOPO/SiO₂-P and CMPO/SiO₂-P adsorbents as well as the TODGA/SiO₂-P adsorbents were used in adsorption/elution experiments described in the following section.

2.2. Adsorption/elution experiments

Adsorption capacity and desorption ratio were obtained through batchwise adsorption/desorption experiments. The optimum concentration of an extractant was determined by using TOPO, CMPO and TODGA/SiO₂-P adsorbent.

0.5 g of TODGA/SiO₂-P adsorbents was contacted with 10 mL of the feed solution containing 10 mM Nd(III), and shaken for 3 h. Then, the adsorbent with Nd(III) was contacted with 10 mL of distilled water for desorption. 0.2 g of TOPO/SiO₂-P and CMPO/SiO₂-P adsorbents were contacted with 4 cm³ of 1 M HNO₃ containing 10 mM Bi(III) and 4.8 M HNO₃ containing 10 mM Nd(III), respectively, and shaken for 3 hours for adsorbing the cations on the adsorbents.

Adsorption capacity and desorption ratio were calculated from metal concentration in the solutions measured by absorption spectroscopy.

2.3. Evaluation of TODGA leakage on gamma irradiation

1 g of TODGA/SiO₂-P adsorbents or SiO₂-P supports and 10 mL of 4.8 M HNO₃ solution were sealed in a glass vial and irradiated with gamma ray from ⁶⁰Co source for 34 h at the dose rate of 3 kGy/h up to 100 kGy. After the irradiation, the amount of leaked TODGA was evaluated from the concentration of total organic carbon (TOC) in the nitric acid solution.

2.4. Column separation experiments

The experimental setup of the column separation experiments is shown in Fig. 1. The reference or the optimized adsorbent was packed in the glass column with water jacket of 1 cmID and 32.5 cm length (1 BV = 25.5 cm³). After conditioning with 4.8 M HNO₃ solution, 1 BV of feed solution, 4 BV of wash solution (2 M HNO₃) and 8 BV of eluent (distilled H₂O) were sequentially supplied to the column. Composition of the simulated high level liquid waste for the feed solution is shown in Table 1. HEDTA as a complexing reagent for Zr or Pd was added to the feed solution to obtain a 0.1 M HEDTA solution in order to avoid adsorption of those elements. During the experiments temperature of the column was controlled at 313 K by the jacket water.

The effluent discharged from the column was fractionally collected by a fraction collector, and concentrations of representative fission product elements (Cs, Sr, Zr, Ce, Eu, Mo, Ru and Pd) contained in the fraction were analyzed by ICP-AES.

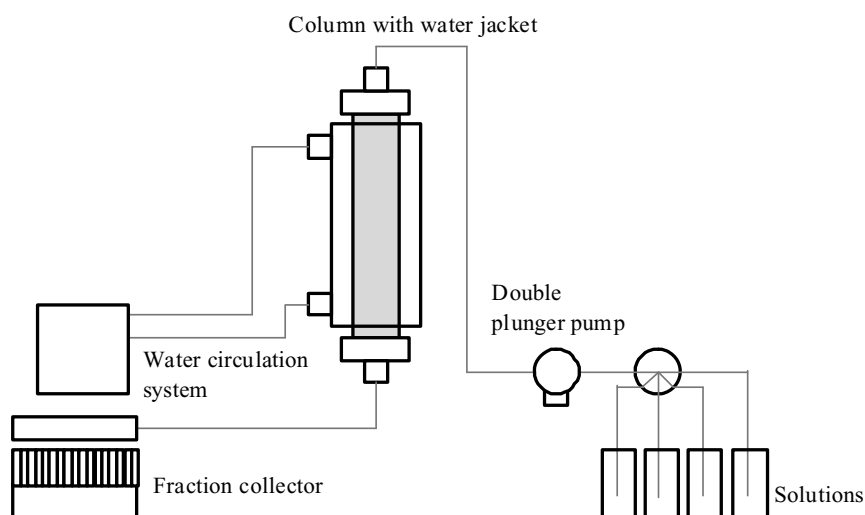


Fig. 1 Experimental setup for the column separation experiments

Table 1 Composition of the feed solution

HNO ₃				HEDTA				
4.8 M				0.1 M				
Se	Br	Rb	Sr	Y	Zr	Mo	Ru	Rh
0.05 g/L	0.02 g/L	0.24 g/L	0.47 g/L	0.28 g/L	0.11 g/L	2.7 g/L	1.0 g/L	0.83 g/L
Pd	Ag	Cd	In	Sn	Sb	Te	Cs	Ba
2.3 g/L	0.23 g/L	0.21 g/L	0.01 g/L	0.14 g/L	0.03 g/L	0.70 g/L	4.8 g/L	1.8 g/L
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
1.2 g/L	2.1 g/L	1.1 g/L	3.9 g/L	1.3 g/L	0.13 g/L	0.18 g/L	0.01 g/L	0.01 g/L

3. Result and discussion

3.1. Adsorption/desorption experiments

Adsorption capacities of CMPO/SiO₂-P and TOPO/SiO₂-P at various concentrations of an extractant impregnated are shown in Fig. 2. For both adsorbents, adsorption capacities increased with increasing concentration of the extractants. The increase in the capacity as a function of impregnated ratio is not constant, and decreased at above 20wt%. These results imply that the efficiency of using an extractant for complexation provides a maximum at 20wt% of extractant concentration. A part of extractant in the adsorbent of >20wt% does not contribute to form adsorption sites for metal. And in the respect of enhancing the diffusion of cations inside the adsorbents, reducing the amount of extractant must be preferable since the reducing is consider to improve hydrophilicity of the adsorbent. In this study, the optimum concentration of extractant impregnated was decided to be 20wt%.

Adsorption capacity and desorption ratio for the TODGA/SiO₂-P are shown in Fig. 3, where the concentration of TODGA impregnated was 20wt%. Concerning cross linkage of polymer, the adsorption capacity for the adsorbents of 10 and 15% were almost identical, although the capacity for 20% was superior to them.

Desorption ratio of Nd apparently reached at an equilibrium in 10 minutes, and it depended on the degree of cross linkage. The adsorbents of 15 and 20% provided lower desorption ratio than that of 10%. Increase in degree of the cross linkage is considered to disturb diffusion of cations inside the adsorbent. Reduction in the amount of adsorbed cations and changes in hydrophobic and swelling properties are considered to have a relationship to the desorption ratio and lead a potential increase of it.

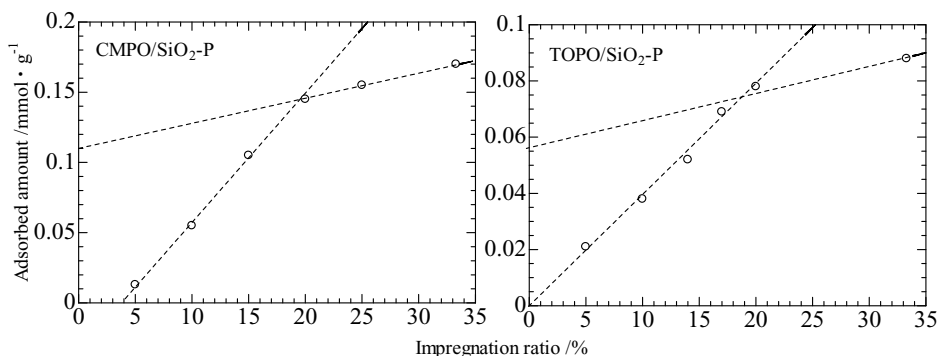


Fig.2 Adsorption capacity of CMPO/SiO₂-P (left) and TOPO/SiO₂-P (right) as a function of the impregnation ratio for an extractant

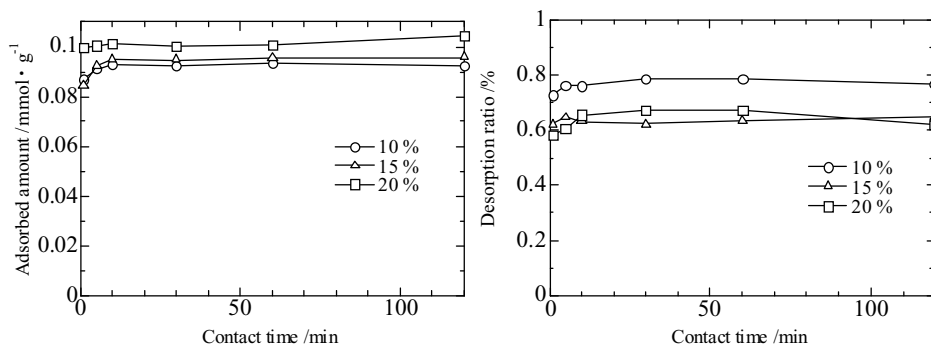


Fig. 3 Adsorption capacity (left) and desorption ratio (right) of TODGA/SiO₂-P in which cross linkage differed

3.2. TODGA leakage on irradiation

TOC measurements on the solution in which the adsorbents were immersed and irradiated with gamma ray showed that the leaked fraction of TODGA after irradiation was less than 0.01% regardless of the TODGA concentration in the adsorbents. Influence of reducing degree of the cross linkage on the stability of extractant must be negligible for the TODGA/SiO₂-P.

3.3. Column separation experiments

According to the results described above on the adsorption/desorption experiments, the appropriate concentration of TODGA and the degree of cross linkage can be concluded to be 20wt% and 10%, respectively.

The elution curves obtained from the column separation experiment using the reference adsorbents ([TODGA]=33.3wt%, degree of the cross linkage=15%) were shown in Fig. 4. Cs, Mo and Ru were not adsorbed by TODGA, and they were washed out by the wash solution. Pd was also eluted with the feed solution, thus effect of chelating with HEDTA for decontaminating Pd was confirmed. Those observations agree with the results of the previous study. Zr was adsorbed by the column and was not stripped despite of the existence of HEDTA. Since accumulation of Zr in the column possibly obstruct a repetitive operation of adsorption and desorption, further optimizations in the flow-sheet to prevent adsorption of Zr or to strip Zr might be required.

Ce was immediately stripped by supplying H₂O and it was separated from other FPs whereas Eu was scarcely eluted through the column operation. According to the published data [3,6,7], MA(III) are expected to be eluted between the peaks of Ce and Eu [8]. This result showed that MA(III) are possibly remained in the column as well as Eu.

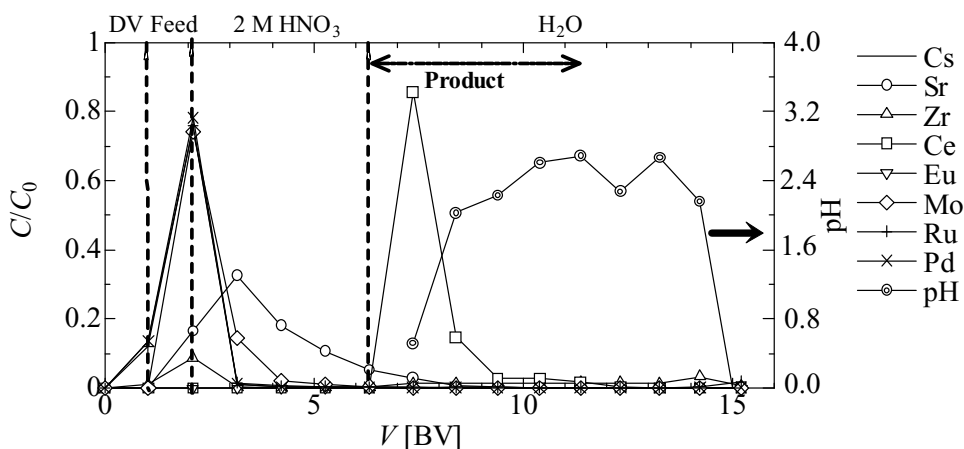


Fig. 4 Elution curves obtained from the column experiments with the reference adsorbents

The elution curves using the improved adsorbent ([TODGA]=20wt%, degree of the cross linkage=10%) are shown in Fig. 5. Different from the elution curves of the reference adsorbent, Eu was successfully stripped by H₂O. However, large part of Ce eluted from the column with the feed solution. The previous report has shown that the lighter Ln(III) were easily stripped from the TODGA/SiO₂-P adsorbent column by supplying H₂O[3,7]. Therefore, decrease in the concentration of TODGA should lead the early breakthrough of Ce as a result of competitive adsorption among Ln(III). The breakthrough of Sr observed in the optimized column experiment

must be due to the same reason. It is considered that MA(III) are adsorbed by TODGA/SiO₂-P adsorbent column, and recovery yield of them should be greater than that obtained in the previous study.

Material balances and decontamination factors (DF) of elements calculated from the elution curves are shown in Table 2. Material balances were the ratios of sum of the eluted amount to the amount fed. In calculation of decontamination factors, MA(III) were assumed to recover at the first 5 BV of the fraction of H₂O eluent .

Desorption property of the TODGA/SiO₂-P adsorbent was successfully improved by optimizing the composition of the adsorbent since the material balance of Eu drastically increased. In addition to that, DF of some elements (Cs, Mo, Ru and Pd) which were not adsorbed by TODGA were also improved by the optimization. 20 % of Ln still remains in the adsorbents and material balances of some elements are still low, thus further optimization of the adsorbents such as improvements in pore and/or particle sizes of SiO₂-P may be required. As well as the additional optimization, separation experiments using a genuine HLLW is also necessary to confirm the improved performance of the adsorbent for MA(III).

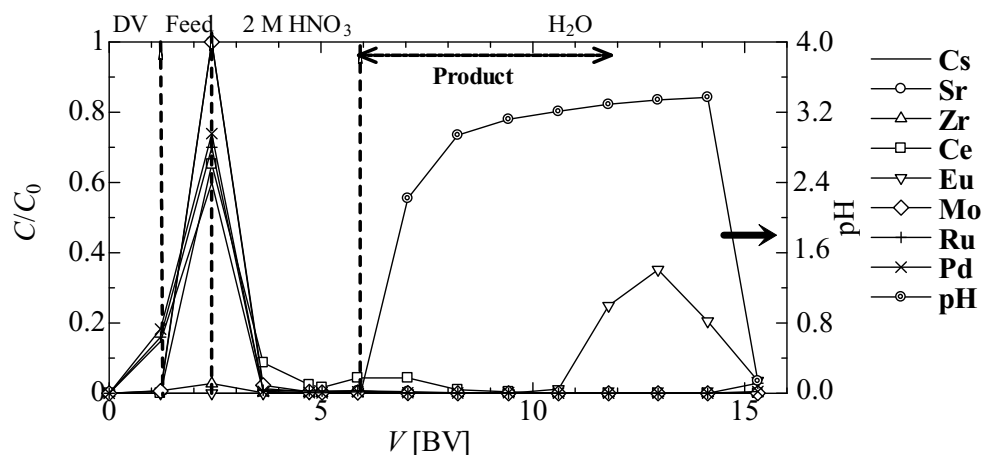


Fig. 5 Elution curves obtained from the column experiments with the improved adsorbents

Table 2 Material balance and decontamination factors obtained by column separation experiments

	Before the optimization		After the optimization	
	Material balance [%]	DF	Material balance [%]	DF
Cs	93.1	289	81.4	9461
Sr	88.6	24	102.8	156
Zr	25.0	14	4.0	384
Ce	106.8	1	85.0	18
Eu	< 1.1	> 269	82.6	4
Mo	98.9	982	103.4	2036
Ru	96.2	88	90.9	1506
Pd	96.8	125	94.2	224

4. Conclusion

The composition of the TODGA/SiO₂-P adsorbent for extraction chromatography technology for MA(III) recovery were optimized to enhance desorption efficiency of MA(III) from the adsorbent. Batchwise adsorption/elution experiments revealed that 20wt% of the adsorbent concentration impregnated and 10% of cross linkage of polymer gave better desorption ratio than the reference adsorbent. Column separation experiments using an inactive simulated solution were also carried out to confirm the effect of the optimization; better recovery yield of Eu and decontamination factors of several elements. Column separation experiments with an active solution containing of MA(III) is needed in order to confirm the improved performance of the adsorbent for MA(III).

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