

Novel Separation of Samarium, Europium and Gadolinium Using a Column Packed with Microcapsules Containing 2-Ethylhexylphosphonic Acid Mono-2-Ethylhexyl Ester

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In this study, we paid attention to separate and recover samarium, europium and gadolinium, which are typical rare-earth metals. Since rare-earth metals have almost the same property, it is very difficult to separate them from each other. Instead of using conventional solvent extraction and ion-exchange methods, a microcapsule method was employed in this work. Chemical method has generally been used in preparing microcapsules. We used here *in situ* polymerization method among them.

In this study, a fundamental investigation of the mutual separation of samarium, europium and gadolinium from an aqueous solution by using microcapsules containing a metal extractant was undertaken. As the extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) was used. The extractant was successfully encapsulated in microcapsules during *in situ* microencapsulation process. Metals extractabilities into the microcapsules were examined from metal ions extraction isotherm. The extraction behaviour of the metals was well explained by using the Langmuir adsorption isotherm model. According to the Langmuir adsorption model, the saturation amount of metal extracted and the extraction equilibrium constant were determined. The microcapsules containing EHPNA were found to be suitable for the extraction of the rare-earth metals. Using a reactor in which two columns packed with the microcapsules are connected in series, the separation and recovery of the metals was examined. In this way, the mutual separation of the rare-earth metals could be almost achieved by feeding a suitable eluent stepwise into the column.

1. Introduction

In recent years, several methods have been in great demand for various functional materials. In particular, rare-earth metals play very important roles as components of electronic products and so on. However, rare-earth metals as well as some other valuable metals cannot be obtained as raw materials in Japan. Therefore, it becomes more important to recover these valuable metals from wastes. The increase in the industrial demands for rare-earth metals will result in an increase in the need for their recycling. From industrial waste treatment processes, dilute aqueous solutions containing rare-earth metals will be obtained. Therefore, it is important to develop a technology to recover and separate rare-earth metals from such dilute solutions. Solvent extraction is an effective process for the treatment of dilute solutions (Narita et al, 2006). However, the conventional solvent extraction technique has some disadvantages, i.e. the formation of third phases and difficulty of back extraction.

For the last several decades, alternative techniques to solvent extraction for recovery of metals from dilute solutions have been developed. Metal adsorption technique using microalgae (Kondo et al, 2012), supported liquid membranes (Fu et al, 2004), emulsion liquid membranes (Kondo and Matsumoto, 1998), solvent impregnated resins (Cortina and Warshawsky, 1997) and microcapsules containing metal extractant (Yoshizawa et al, 1995) are typical examples. Among these techniques, we have investigated a microcapsule method to recover and separate precious metals (Kondo et al, 2010). The metals are

extracted by the microcapsules to quite high loadings. In addition, the separation of the precious metals could be achieved by using a column packed with the microcapsules.

In this study, we focused on the extraction and the separation of the rare-earth metals using microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) as an extractant. Using a reactor in which two columns packed with the microcapsules containing EHPNA are connected in series, the separation and the recovery of samarium, europium and gadolinium was examined.

2. Experimental

2.1 Reagents

EHPNA was kindly supplied from Daihachi Chemical Industry Co., Ltd. (Osaka, Japan). This was used without further purification. Divinylbenzene (DVB), employed as a monomer to form the shell of the microcapsule, was used after distillation to remove contaminants. Toluene was used as the diluent for the extractant. 2,2'-Azobis(2,4-dimethylvaleronitrile) (ADV N) was used as the polymerization initiator. This was a special grade chemical and used without further purification.

Aqueous solutions were prepared using 100 mol/m³ HCl and 100 mol/m³ CH₃COONa containing the desired amount of metal ions. The pH of the aqueous solutions was adjusted by using a pH meter (Horiba F-21). All of the metal chlorides used were of special grade chemicals. In this study, three metal ions (Sm³⁺, Eu³⁺ and Gd³⁺) were used as model species of rare-earth metals.

2.2 Preparation of microcapsules

The reactor for preparation of the microcapsules was a mixing vessel with four baffle plates having a capacity of 1 × 10⁻³ m³. The continuous phase was 900 g distilled water containing 2% w/w Arabic gum, which is used as a dispersion stabilizer. It was stirred using a flat paddle in the vessel. After the temperature of the continuous phase reached 343 K, the dispersed phase consisting of DVB, ADVN, toluene and EHPNA was added to the continuous phase. The reactor was purged with nitrogen gas and the contents were agitated at 300 rpm for 3 h at 343 K under nitrogen atmosphere to make the microcapsules through *in-situ* radical polymerization of DVB. The composition of the dispersed phase is given in Table 1. The obtained microcapsules were collected by suction filtration, washed with distilled water, and then dried at room temperature.

Table 1: Preparation condition of MC

	Materials	weight
Continuous phase	Distilled water	882 g
	Arabic gum	18.0 g
Dispersed phase	DVB	15.0 g
	ADV N	3.6 g
	EHPNA	18.8 g
	Toluene	18.8 g

2.3 Extraction equilibria

Extraction equilibrium experiments were carried out batchwise: 0.05 g microcapsules containing EHPNA and 10 cm³ of aqueous solution containing each metal ion were contacted in a glass tube for over 24 h to attain equilibrium. The initial metal concentration was 1.0 mol/m³ for all metals. The glass tubes were shaken in a thermostat bath at 303 K. The pH and the metal concentration in the aqueous solution before and after equilibrium were measured with a pH meter and by inductively coupled plasma spectrometry (ICP-AES; ICPS-8000, Shimadzu Corp.), respectively. The metal concentration extracted into the microcapsules was calculated from the mass balance before and after equilibrium.

Extraction isotherms for the metal ions using the microcapsules containing EHPNA were determined. The temperature was kept constant at 303 K during the experiments. The pH of the aqueous solution before extraction of the metals was 3.5. The pH change in the aqueous solution during the extraction was within 0.1. The resulting isotherms were analyzed by using the following Langmuir adsorption isotherm model.

$$q = \frac{Kq_{\infty}C_{eq}}{1 + KC_{eq}} \quad (1)$$

Where K and q_{∞} are the apparent extraction equilibrium constant and the saturation amount of metal extracted, respectively, and C_{eq} is the metal concentration at equilibrium. The Langmuir constants, K and q_{∞} , were determined from the reciprocal plot of Equation (1) using the least square method. The extraction ability of each metal was easily estimated from the K value.

2.4 Column operation

A glass column of 15 mm inner diameter packed with 5.0 g of microcapsules containing the extractant was used. The bed height of the column was about 50 mm. The experimental apparatus was composed of two columns connected in series.

2.4.1 Metal adsorption to the column

After the columns had been conditioned, the aqueous solution containing three metal ions was continuously introduced into the column at a constant flow rate of 2.0 mL/min. The concentration of each metal ion was $5.0 \times 10^{-3} \text{ mol/dm}^3$. The pH of the aqueous solution was 3.0, which was adjusted by using $0.1 \text{ mol/dm}^3 \text{ HCl}$ and $0.1 \text{ mol/dm}^3 \text{ CH}_3\text{COONa}$ aqueous solutions. The samples exiting the column were collected at appropriate time intervals. The metal concentrations in the samples were measured by ICP-AES and so the breakthrough curves were obtained.

2.4.2 Metal elution from the column

Thereafter, the elution and the separation of the metals from the column were investigated. The column in which the metal ion loaded microcapsules were packed was firstly rinsed with distilled water, and then the metal ions were washed out with a stripping solution. In this study, highly acidic hydrochloric acid solution was used as the stripping solution. No leakage of the extractant from the column was observed under the experimental conditions. The metal elution experiments were carried out in various modes as will be described in subsection 3.2.2.

3. Results and discussion

3.1 Extraction equilibria

As mentioned before, it was found that the microcapsules containing EHPNA are suitable for extraction of the rare-earth metals. In addition, it was found that the extractability of each metal ion increases with increasing the pH of the aqueous solution. Figure 1 shows the adsorption isotherm of samarium. As to europium and gadolinium, similar adsorption behaviours to samarium were obtained.

From these results of the extraction isotherms for the metals with the microcapsules containing EHPNA, the Langmuir constants were determined and are given in Table 2. As is expected, the values of the apparent extraction equilibrium constant, K and the saturation amount of metal extracted, q_{∞} were increased with increasing in pH value for each metal.

3.2 Column operation

3.2.1 Metal adsorption to the column

Figure 2 shows the breakthrough curves of the metal ions when using only one column packed with the microcapsules. As shown in Figure 2, the adsorption behaviours of Sm^{3+} , Eu^{3+} and Gd^{3+} are very similar to each other so that the separation of the three metal ions was very difficult in this adsorption step. The results were as expected because the properties of the three metals are almost the same.

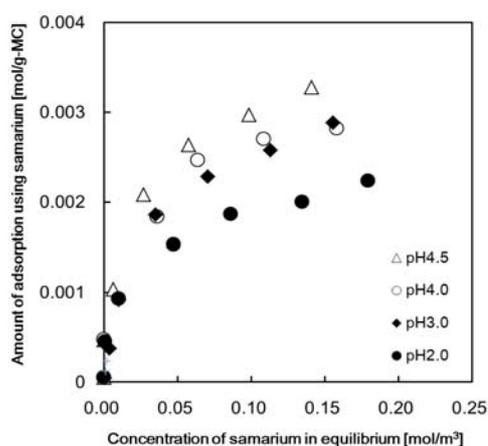


Figure 1: Adsorption isotherm of samarium

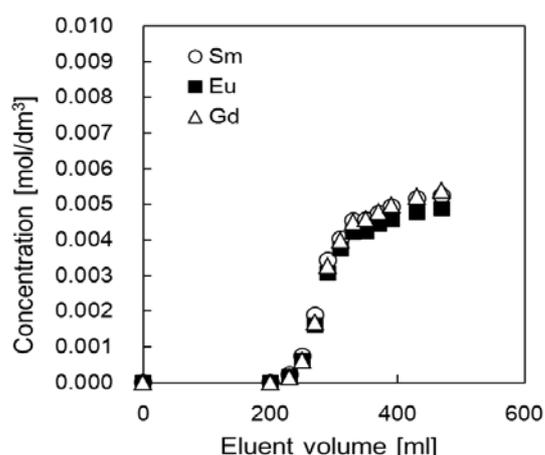


Figure 2: Breakthrough curve of metals

Table 2: Langmuir adsorption constants, q_{∞} and K for each metal

pH	Samarium		Europium		Gadolinium	
	q_{∞} [mol/g-MC]	K [(mol/m ³) ⁻¹]	q_{∞} [mol/g-MC]	K [(mol/m ³) ⁻¹]	q_{∞} [mol/g-MC]	K [(mol/m ³) ⁻¹]
2.0	2.55×10^{-3}	2.11×10	1.47×10^{-3}	5.82×10	2.86×10^{-3}	3.53×10
3.0	3.10×10^{-3}	2.89×10	1.59×10^{-3}	9.46×10	3.14×10^{-3}	3.65×10
4.0	3.33×10^{-3}	3.73×10	2.15×10^{-3}	2.50×10^2	3.19×10^{-3}	4.14×10
4.5	4.11×10^{-3}	4.45×10	2.51×10^{-3}	3.92×10^2	3.58×10^{-3}	5.05×10

3.2.2 Metal elution from the column

Figure 3 shows the elution curves of the metals extracted in the column packed with the microcapsules (Figure 2) when using HCl solution of pH 1.15. We have tried a similar metal elution experiment using HCl solution of pH 0.95, but the separation efficiency between the three metal ions was not so good. It was found from Figure 3 that the existing ratio of Sm³⁺ in the solution eluted from the column was about 91%. And those of Eu³⁺ and Gd³⁺ were 8% and 1%, respectively.

In order to enhance the separation efficiency, the elution experiment using the two columns in which the three metals were loaded was examined. Figure 4 shows the experimental result in which 93 % of Sm³⁺ was desorbed together with 56 % of Eu³⁺ and 23 % of Gd³⁺ from the columns. The existing ratio of Sm³⁺ in the solution eluted from the column was 55 % which showed that the separation was not enough. The effluent volume 1000 mL from the column in Figure 4 is named Solution 1.

Figure 5 shows the result in the case that Solution 1 was supplied to the column with an adjusted pH to 1.15. As shown in Figure 5, the recovery ratios of the metals were 99 % for Sm³⁺, 79 % for Eu³⁺ and 9.5 % for Gd³⁺, respectively.

The result in the case that a solution containing only Sm³⁺ and Eu³⁺ was supplied to the column is shown in Figure 6. The separation between Sm³⁺ and Eu³⁺ was achieved almost completely in this operation and the recovery ratio of each metal ion was 97 % for Sm³⁺ and 39 % for Eu³⁺, respectively.

The result in the case that a solution containing only Eu³⁺ and Gd³⁺ was supplied to the column is shown in Figure 7. It was found from Figure 7 that the separation between Eu³⁺ and Gd³⁺ was incomplete. And the recovery ratio of each metal ion was almost 100 % for Eu³⁺ and 99 % for Gd³⁺, respectively.

Taking the result of Figure 7 into consideration, the experiment changing the pH in the feed solution containing only Eu³⁺ and Gd³⁺ was examined. The result in the case that the pH of the feed solution was 0.95 is shown in Figure 8 where the two elution curves (Eu³⁺ and Gd³⁺) were overlapped showing that the separation between two metal ions was also incomplete. So we separate the eluted solution from the column into two parts; one is Eu³⁺ rich solution (A) and the other is Gd³⁺ rich solution (B).

The result in the case that the solution A whose pH is 1.05 was supplied to the column is shown in Figure 9. The recovery ratio of each metal ion was almost 100 % for Eu³⁺ and 98 % for Gd³⁺, respectively, but Eu³⁺ and Gd³⁺ were not separated completely in each other.

The result in the case that the solution B whose pH was 1.05 was supplied to the column is shown in Figure 10. The recovery ratio of each metal ion was almost 100 % for Eu³⁺ and 97 % for Gd³⁺, respectively. We could conclude from the results of Figure 10 that Eu³⁺ and Gd³⁺ were separated almost completely in each other.

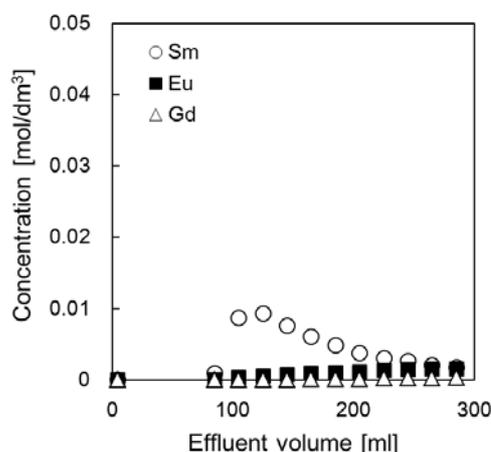


Figure 3: Elution curve of metals
(Eluent: pH 1.15 HCl, Flow rate: 2.0 mL/min)

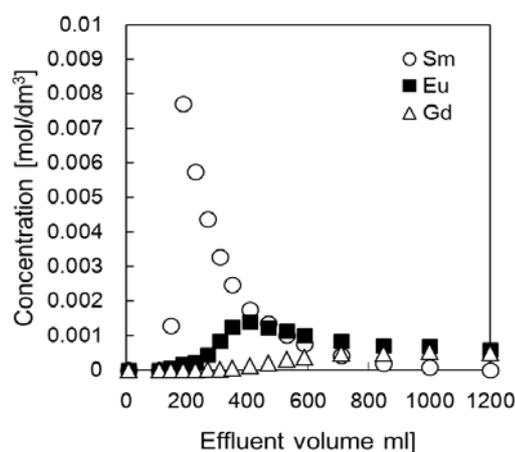


Figure 4: Elution curve of metals (2 columns,
Eluent: pH 1.15 HCl, Flow rate: 2.0 mL/min)

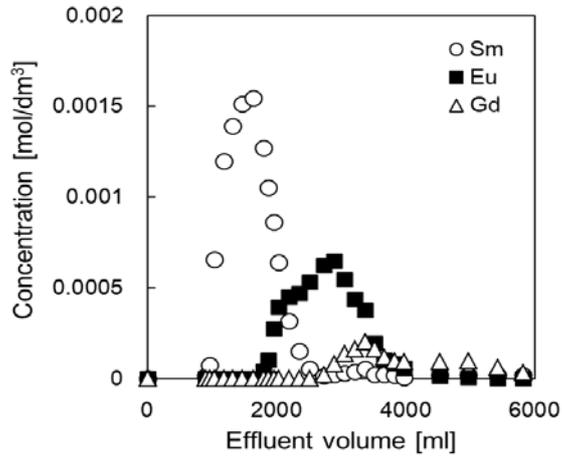


Figure 5: Elution curve of metals (2 columns, Eluent: pH 1.15 HCl, Flow rate: 2.0 mL/min)

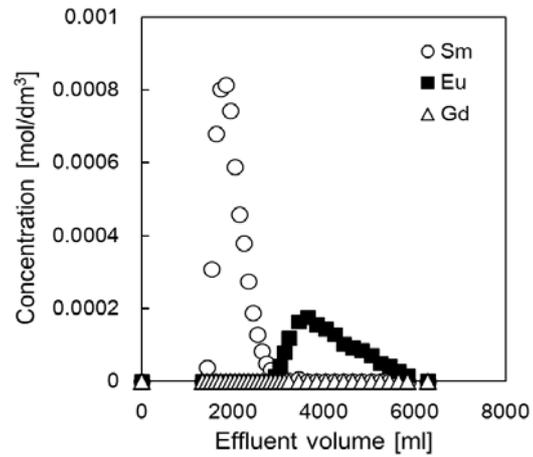


Figure 6: Elution curve of metals (2 columns, Eluent: pH 1.15 HCl, Flow rate: 2.0 mL/min)

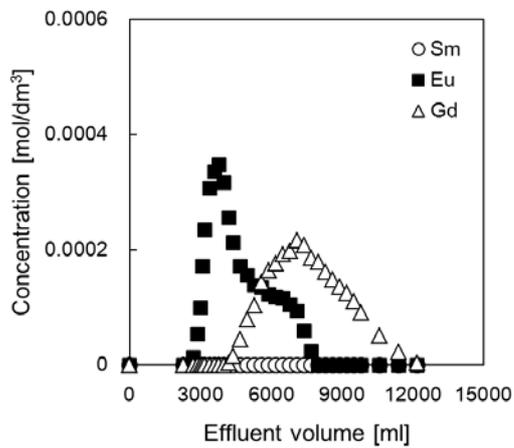


Figure 7: Elution curve of metals (2 columns, Eluent: pH 1.15 (HCl+CH₃COONa), Flow rate: 2.0 mL/min)

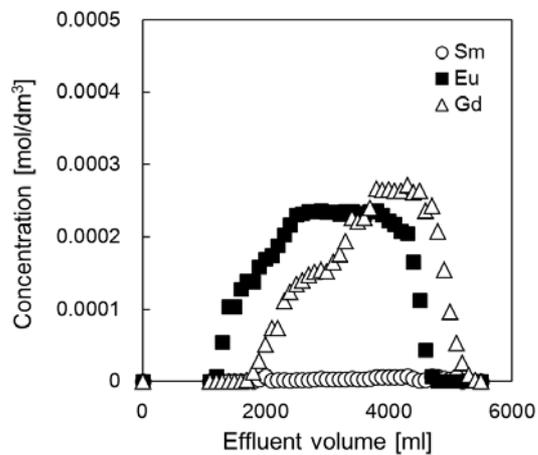


Figure 8: Elution curve of metals (2 columns, Eluent: pH 0.95 HCl, Flow rate: 2.0 mL/min)

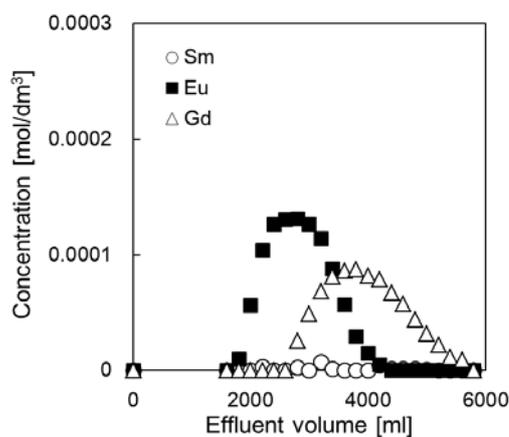


Figure 9: Elution curve of metals (2 columns, Eluent: pH 1.05 (HCl+CH₃COONa), Flow rate: 2.0 mL/min)

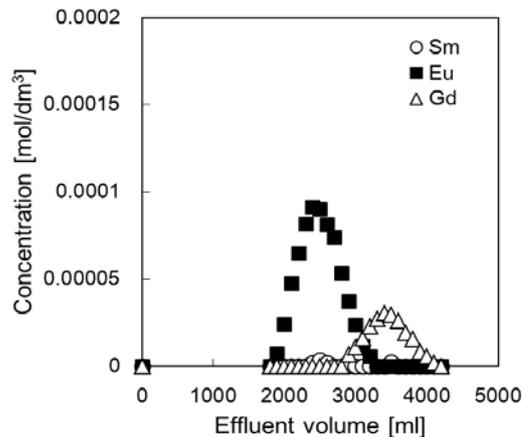


Figure 10: Elution curve of metals (2 columns, Eluent: pH 1.05 (HCl+CH₃COONa), Flow rate: 2.0 mL/min)

As mentioned above, we could perform approximately the separation of Sm^{3+} , Eu^{3+} and Gd^{3+} by using the microcapsules method proposed here.

4. Conclusions

In this study, the extraction and separation of rare-earth metals, that is, Sm^{3+} , Eu^{3+} and Gd^{3+} by using the microcapsules containing EHPNA was investigated. As the result, the following information was obtained.

(1) The extraction behaviour of the metals into the microcapsules was well explained by using the Langmuir adsorption isotherm model. The values of the apparent extraction equilibrium constant, K and the saturation amount of metal extracted, q_{∞} were increased with increasing in pH value for each metal.

(2) By using a reactor in which two columns packed with the microcapsules containing EHPNA connected in series, the mutual separation of the rare-earth metals could be almost achieved by feeding a suitable eluent into the column. Firstly, by feeding the solution containing the three metals whose pH was adjusted to 1.15 to the column, Sm^{3+} was almost completely separated from Eu^{3+} and Gd^{3+} . Next, by feeding the solution containing only Eu^{3+} and Gd^{3+} whose pH was 1.05 to the column, the results in which the recovery ratio of each metal ion was almost 100 % for Eu^{3+} and 97 % for Gd^{3+} were obtained.

The information obtained in the study will through new light upon the separation technique of rare-earth metals from other ones in the field of hydrometallurgy or in the recycling of such metals from waste materials. Conclusively, the microcapsule method proposed in this work is a superior one to the solvent extraction and ion-exchange methods.

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