Separation and Recovery of Scandium and Yttrium from Aqueous Chloride Media by Integrated Ion Exchange Method

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Separation of scandium (Sc) and yttrium (Y) using solvent-impregnated resin (SIR) containing bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) along with 1-octanol as a modifier was investigated. 1-Octanol was added to enhance stripping efficiency, since stripping of heavy rare earths from the organic solution containing organophosphorus extractants is difficult. The coated SIR was applied to both batch and chromatographic recovery of Sc and Y. The adsorption of Sc followed the Langmuir isotherm model. Separation of Sc from Y was achieved by employing chromatographic adsorption system together with quantitative elution from SIR by 5 mol/L HCl.

1. Introduction

Scandium (Sc) and yttrium (Y) are parts of rare earths, providing excellent characteristics for industrial applications, such as batteries and laser crystals. Although Sc is abundant in the earth's crust, it is produced only as a by-product during processing of various ores at low concentrations, or in combination with a variety of minerals, not only as a pure metal [1,2]. In countries such as Japan, which has the world’s second-largest demand for rare earths, most of which are imported from China, the development of highly efficient separation and recovery processes from waste materials has become critical in terms of resource sustainability and securement.

Separation of rare earths is generally performed by hydrometallurgical processes, such as solvent extraction and ion exchange. Solvent extraction is widely used due to its advantage such as high speed, simple processing, and scalability. However, it is environmentally harmful, since it requires a large amount of organic solvent [3-5]. Ion exchange has lower selectivity than solvent extraction. However, owing to low environmental load, high adsorption capacity from dilute solution, and easy handling, various types of ion exchange resins were investigated for this purpose [6-8].

Solvent impregnated resin (SIR) is an alternative separation method that is environmentally friendly and relatively easy to prepare, incorporating the unique features and advantages bridging solvent extraction and ion exchange. The main disadvantage of SIR is however the loss of extractant from the resin due to the solubility of the extractant to the aqueous phase, which can be suppressed by coating with polymer and chemical crosslinking [9-11].

Generally, organophosphorus extractants are employed to separate rare earths. However, stripping of heavy rare earths from loaded organophosphorus extractants is quite difficult. Although stripping of metals...
from phosphinic acid extractant is easier than those from phosphoric acid and phosphonic acid extractants, because of low acidity, we found that the highest stripping rate of Sc with hydrochloric acid from the loaded organic phase containing phosphinic acid extractant was still less than 80% [12-14]. Considerable enhancement in stripping efficiency could be attained in organophosphorus extractant system by adding a modifier into the organic phase, despite a small loss of loading capacity, since such modifier prevents dimerization of the extractant and formation of metal-extractant complexes. In the stripping of Sc in the solvent extraction system, 1-octanol as a modifier was added to the organic phase to suppress the Sc extraction as well as to enhance the stripping efficiency in a multistage process [16].

In the present study, the extraction and stripping of Sc and Y by SIR have been investigated, employing bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) along with 1-octanol as the modifier. SIR was employed in both batchwise adsorption and chromatographic separation of Sc from Y.

2. Experiments

2.1 Reagents

Cyanex 272 was supplied by Cytec Solvay Japan Co., Ltd (Tokyo, Japan). Purities of the extractant were measured by potentiometric titration with NaOH, to be determined as 87.1 wt% with 12.9 wt% of tris(2,4,4-trimethylpentyl)phosphine oxide. Scandium oxide and yttrium oxide were supplied by Nippon Yttrium Co., Inc. (Fukuoka, Japan), and were used followed by dissolving in 1 mol/L HCl solution. DIAION HP2MG (macroporous methacrylate polymeric resin) was supplied by Mitsubishi Chemical Corporation (Tokyo, Japan). All other organic and inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents.

2.2 Preparation of coated SIR

Preparation of SIR and coating of SIR were carried out in the manner described in the previous work [15]. The support resin, HP2MG (40 g), was first washed by dipping in methanol (400 mL) and dried overnight. Washed HP2MG (40 g) was immersed in a solution of acetone containing different amounts of Cyanex 272 and 1-octanol (50 mL) for 24 h. Concentration of Cyanex 272 and 1-octanol used for the preparation of SIR in the present work are shown in Table 1. Acetone was then completely evaporated to produce an SIR impregnated with Cyanex 272 and 1-octanol.

Coating of SIR was then carried out using polyvinyl alcohol (PVA, average polymerization degree 2000) and glutaraldehyde (GA). The prepared SIR (3 g) was immersed in an aqueous solution (50 mL) containing 3 wt% PVA and 1 wt% acetic acid and the mixture was shaken for 17 h. The resulting suspension was then mixed with 1 mol/L KCl aqueous solution (10 mL) and the mixture was shaken for 24 h. The pretreated SIR was filtered, followed by adding 0.32 mol/L H2SO4 solution (10 mL) and standing for 1 hour. Then 0.32 mol/L GA solution (10 mL) was added and the mixture was shaken for 24 h to complete crosslinking. The coated SIR obtained was filtered, washed with deionized water, and then dried. SIR used in this study was all coated SIR.

2.3 Determination of impregnation amount of Cyanex 272

A piranha solution was prepared by mixing 15 mL of concentrated H2SO4 in 5 mL of 30% H2O2. SIR (20 mg), before coating, was added to 20 mL of the piranha solution, and the resin was completely dissolved by heating and stirring at 323 K using a hot stirrer. Concentration of P in the resultant solution was determined
by ICP-AES (Shimadzu ICPE-9000). Since one Cyanex 272 molecule has one P molecule, the impregnation amount of Cyanex 272 was calculated by the following Eq.(1).

\[
\text{Impregnation amount of Cyanex 272 (mmol/g)} = \frac{[P]}{w} \cdot \frac{20}{1000}
\]  

where \([P]\) is the concentration of P measured by ICP-AES (mmol/L), \(w\) is the amount of SIR (g). The impregnation amount of 1-octanol was determined by the material balance after subtracting the impregnation amount of acetone.

\[
\text{Impregnation amount of 1-octanol (mmol/g)} = \frac{w_{\text{eq}} - w_{\text{ini}} - w_{\text{sol}} - I_{\text{Cyanex272}} \cdot M_{\text{Cyanex272}} \cdot w}{M_{1\text{-octanol}}} 
\]

where \(w_{\text{eq}}\) is the weight of resin after impregnation (g), \(w_{\text{ini}}\) is the weight of resin before impregnation (g), \(w_{\text{sol}}\) is the weight of acetone in the resin (g), \(I_{\text{Cyanex272}}\) is the impregnation amount of Cyanex 272 (mmol/g), \(M_{\text{Cyanex272}}\) is the molecular weight of Cyanex 272 (g/mol), and \(M_{1\text{-octanol}}\) is the molecular weight of 1-octanol (g/mol). The impregnation amount of SIR determined is summarized in Table 1.

| Organic solvent (Cyanex 272/1-octanol) | Impregnation amount of Cyanex 272 (mmol/g) | Impregnation amount of 1-octanol (mmol/g) |
|--------------------------------------|------------------------------------------|-----------------------------------------|
| (a) 0.05 mol/L/0.00 mol/L            | 0.74                                     | 0                                       |
| (b) 0.05 mol/L/0.01 mol/L            | 0.76                                     | 0.34                                    |
| (c) 0.05 mol/L/0.03 mol/L            | 0.80                                     | 0.74                                    |

### 2.4 Batch adsorption

Aqueous solution of the rare earths of 1 mmol/L was prepared with HCl solution, and the pH was adjusted using HCl and NaOH. The SIR (20 mg) was added to 20 mL of aqueous solution in a 50 mL Erlenmeyer flask, and the suspended mixture was shaken at 298 K for 24 h. After filtering the resin, the concentrations of the metal ions were determined with ICP-AES. Equilibrium pH was measured by pH meter (Horiba F-74). The adsorption amount of the rare metals, \(q\) (mmol/g), is defined as:

\[
q = \frac{([M^{3+}]_{\text{ini}} - [M^{3+}]_{\text{eq}}) \cdot L}{w}
\]

where \([M]_{\text{ini}}\) and \([M]_{\text{eq}}\) are initial and equilibrium concentrations of metals in the solution (mmol/L), respectively, \(L\) is the volume of the solution (L), and \(w\) is the weight of the resin (g).

Elution experiment was performed by immersing 20 mg of metal loaded SIR from batch experiment to 20 mL of 1 – 3 mol/L HCl in a 50 mL Erlenmeyer flask. The suspended mixture was shaken at 298 K for 24 h. After filtering the resin, the concentration of the metal ions was determined with ICP-AES. The elution rate was calculated by the Eq.(4):

\[
\text{Elution rate (\%)} = \frac{[M^{3+}] \cdot L}{q \cdot w} \times 100
\]
2.5 Column adsorption

SIR (weight = 1.0 g, wet volume = 2.71 mL) was packed into a glass column of 100 mm in length and 8 mm in diameter, and then deionized water was fed to the column to wash the adsorbent for 12 h. Aqueous feed solution containing [Sc^{3+}] = [Y^{3+}] = 1 mmol/L at pH_{ini} = 1.45 was fed to the column at flow rate of 0.18 mL/min {space velocity (S.V.) = 6 h^{-1}}, using a peristaltic pump (EYELA KP-11). The metal ions loaded into the columns were eluted with 5 mol/L HCl, determined by the preliminary study comparing various acids and bases. The effluents were collected with a fraction collector (EYELA DC-1500). The number of bed volumes of the effluent is defined as:

\[ \text{Bed Volume} = \frac{v \cdot t}{V} \quad (5) \]

where \( v \), \( t \), and \( V \) are the flow rate of the solution (mL/min), time the solution was applied (min), and the wet volume of the adsorbent (mL).

3. Results and Discussion

3.1 Batchwise adsorption of Sc and Y

The SIRs prepared in the present work were first applied for batchwise adsorption of Sc and Y. Figure 1 shows the effect of pH on the adsorption amount of Sc and Y. In all cases, almost no adsorption of Y was observed, while Sc was adsorbed with high adsorption amount in the pH range investigated. When comparing the adsorption amount of Sc with the different SIRs, the adsorption amount was slightly decreased by increasing the amount of 1-octanol in the SIR. However, the effect of 1-octanol to decrease in the adsorption of Sc is decreased compared with that observed in the conventional solvent extraction system [16]. The decrease in the adsorption/extraction ability for metals by adding 1-octanol is caused by the decrease in the dimerization of the extractant. In the SIR system, however, most of the diluent evaporated, leading the extractant exists as monomeric species in the support resin, and thus the effect of addition of 1-octanol was decreased.

Adsorption isotherms of Sc with the SIRs were then investigated at equilibrium pH = 1.58 ± 0.07, 1.54 ± 0.06, 1.53± 0.06, respectively. The isotherms obtained are shown in Figure 2. Assuming that the adsorption is of Langmuir mechanism, as shown in Eq. (6),

\[ q = \frac{q_0 \cdot K \cdot [M]}{1 + K \cdot [M]} \quad (6) \]

then linearized Langmuir equation can be obtained, as Eq. (7).

\[ \frac{[M]}{q} = \frac{1}{q_0} [M] + \frac{1}{q_0 \cdot K} \quad (7) \]

where \( q_0 \) is the maximum adsorption amount (mmol/g) and \( K \) is the adsorption equilibrium constant (L/mmol). The linearized relationship of the adsorption isotherm data was also shown in Figure 2, and the data fitted well to the Langmuir adsorption model. The maximum adsorption amount and adsorption equilibrium constant are summarized in Table 2. Almost the same maximum adsorption amount was obtained with SIR (a) and (b), while it is dramatically decreased in the case of SIR (c). In the previous work on the solvent extraction of Sc and Y by Cyanex272 as an extractant and 1-octanol as a modifier [16], the stoichiometry of extractant to metal ion in the metal complex is 6:1 (form ScR\_3(RH)\_3). In this work, the stoichiometry of
extractant to metal ion was almost 4:1 (form ScR_3RH). This means that insufficient stoichiometry of extractant to metal ion is allowed in the SIR micropore.

Figure 1. Effect of pH on adsorption of Sc and Y by SIRs with different concentrations of organic solvent (Cyanex 272/1-octanol); (a) 0.05 mol/L/0.00 mol/L (b) 0.05 mol/L/0.01 mol/L, and (c) 0.05 mol/L/0.03 mol/L.

Figure 2. Langmuir isotherm model of SIRs with different concentrations of organic solvent (Cyanex 272/1-octanol); (a) 0.05 mol/L/0.00 mol/L (b) 0.05 mol/L/0.01 mol/L, and (c) 0.05 mol/L/0.03 mol/L.

Table 2. Maximum adsorption amount and adsorption equilibrium constant of Sc with SIRs.

| SIR                  | q_0 (mmol/g) | K (L/mmol) |
|----------------------|--------------|------------|
| (a) 0.05 mol/L/0.00 mol/L | 0.179±0.043  | 31.6±0.8   |
| (b) 0.05 mol/L/0.01 mol/L | 0.176±0.050  | 32.1±1.0   |
| (c) 0.05 mol/L/0.03 mol/L | 0.124±0.017  | 33.1±1.0   |

Elution of Sc from the loaded SIRs with different concentration of HCl was then investigated. The elution rate obtained is summarized in Figure 3. In all SIRs, the elution rate was increased with increasing
HCl concentration, although quantitative elution was not achieved from SIRs (a) 0.05 mol/L/0.00 mol/L or (b) 0.05 mol/L/0.01 mol/L. In the case of the SIR (c) 0.05 mol/L/0.03 mol/L; however, complete elution was achieved with 5 mol/L HCl solution. These results are consistent to the maximum adsorption amount shown in Table 2, indicating excess amount of 1-octanol in the SIR can decrease adsorption ability of Sc and can therefore increase elution rate of Sc.

Figure 3. Elution rate of Sc with HCl solution from SIRs impregnated with different concentration of organic solvent (Cyanex 272/1-octanol); (a) 0.05 mol/L/0.00 mol/L (b) 0.05 mol/L/0.01 mol/L, and (c) 0.05 mol/L/0.03 mol/L.

3.2 Column adsorption of Sc and Y

Column adsorption of Sc and Y from binary solution was investigated. In this case, the SIR (b) 0.05 mol/L/0.01 mol/L was used as adsorbent, and adsorption – elution processing was repeated for three times. Adsorption was carried out by frontal mode, and then the loaded metals were eluted by 5 mol/L HCl solution. Figure 4 shows breakthrough and elution curves of the metals in each cycle. In the case of the 1st cycle, Sc was completely adsorbed until bed volume of ca. 40, while Y was hardly adsorbed and was immediately broken through. Complete elution of both metals was also achieved with 5 mol/L HCl solution. In the cases of the 2nd and 3rd cycles, however, adsorption amount of Sc was decreased, compared to the 1st cycle, to 84% and 69%, respectively. In addition, elution rate of Sc was also decreased to 87% and 85%. This might be due to the leakage of 1-octanol, and incomplete elution of Sc at the 2nd cycle leads dramatical decrease in the adsorption amount in the 3rd cycle.
Figure 4. Breakthrough and elution curves of Sc and Y with SIR impregnated with different concentrations of organic solvent (Cyanex 272/1-octanol); (b) 0.05 mol/L/0.01 mol/L. (a) 1st cycle (b) 2nd cycle (c) 3rd cycle.

4. Conclusion

Separation and recovery of Sc and Y with SIR impregnating Cyanex 272 together with 1-octanol was investigated with the following results. Sc was successfully adsorbed with the all SIRs, while Y was hardly adsorbed. The adsorption amount of Sc was decreased with SIR (c) 0.05 mol/L/0.03 mol/L, and thus complete elution of Sc from the adsorbent was achieved with 5 mol/L HCl. Adsorption of Sc by SIRs was of Langmuir adsorption model. SIR could be applied for chromatographic separation of Sc and Y. Sc was selectively adsorbed with SIR by frontal mode operation, while Y was hardly adsorbed. Sc adsorbed was completely eluted with 5 mol/L HCl. The adsorption amount and elution rate were however decreased with repeated use of SIR, likely due to the leakage of 1-octanol during the processing.

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