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Separation of rare earths in nitric acid medium by a novel silica-based pyridinium anion exchange resin

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Abstract

To separate rare earths in nitric acid medium by anion exchange process, a novel silica-based macro-reticular anion exchange resin (SiPyR-N4) with pyridinium as functional group has been synthesized. It was found that the SiPyR-N4 resin exhibits a quite strong adsorption for some rare earths especially the light rare earth elements such as La, Ce, Pr, Nd and Pm whose distribution coefficients onto SiPyR-N4 reach 10–25 dm^3/kg-resin, which are much higher than the reported values for these elements with conventional anion exchange resins. The results from the column experiments show that the rare earths can be separated into the three groups: light, moderate and heavy rare earths and, a perfect separation between La–Pr group and Sm–Gd group can be achieved.

Keywords: Metals; Polymers; Molecule

1. Introduction

Although an ion exchange process has many advantages such as organic solvent free and little waste generation, compacted equipment, simple operation procedure and economical improvement [1–3], ion exchange technology has not been applied for industrial use as a main rare earths separation process due to its slow adsorption and elution kinetics for conventional anion exchange resins with quaternary ammonium as functional group [4,5], and to the instability of organic resin in a strong acid medium. Generally, anion exchange resins are polymer-based matrix with which a column separation is affected by the swelling and the pressure drop associated with liquids change. In addition, the commercially available ammonium group resins degrade easily in nitric acid under certain conditions. In contrast, SiPyR-N4 is a silica-based matrix, which has fast adsorption kinetics, low swelling and pressure drop. It exhibits a quite strong adsorption for some rare earths especially the light rare earth elements such as La, Ce, Pr, Nd, and Pm [6]. Furthermore, it has high chemical stability in nitric acid medium because of pyridinium as the functional group in the aromatic ring [7,8]. Therefore, adsorption and separation behaviors for rare earths in nitric acid medium were investigated by using this novel anion exchange resin, SiPyR-N4.

2. Experimental

2.1. Synthesis of silica-based pyridinium anion exchange resin

Silica particles with a diameter of 37–74 μm, mean pore size of 600 nm and porosity of 69% were chosen as a support for the polymer resin. The silica particles were placed in a rotary evaporator flask followed by evacuation using vacuum pump. A mixture of monomers (85 wt.% vinyl pyridine and 15 wt.% *m*/*p*-divinylbenzene), initiators (α,α-azobisisobutyronitrile and 1,1′-azobiscyclohexane-1-carbonitrile) and diluents (acetophenone and diethyl phthalate) was then sucked into the flask. After that, the flask was

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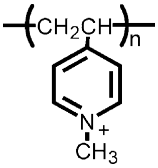
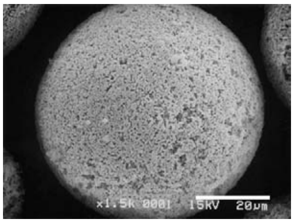
Table 1
Structure and properties of SiPyR-N4

Functional group	
SEM photograph	
Bead diameter (µm)	37–74
Total capacity (mequiv./g-resin)	4.5
Quaternary capacity (mequiv./g-resin)	4.5
Impregnated polymer ratio (wt.%)	27

rotated so that pores of silica were filled with the mixture completely. Hereafter, the flask was filled with nitrogen gas, and was heated slowly in silicone-oil bath at a rising temperature up to 363 K, at which the temperature was kept constant for 20 h for complete polymerization. The resulting silica grafted anion exchange resin was then washed with water and acetone, respectively, for several times and converted to quaternary ammonium salt by reacting with dimethylsulphate. The content of polymer resin embedded in the silica was measured as 27 wt.% by thermo-gravimetric analysis (TGA).

Total exchange capacity of the resin was determined as 4.5 mequiv./g-resin and quaternary rate was almost 100%, which indicates that tertiary polyvinyl pyridine was completely converted to quaternary ammonium salt. Table 1 shows the structure and photos of the synthesized resin.

2.2. Adsorption experiment

The metal ions used for distribution coefficients measurement were La(III), Ce(III), Pr(III), Nd(III), Eu(III), Dy(III), Y(III) in nitric acid medium. The distribution coefficient values were measured by batch adsorption experiment. Prior to the adsorption of rare earth metal ions, the resin was conditioned with nitric acid solutions with concentration of 0.1–9 mol/dm^3. About 1 g of the resin in NO_3-form and 20 cm^3 of rare earth solution containing 10 mol/dm^3 of each metal were placed in a glass flask and shaken mechanically at the constant temperature of 298 K in a water bath till an equilibrium state was reached. The solution was then separated by filtration and, the concentrations of metals before and after the adsorption were measured by ICP spectroscopy (Seiko Instruments Inc., SPS 5000). The resin was washed with diluted nitric acid and distilled water and then finally dried at 333 K for 10 h.

The distribution coefficients (K_d) were calculated according to the following equation:

$$K_d = \frac{C_0 - C_S}{C_S} \times \frac{V_S}{W_R} \quad (1)$$

where C_0 and C_S stand for the metal ion concentration in the aqueous solution before and after the adsorption, respectively, W_R stands for the weight of the dry resin and V_S for the volume of the aqueous phase.

2.3. Column separation experiment

Column separation experiments were conducted using a pressure-resistant Pyrex-glass column with 10 mm inner diameter and 500 mm long. Fig. 1 shows the schematic diagram of the equipments for column separation experiments.

SiPyR-N4 anion exchange resin was packed into the column in slurry state at 0.1 MPa. The bed volume of SiPyR-N4 resin in the column was about 35 cm^3. The SiPyR-N4 packed column was kept at a constant temperature with water jackets. Prior to the introduction of sample solution, the SiPyR-N4 was conditioned by passing 250 cm^3 of HNO_3 solution with a certain concentration through the column. In the separation experiment, a sample solution containing some typical rare earth elements were 5 mmol/dm^3 in 3.0–6.0 mol/dm^3 HNO_3. A 20 cm^3 portion of this solution was fed to the column at a constant linear flow rate of 2.5 cm/min. Then the eluent and washing solutions were passed through the column, successively. The effluents from the column were collected using an auto-fractional collector in 5 cm^3 aliquots. The metal ion

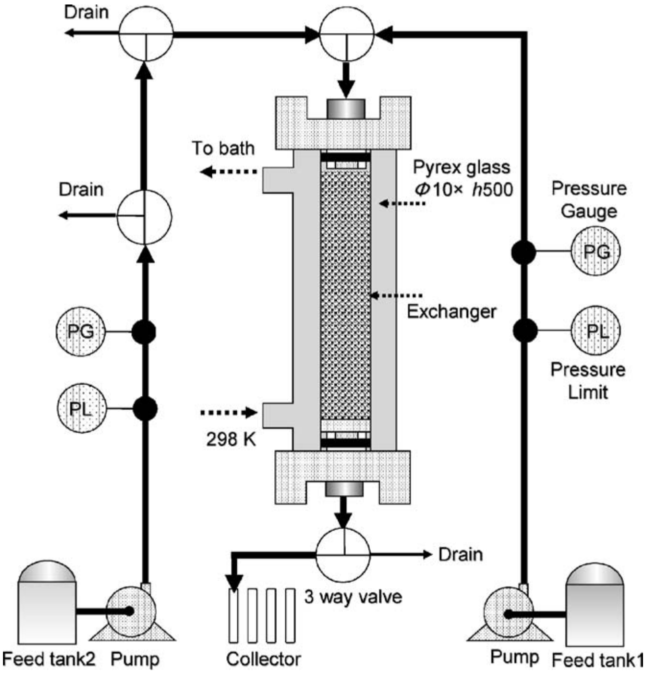


Fig. 1. Schematic diagram of the column apparatus for separation experiments.

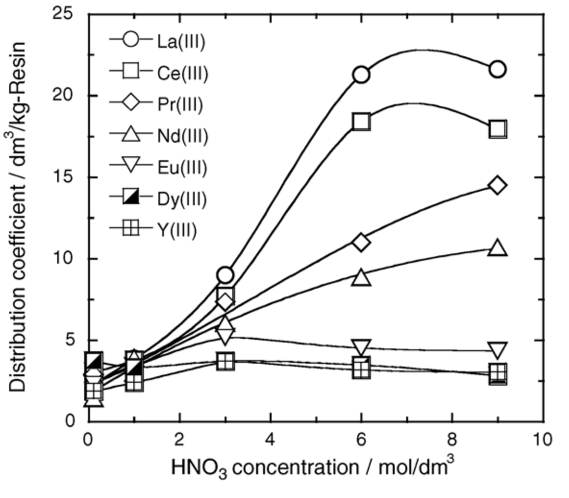
concentrations in each fraction were analyzed by ICP spectroscopy.

3. Results and discussion

3.1. Adsorption behavior of SiPyR-N4 resin

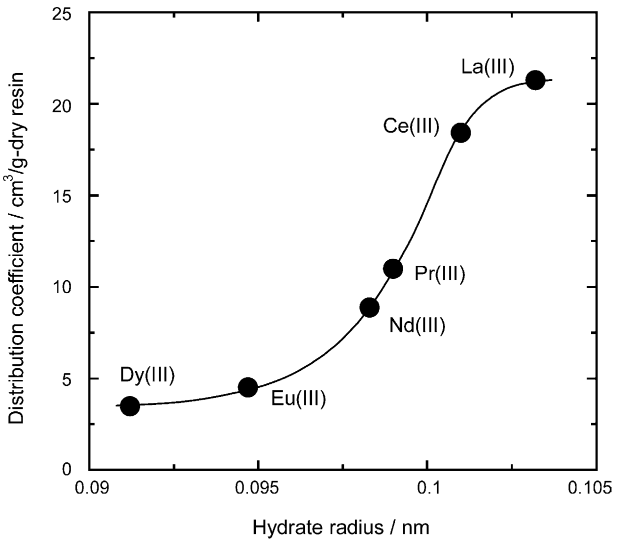
Fig. 2 shows the distribution coefficients for rare earths in nitric acid solutions with various concentrations from 0.1 to 9 mol/dm^3. As can be seen in Fig. 2, the SiPyR-N4 resin exhibits a quite strong adsorption to some rare earths especially the light rare earth elements such as La(III), Ce(III), Pr(III), Nd(III) and Pm(III) with which the distribution coefficients reach 10–25 dm^3/kg-resin, which is several times higher than that of heavy rare earth elements and much higher than the values reported for these elements with conventional anion exchange resins [4,5]. In addition, it is also found that the adsorption of these elements is promoted by the increasing nitric acid concentration up to ca. 6 mol/dm^3. From the above results it was found that the rare earths can be separated into the two or three groups: light and heavy, or light, moderate and heavy rare earths in concentrated nitric acid medium using SiPyR-N4 packed column.

A relationship between the distribution coefficient in 6 mol/dm^3 nitric acid medium and the hydrate radius of rare earth ions is illustrated in Fig. 3. As can be seen in Fig. 3, the adsorption affinity to the SiPyR-N4 resin increases markedly with the increase in ionic radius of the rare earths, especially, the light rare earth elements, which is probably attributed to the lanthanoid contraction, resulting in an increase in the charge density and a difficulty to hydration in nitric acid medium of high concentration.



[Ln] = 10 mmol/dm^3, Temp. : 298 K, Adsorption time : 2 hr

Fig. 2. Distribution coefficients of rare earths with SiPyR-N4 resin in nitric acid solutions.



[Ln] = 10 mmol/dm^3, [HNO$_3$] =6 mol/dm^3

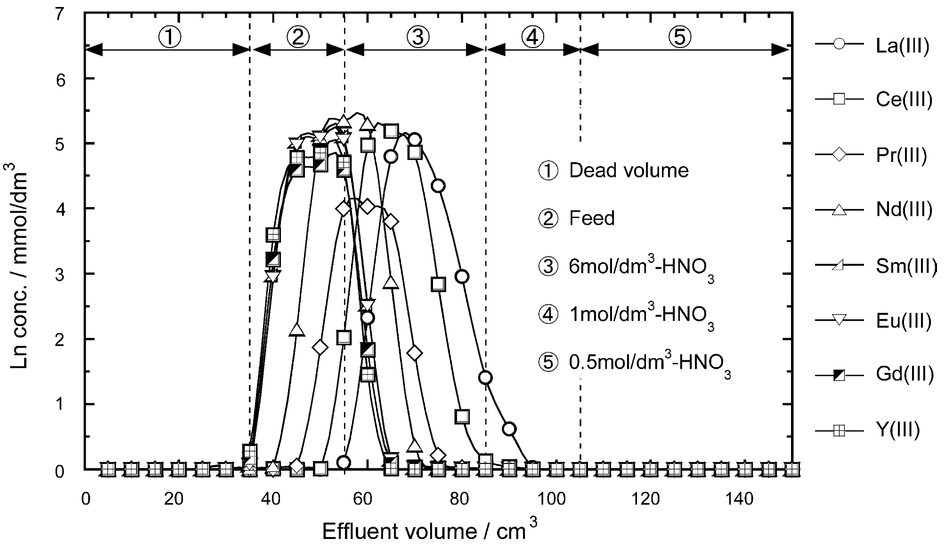
Adsorption time : 2hr, Temperature : 298K

Fig. 3. Distribution coefficients against the hydrate radius of the rare earths in 6 mol/dm^3 nitric acid.

3.2. Separation behavior of the rare earth elements

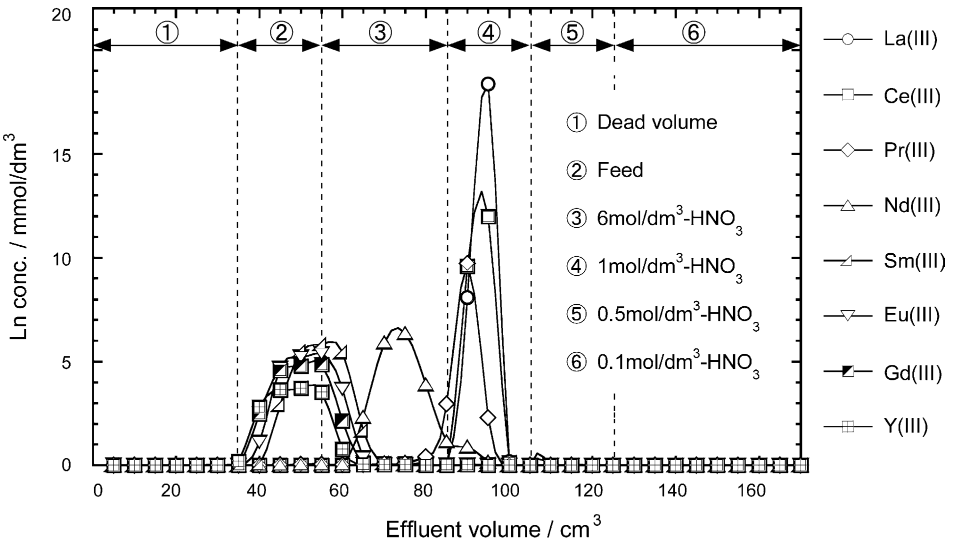
To investigate the separation behavior of some typical rare earth elements, separation experiments using SiPyR-N4 packed column were carried out for the rare earths in nitric acid solutions with various concentrations. Fig. 4 shows the plots of the concentration profiles of rare earths in the effluent from the column against the effluent volume, in which La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Y(III) in 3 mol/dm^3 nitric acid was used as the feed solution. As can be seen in Fig. 4, the heavy rare earth elements such as Sm(III), Eu(III), Gd(III) and Y(III) (similar to heavy rare earths) show almost no adsorption, and the light rare earth elements show only slight adsorption, which indicates that the separation of the rare earths in 3 mol/dm^3 nitric acid is difficult due to their close distribution coefficients (i.e., 3–8 dm^3/kg-resin).

Fig. 5 shows the results obtained from the column separation experiment for rare earths in 6 mol/dm^3 nitric acid. As can be seen in Fig. 5, the heavy rare earth elements, Sm(III), Eu(III), Gd(III) and Y(III) show almost no adsorption, and the moderate rare earth such as Nd(III) shows a slight adsorption in 6 mol/dm^3 nitric acid medium, resulting in an elution off of Nd(III) with the 6 mol/dm^3 nitric acid rinse solution. In contrast, the light rare earths such as La(III), Ce(III) and Pr(III) were fairly strongly retained by the SiPyR-N4 resin, and the adsorbed ions were effectively eluted by using 1 mol/dm^3 of nitric acid as an eluent. Therefore, the rare earths were separated into the three groups: light, moderate and heavy rare earths, respectively, and a perfect separation between La–Pr group and Sm–Gd group in 6 mol/dm^3 nitric acid solution was achieved.



Feed : [Ln] = 5mmol/dm^3, [HNO$_3$] = 3mol/dm^3, Flow Rate: 2.5cm/min, Temp.: 298K

Fig. 4. Concentration profiles of the rare earths in the effluent from column (3 mol/dm^3 nitric acid).



Feed : [Ln] = 5mmol/dm^3, [HNO$_3$] = 6mol/dm^3, Flow Rate: 2.5cm/min, Temp.: 298K

Fig. 5. Concentration profiles of the rare earths in the effluent from column (6 mol/dm^3 nitric acid).

4. Conclusions

A novel SiPyR-N4 resin has been synthesized and characterized for its adsorption and separation behavior for the rare earths. SiPyR-N4 resin exhibits a quite strong adsorption for some rare earths especially the light rare earth elements with which the distribution coefficients reach 10–25 dm^3/kg-resin, which is several times higher than that of heavy rare earth elements and much higher than the values obtained from the conventional anion exchange resins. The adsorption behavior was presumed to relate to the lanthanoid contraction, which results in a different charge density of the rare earth ions.

The results of column separation experiments indicate that the rare earths can be separated into the three groups: light, moderate and heavy rare earths, respectively. A perfect separation between La–Pr group and Sm–Gd can be achieved.

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