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Novel Phosphoric and Phosphonic Acid Type Ion Exchange Resin for Separation of Rare Earth Metals

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Novel phosphoric and phosphonic acid type ion exchange resins were synthesized as impregnation type resins and surface functional group type resins in the present work, and their adsorption and separation abilities for rare earth metals were investigated. The impregnation type resins were synthesized using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) as a porogen during the synthesis of polymer beads, while the surface functional group type resins were synthesized by immobilizing the phosphoric acid ester ligand onto polymer beads. All ion exchange resins exhibited adsorption ability for dysprosium. The separation abilities for dysprosium and europium with the impregnation type resins were consistent with those with the conventional solvent-impregnated resin containing PC-88A, while almost no selectivity was obtained with the surface functional group type resins. The impregnation type resin can be applied to column operation, and the selective adsorption of dysprosium over neodymium can be achieved by combining a scrubbing method.

1. Introduction

Rare earth metals are critical for recent advanced technologies, and their high purity is required. A hydrometallurgical separation process is generally applied for the separation of rare earth metals. The main hydrometallurgical separation processes for rare earth metals are liquid-liquid extraction and ion exchange. In the case of liquid-liquid extraction, acidic organophosphorus compounds, such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), exhibit high selectivity for rare earth metals [1].

Liquid-liquid extraction is widely applied to the industrial-scale separation and recovery of metals, since it has the advantages of straightforward, large-scale, and continuous operation. However, a large amount of organic diluent is required to dissolve both the extractant and the extracted species. In addition, although this method is effective for treating concentrated solutions, it is not suitable for dilute solutions. When recovering metals from waste materials, the concentrations of the target metals in the leaching solution are generally dilute, often making liquid-liquid extraction difficult to apply [2].

Ion exchange has the advantages that no organic solvent is required during operation and that dilute solutions can be treated. However, ion exchange resins with selectivity for rare earth metals have seldom been reported, and a complexing agent for rare earth metals, such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA), is required [3]. Acidic organophosphorus ligands are considered promising due to their high selectivity for rare earth metals in liquid-liquid extraction systems, but no commercially available ion exchange resin incorporates these ligands. Although several ion exchange resins have aminophosphoric acid or aminophosphonic acid ligands, such as Duolite C467, Ambersep IRC747UPS, and Purolite S950, they show poor selectivity for rare earth metals [4]. A solvent-impregnated resin (SIR) containing an acidic organophosphorus compound extractant is a potential adsorbent for the separation of rare earth metals [3]. However, the impregnated extractant leaks from the SIR during the operation. To address this issue, the surface of the SIR has been coated with a crosslinked water-soluble polymer to prevent extractant leakage [5].

In the present work, novel phosphoric and phosphonic acid type ion exchange resins were synthesized, and their adsorption and separation behaviors for three rare earth metals, dysprosium (Dy), europium (Eu), and neodymium (Nd), were investigated. Two impregnation type resins containing PC-88A and three surface functional group type resins with a phosphoric acid ester ligand on the polymer surface were synthesized. Batchwise adsorption experiments were then conducted using the synthesized resins, and the results were compared with those for the SIR [5]. The adsorption kinetics and isotherms of Dy with the new ion exchange resins were also investigated. The effect of pH on Dy adsorption was examined in single and binary systems (Dy/Eu and Dy/Nd). Finally, the new ion exchange resins were applied to column operation for the Dy single system and Dy/Eu and Dy/Nd binary systems. The separation of Dy and Nd, a key pair for recovering metals from waste Nd magnet, was further evaluated using a scrubbing method [6].

2. Experimental

2.1 Reagents

$EuCl_3 \cdot 6H_2O$ and 99% phosphoric acid were purchased from Sigma-Aldrich Japan (Tokyo, Japan), and $NdCl_3 \cdot 6H_2O$ was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Divinylbenzene (DVB-570) was purchased from NIPPON STEEL Chemical & Material Co., Ltd. (Tokyo, Japan), 75% benzoyl peroxide and sulfuric acid were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan), and hydroxypropyl methylcellulose (METOLOSE 65SH-50) was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Diaion HP2MG, a methacrylic ester copolymer with no ion exchange functional groups, and SEPABEADS FPEP13L, an epoxy type methacrylic ester copolymer with no ion exchange functional groups, were supplied by Mitsubishi Chemical Co. (Tokyo, Japan). PC-88A was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) for the preparation of ion exchange resins KH001 and KH002, and from Daihachi Chemical Co., Ltd. (Osaka, Japan) for the preparation of SIR. Monobutyl phosphate (MP-4) and monoisodecyl phosphate (MP-10) were purchased from Daihachi Chemical Co., Ltd. All other organic and inorganic reagents were of analytical grade and purchased from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan).

Feed aqueous solutions containing rare earth metals were prepared by dissolving rare earth chlorides in deionized water. The pH of the feed solution was adjusted by adding HCl or NaOH at appropriate concentrations.

2.2 Synthesis of new ion exchange resins and preparation of SIR

The new ion exchange resins, KH001 – KH006, and SIR were prepared as follows. The structures of KH001 – KH006 are shown in Figure 1.

2.2.1 KH001 and KH002

KH001 and KH002 were synthesized using PC-88A as a porogen during the synthesis of polymer beads. A dispersed phase was prepared by mixing divinylbenzene (30 g), 75% benzoyl peroxide (0.40 g), and PC-88A (30 g), and a continuous phase was prepared by dissolving hydroxypropyl methylcellulose (0.30 g) in deionized water (171 mL). The dispersed phase was added to the continuous phase, and the mixture was heated from 25 °C to 82 °C over 2 h and then kept at 82 °C for 6 h. The resultant suspended mixture was filtered, and the product was washed with 180 g of deionized water four times, then dried in a vacuum dry oven at 50 °C for 8 h (KH002). In the case of KH001, the surface of the resin was coated with crosslinked hydroxypropyl methylcellulose. The same dispersed and continuous phases were mixed and heated. After 2 h, 25% glutaraldehyde solution (10.9 g) and 98% sulfuric acid (1.58 mL) diluted with deionized water (40 mL) were added to crosslink the hydroxypropyl methylcellulose, and the temperature was kept at 82 °C for 6 h. The obtained resins (1.00 g) were washed with methanol (10 mL) four times to remove the impregnated PC-88A, then dried in a vacuum dry oven at 50 °C for 8 h. The amounts of impregnated PC-88A, determined from the weight difference, were 1.86 mmol/g for KH001 and 1.79 mmol/g for KH002. The sizes of 100 randomly selected particles of the synthesized resins were measured using an optical microscope (SMZ1500, Nikon, Tokyo, Japan), and the average particle size was calculated as the volume median diameter. Additionally, the effective size was determined as the particle size at which the cumulative volume reached 90% (D_{90}). The uniformity coefficient was determined by dividing the particle size at which the cumulative volume reached 40% (D_{40}) by D_{90}. The average particle size, effective size, and uniformity coefficient of the resins are summarized in Table 1.

2.2.2 KH003 and KH004

SEPABEADS FPEP13L (15 g), toluene (75 mL), and MP-4 (13.3 g) for KH003 or MP-10 (23.4 g) for KH004 were mixed, and the mixture was heated from 25 °C to 102 °C over 2 h and then kept at 102 °C for 6 h. The resultant suspended mixture was filtered, and the product was washed with 75 mL of methanol twice.

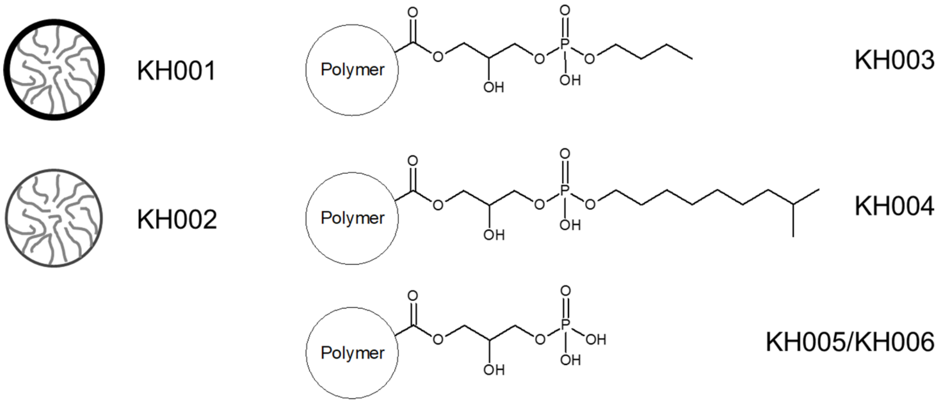

Figure 1. Structures of KH001 – KH006.

Table 1. Average particle size, effective size, and uniformity coefficient of the ion exchange resins.

Resin	Average particle size	Effective size	Uniformity coefficient
KH001	371 μm	295 μm	1.30
KH002	371 μm	297 μm	1.29
KH003	323 μm	222 μm	1.52
KH004	349 μm	283 μm	1.27
KH005	153 μm	117 μm	1.36
KH006	148 μm	118 μm	1.32

The product was then suspended in 75 mL of deionized water, then packed into a column and washed with 1 L of deionized water. After washing, the product was dried in a vacuum dry oven at 50 °C for 8 h. The average particle size, effective size, and uniformity coefficient of the resins were determined in the same manner as in Section 2.2.1 and are summarized in Table 1.

2.2.3 KH005 and KH006

KH005 and KH006 were essentially the same resin but with different concentrations of phosphoric acid used in the preparation. SEPABEADS FPEP13L (15 g), toluene (75 mL), and 99% phosphoric acid (8.9 g) for KH005 or 85% phosphoric acid (10.4 g) for KH006 were mixed, and the mixture was heated from 25 °C to 102 °C over 2 h and then kept at 102 °C for 6 h. The resultant suspended mixture was filtered, and the product was washed with 75 mL of methanol twice. The product was washed and dried in the same manner as for KH003 and KH004. The average particle size, effective size, and uniformity coefficient of the resins were determined as before and are summarized in Table 1.

2.2.4 Preparation of solvent-impregnated resin

SIR was prepared in the same manner as reported previously [5]. HP2MG (40 g) was washed with methanol (250 mL), and the resin was dried *in vacuo*. The washed HP2MG (2.5 g) was then immersed in 50 mL of 0.10 mol/L PC-88A–toluene solution overnight. After impregnation, the toluene was evaporated using an evaporator (EYELA OSB-2200), and the resin was dried overnight to obtain SIR. The amount of impregnated PC-88A was 2.06 mmol/g. The resultant SIR (3.0 g) was immersed in an aqueous solution (50 mL) containing 1.0 g of acetamide and 3.0 wt% polyvinyl alcohol (polymerization degree of ca. 2000), and the mixture was shaken for 17 h. Then, 1.0 mol/L potassium chloride (10 mL) was added to the solution, which was shaken for 24 h. The resultant SIR was filtered and resuspended in 0.32 mol/L sulfuric acid solution (10 mL) for 1 h. Finally, 0.32 mol/L glutaraldehyde solution (10 mL) was added, followed by shaking for 24 h to crosslink the polyvinyl alcohol. The coated SIR was vacuum-filtered and washed with deionized water.

2.3 Batchwise adsorption of Dy, Dy/Eu, and Dy/Nd

Batchwise adsorption experiments were conducted by shaking 10 mL of an aqueous feed solution with 20 mg of each adsorbent at 25 °C using a thermostatic mechanical shaker. A Dy single system and Dy/Eu and Dy/Nd binary systems were investigated. In the equilibrium studies with KH001, KH002, KH005, and KH006, the suspended mixtures were added to test tubes, which were set horizontally in the thermostatic mechanical shaker and shaken at 100 rpm, since the specific gravities of these ion exchange resins were low, making it difficult to submerge them in the feed solution. In the equilibrium studies with KH003, KH004,

Table 2. Conditions for the batchwise equilibrium studies.

Resin	Container	Shaking rate	Shaking time
KH001	Test tube	100 rpm	> 24 h
KH002	Test tube	100 rpm	> 24 h
KH003	Erlenmeyer flask	150 rpm	> 48 h
KH004	Erlenmeyer flask	150 rpm	> 48 h
KH005	Test tube	100 rpm	> 60 h
KH006	Test tube	100 rpm	> 60 h
SIR	Erlenmeyer flask	150 rpm	> 24 h

and SIR, the suspended mixtures were added to Erlenmeyer flasks, which were shaken at 150 rpm with the thermostatic mechanical shaker. Detailed conditions for the equilibrium studies are summarized in Table 2. In the kinetic study, all samples were added to test tubes and shaken at 100 rpm to ensure the same experimental conditions.

For the Dy single system, the feed Dy concentration was set at ca. 1.0 mmol/L to study the kinetic and pH effects, while concentrations ranging from 0.2 to 17.4 mmol/L were used to obtain the adsorption isotherms. For the Du/Eu and Dy/Nd binary systems, the feed concentrations of both metals were set at ca. 1.0 mol/L. After shaking each suspended mixture, the aqueous solution was filtered, and the pH was measured by a pH meter (Horiba F-72). The concentrations of rare earth metal ions were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES; ICPE-9000, Shimadzu, Kyoto, Japan). The adsorption of rare earth metals was calculated as follows:

$$q\ (\text{mmol/g}) = \frac{([\text{Ln}]_{\text{feed}} - [\text{Ln}]_{\text{eq}}) \cdot V}{w} \qquad (1)$$

where $[\text{Ln}]_{\text{feed}}$ and $[\text{Ln}]_{\text{eq}}$ denote the initial and equilibrium concentrations of rare earth metals (mmol/L), respectively, V is the volume of aqueous solution (L), and w is the mass of adsorbent (g). Leakage of PC-88A from KH001, KH002, and SIR was determined by measuring the phosphorus concentration in the aqueous solution after measuring adsorption using ICP-AES.

2.4 Chromatographic adsorption of rare earth metals

Chromatographic adsorption of the rare earth metals with KH001 was investigated. The feed solutions were the Dy single system ($[\text{Dy}]_{\text{feed}}$ = ca. 2.5 mmol/L, pH_{feed} = 3.00), the Dy/Eu binary solution ($[\text{Dy}]_{\text{feed}}$ = $[\text{Eu}]_{\text{feed}}$ = ca. 2.5 mmol/L, pH_{feed} = 3.00), and a simulated leaching solution of waste Nd magnet ($[\text{Dy}]_{\text{feed}}$ = ca.1 mmol/L, $[\text{Nd}]_{\text{feed}}$ = ca. 5 mmol/L, pH_{feed} = ca. 1.45) [6]. For the Dy single solution and Dy/Eu binary solution, 2.0 g of KH001 (dry volume = 3.8 mL) was packed into a glass column (length: 10 cm, inner diameter: 10 mm), through which the feed solution was then fed upward using a dual-plunger pump (KP-21, Flom, Tokyo, Japan) at flow velocities of 0.157 – 0.960 mL/min (S.V. = 2.47 – 15.2 /h) for the Dy single solution and 0.157 mL/min (S.V. = 2.47 /h) for the Dy/Eu binary solution. The space velocity (S.V.) was defined as follows:

$$\text{S.V.}\ (\text{/h}) = \frac{v}{V_{\text{resin}}} \qquad (2)$$

where v is the flow rate of the feed solution (mL/h) and V_{resin} is the dry volume of KH001 in the column (mL) because the wet volume could not be measured due to the low specific gravity of KH001.

For the simulated leaching solution of waste Nd magnet, 1.0 g of KH001 (dry volume = 1.95 mL) was packed into a glass column (length: 10 cm, inner diameter: 10 mm), through which the feed solution was then fed upward using a dual-plunger pump at a flow velocity of 0.240 mL/min (S.V. = 7.38 /h). After adsorption reached saturation, deionized water was fed into the column to wash out the excess feed solution remaining in the column. Elution was then conducted with 2 mol/L HCl. Scrubbing was also performed to improve the separation of Dy and Nd. In this case, adsorption was performed by feeding the feed solution until the bed volume reached 88.6, and then scrubbing solution containing 0.0551 mmol/L Eu ($\mathrm{pH}_{\mathrm{scrubbing,feed}}$ = 1.45) was fed into the column. After scrubbing, deionized water was fed into the column, followed by elution with 2 mol/L HCl.

The effluent was collected using a fraction collector (EYELA DC-1500), and the rare earth ion concentrations were determined using ICP-AES. The bed volume of the effluent was calculated as

$$\text{Bed Volume }(-) = \frac{v \cdot t}{V_{\mathrm{resin}}} \tag{3}$$

where t denotes the time over which the feed solution was supplied (h).

3. Results and Discussion

3.1 Adsorption kinetics of Dy

The adsorption kinetics of Dy on the ion exchange resins were investigated. Figures 2a and 2b show the time-course variation of Dy adsorption with the resins. Pseudo-first-order and pseudo-second-order

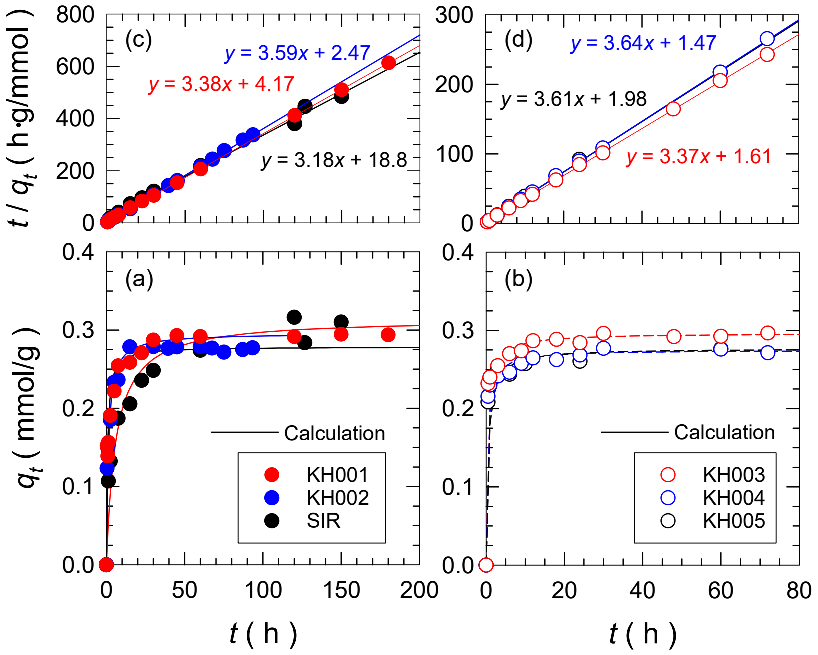

Figure 2. Time-course variation of the adsorption of Dy with the ion exchange resins and corresponding linear relationships for adsorption with pseudo-second-order kinetics. The values calculated from the pseudo-second-order rate model are shown as solid and dotted lines. $[\mathrm{Dy}]_{\mathrm{feed}}$ = 1.03 mmol/L for KH001 and KH002, 1.01 mmol/L for KH003 and KH004, and 0.997 mmol/L for KH005 and SIR. $\mathrm{pH}_{\mathrm{feed}}$ = 3.5.

Table 3. Adsorption rate constants for the ion exchange resins.

Resin	k (g/mmol·h)	Resin	k (g/mmol·h)
KH001	2.74	KH004	8.99
KH002	5.21	KH005	6.57
KH003	7.06	SIR	0.536

models were used to analyze the data, and the adsorption kinetics were determined to be pseudo-second-order, as given by

$$\frac{dq}{dt} = k(q_{\mathrm{eq}} - q_t)^2 \tag{4}$$

where k is the pseudo-second-order rate constant (g/(mmol·h)) and q_{eq} and q_t are the amounts of Dy adsorbed (mmol/g) at equilibrium and at time t (h), respectively [7]. Integrating eq. (4) yields the following linear form of the pseudo-second-order model:

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{k{q_{\mathrm{eq}}}^2} + \frac{1}{q_{\mathrm{eq}}}t \tag{5}$$

The linearized relationships for the adsorption of Dy are shown in Figures 2c and 2d. For all systems, t and t/q_{t} were linearly related, indicating pseudo-second-order kinetics for the adsorption of Dy. The adsorption of the rare earth metal by all ion exchange resins therefore occurred via ion exchange [7]. Table 3 shows the obtained adsorption rate constants (k). For the surface functional group type resins, the adsorbate ions diffuse into the pores of the resin. However, for the impregnation type resins, the adsorbate ion must penetrate into the resin for complexation with PC-88A inside the resin. The rate constants of the surface functional group type resins (KH003, KH004, KH005) are therefore higher than those of the impregnation type resins (KH001,

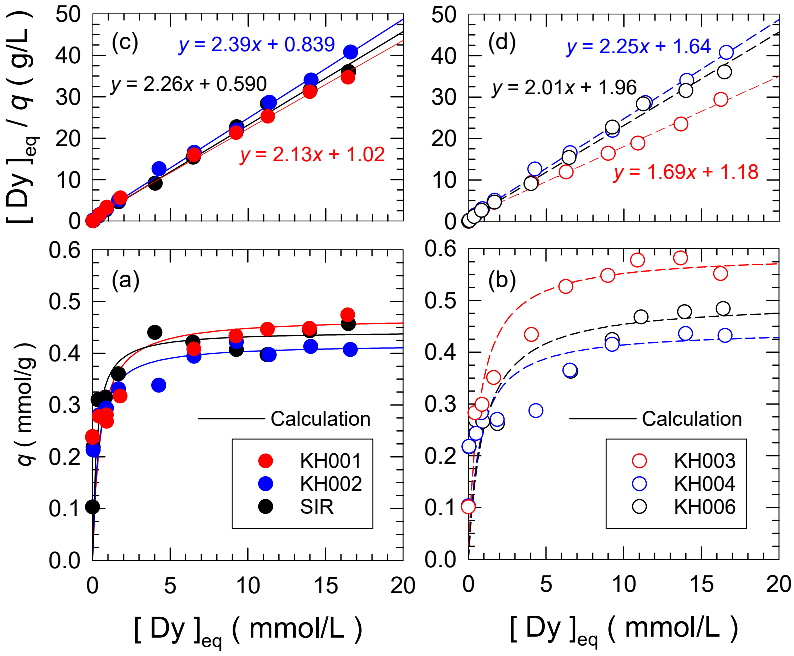

Figure 3. Adsorption isotherms for Dy and linearized Langmuir plots of the adsorption isotherms. The values calculated from the Langmuir adsorption model are shown as solid and dotted lines.

KH002). The rate constant of KH001 is smaller than that of KH002, since the surface of KH001 is coated with crosslinked hydroxypropyl methylcellulose. However, the rate constant of KH001 is much higher than that of SIR, indicating that the new ion exchange resins have superior kinetics for the adsorption of rare earth metals.

3.2 Adsorption isotherms of Dy

The adsorption isotherms of Dy for each ion exchange resin were investigated at pH_{eq} = ca. 2.8 (Figures 3a and 3b). The adsorption isotherms of all adsorbents fit well with the linear relationship predicted by the Langmuir mechanism, as shown in Figures 3c and 3d. The saturated adsorption amounts (q_s) and adsorption constants (K) for Dy are summarized in Table 4. The amounts of saturated adsorption are comparable, except for that of KH003, which is higher. Although the reason for the high saturated adsorption of KH003 is unclear in the present work, a possible reason is that a larger amount of the functional group was immobilized.

Table 4. Saturated adsorption amounts and adsorption constants.

Resin	pH_{eq}	q_s (mmol/g)	K (L/mmol)
KH001	2.81 ± 0.03	0.469	2.09
KH002	2.79 ± 0.03	0.418	2.85
KH003	2.78 ± 0.04	0.591	1.43
KH004	2.81 ± 0.06	0.444	1.37
KH006	2.78 ± 0.05	0.498	1.02
SIR	2.75 ± 0.04	0.443	3.83

3.3 Adsorption of Dy/Eu and Dy/Nd in binary systems

The adsorption of Dy and Eu in binary systems by the ion exchange resins was investigated. Figure 4 shows the effect of pH on the adsorption of Dy and Eu by the impregnation type resins (KH001, KH002, SIR). Dy was selectively adsorbed over Eu for the impregnation type resins, consistent with the behavior of the conventional liquid-liquid extraction system with PC-88A [8]. The separation abilities with KH001 and KH002 were similar to that with SIR. The leakage of PC-88A from the adsorbents is also shown in Figure 4. The leakage from KH001 and KH002 was less than 0.5%, with almost no difference between them, even though the KH001 surface was coated with crosslinked hydroxypropyl methylcellulose. Therefore, surface coating of the new impregnation type ion exchange resin is unnecessary, as PC-88A is impregnated inside the resin. The leakage of PC-88A from SIR was 0.6 – 1.8%, although its surface was also coated with the crosslinked polyvinyl alcohol to suppress leakage [5]. KH001 and KH002 thus exhibit much greater stability than SIR.

Figure 5 shows the effect of pH on the adsorption of Dy and Eu by the surface functional group type resins (KH003, KH004, KH005). In these cases, the adsorption behavior of the two metals is almost identical, indicating relatively low separation abilities for the rare earth metals with the surface functional group type resins. The separation ability for the rare earth metals is not achieved with a single phosphoric acid ester-based functional group, but rather with multiple phosphoric acid ester-based functional groups or the inclusion of alkyl side chains of the acidic organophosphorus compounds.

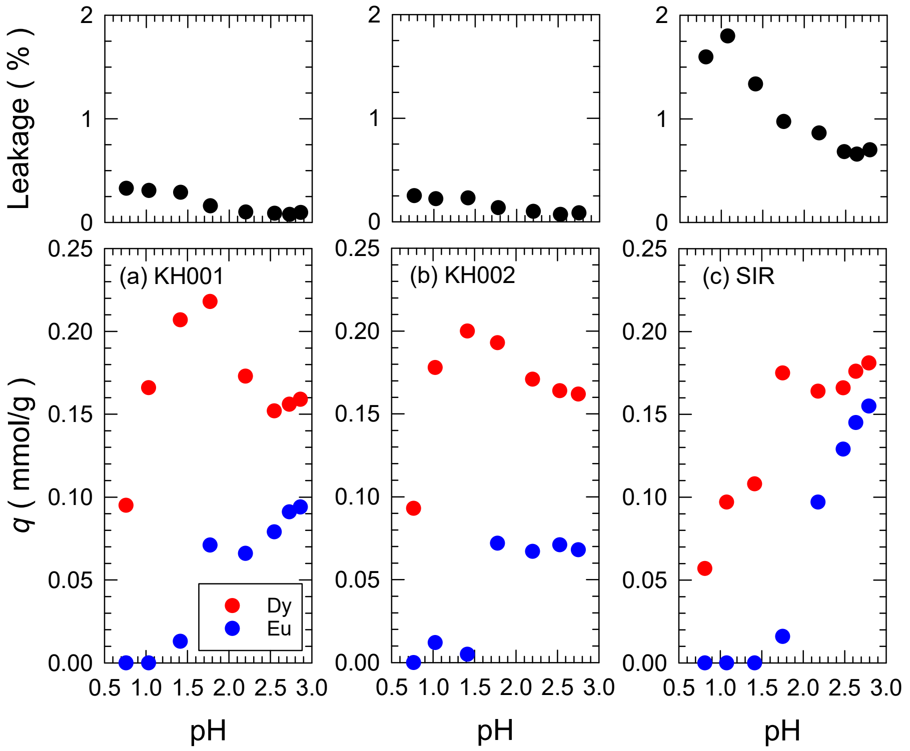

Figure 4. Effect of pH on the adsorption of Dy and Eu in the binary systems with (a) KH001, (b) KH002, and (c) SIR. $[Dy]_{feed}$ = 0.982 mmol/L and $[Eu]_{feed}$ = 0.995 mmol/L.

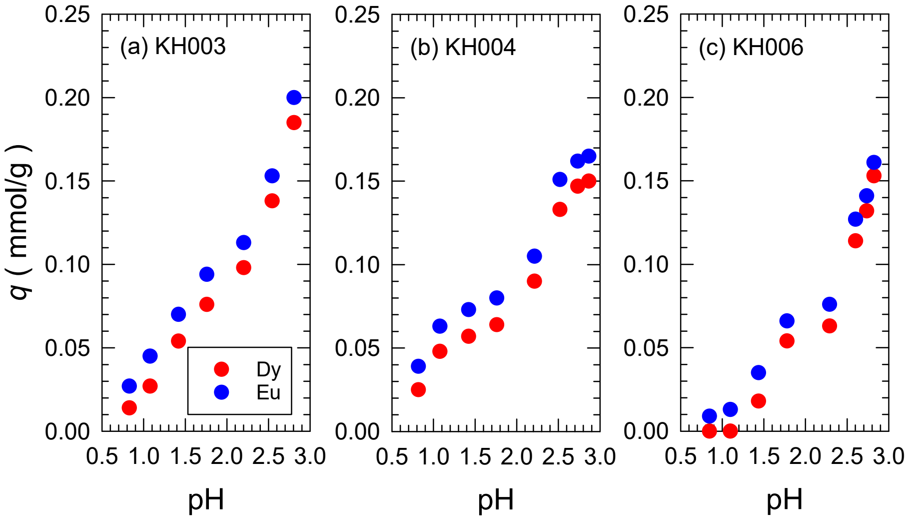

Figure 5. Effect of pH on the adsorption amount of Dy and Eu in the binary systems with (a) KH003, (b) KH004, and (c) KH006. $[Dy]_{feed}$ = 0.982 mmol/L and $[Eu]_{feed}$ = 0.995 mmol/L.

Batchwise adsorption of Dy and Nd from the binary solution was also investigated. Based on the results obtained from the Dy/Eu system, only KH001 was used due to its separation ability for the rare earth metals. Figure 6 shows the effect of pH on the adsorption of Dy and Nd. The selective adsorption of Dy proceeded in a similar manner to the Dy/Eu binary solution, particularly around a pH of 1.5.

3.4 Column adsorption of Dy single solution and Dy/Eu binary solution

Based on the batchwise studies, KH001 was applied to the column adsorption system. Figure 7 shows the breakthrough curves of Dy for the single solution and different S.V. values. KH001 proved effective for the column operation. The breakthrough point decreased with increasing S.V. The breakthrough curves for S.V. = 2.47, 5.05, and 7.69 were S-shaped with an inflection point, while those for S.V. = 9.95 and 15.2 were convex upwards. KH001 should therefore be used at S.V. < ca. 7.5.

Column adsorption of the Dy/Nd binary solution with KH001 was then investigated. Figure 8 shows the breakthrough and elution curves for the metals. Both metals were adsorbed by KH001, with the adsorption amounts calculated from the breakthrough curves as 0.148 mmol/g for Dy and 0.112 mmol/g for Eu. The loaded metals were quantitatively eluted with 2 mol/L HCl. However, the metals could not be separated using the conventional frontal separation method.

3.5 Separation of Dy from simulated leaching solution of waste Nd magnet

Finally, the separation of Dy from the simulated leaching solution of waste Nd magnet was investigated using the column system. Figure 9 shows the breakthrough and elution curves of Dy and Nd for the conventional frontal separation method. Dy was almost completely adsorbed up to a bed volume of ca. 80, after which breakthrough occurred. Nd was adsorbed up to a bed volume of ca. 15 before breaking through. After the breakthrough of Nd, the adsorbed Nd and the Dy in the feed solution were displaced, causing the concentration of Nd in the effluent to exceed that in the feed solution. The loaded Dy and Nd were quantitatively eluted with 2.0 mol/L HCl. The amounts of eluted Dy, calculated from the elution curves, were 0.248 mmol/g and 0.00752 mmol/g, respectively. The purity of Dy in the eluent was therefore 97.1% by the conventional frontal adsorption method.

Scrubbing is used to purify loaded metals by displacing less selective metals with a more selective

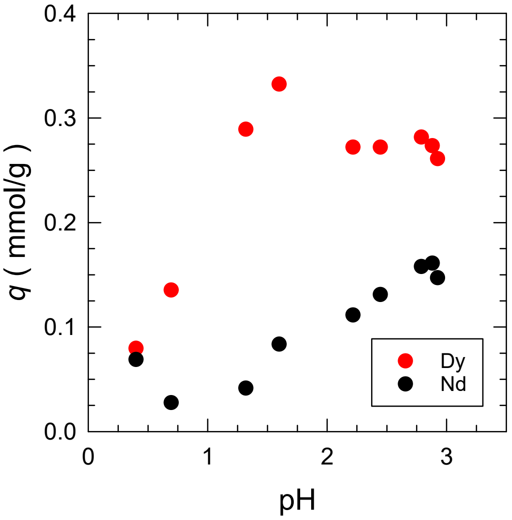

Figure 6. Effect of pH on the adsorption of Dy and Nd in the binary systems with KH001. $[Dy]_{feed}$ = 1.10 mmol/L and $[Nd]_{feed}$ = 1.15 mmol/L.

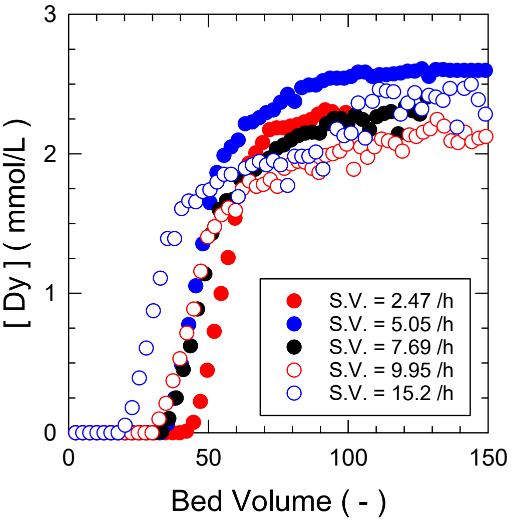

Figure 7. Effect of space velocity on the breakthrough curve of Dy from the single Dy solution. $[Dy]_{feed}$ = 2.28 mmol/L (S.V. = 2.47 /h), 2.71 mmol/L (S.V. = 5.05 /h), 2.40 mmol/L (S.V. = 7.69 /h), 2.16 mmol/L (S.V. = 9.95 /h), and 2.35 mmol/L (S.V. = 15.2 /h) and pH_{feed} = 3.00.

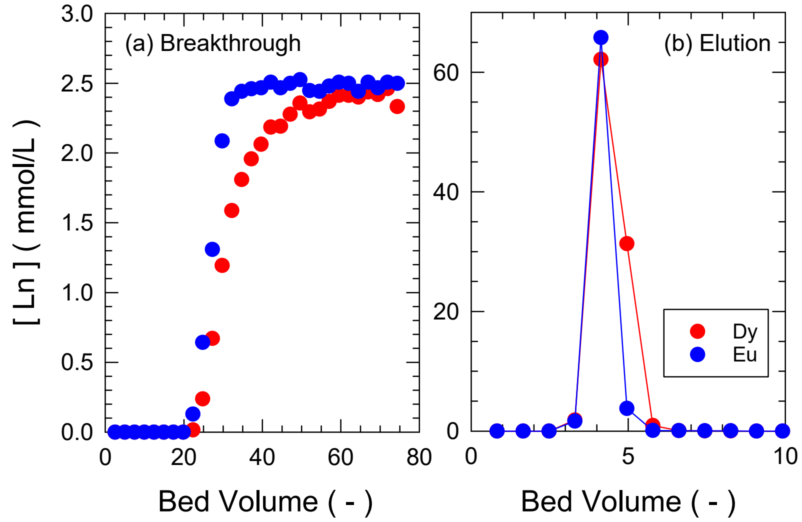

Figure 8. (a) Breakthrough and (b) elution curves of Dy and Eu from the Dy/Eu binary solution. $[Dy]_{feed}$ = 2.60 mmol/L, $[Eu]_{feed}$ = 2.55 mmol/L, pH_{feed} = 3.00, and S.V. = 2.48 /h.

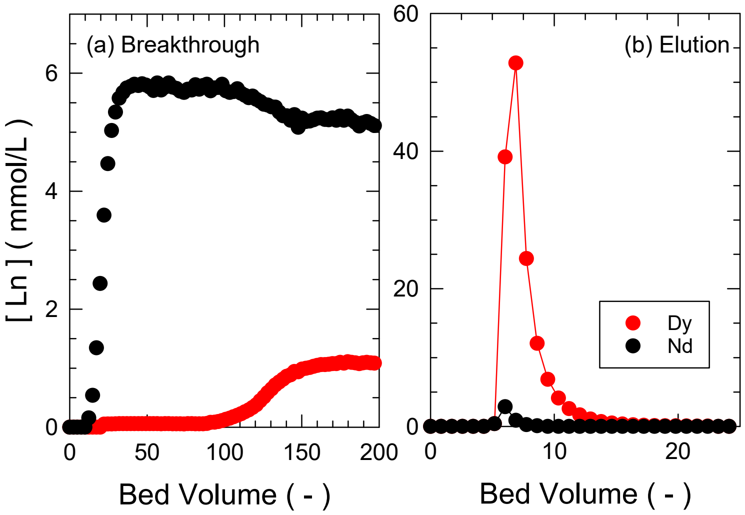

Figure 9. (a) Breakthrough and (b) elution curves of Dy and Nd from the simulated leaching solution of waste Nd magnet. $[Dy]_{feed}$ = 1.05 mmol/L, $[Nd]_{feed}$ = 4.89 mmol/L, pH_{feed} = 1.46, and S.V. = 7.38 /h.

metal in the scrubbing solution, and is mainly used in liquid-liquid extraction processes [9,10]. In the present work, scrubbing was applied to the column system to remove the adsorbed Nd. Adsorption was performed until the bed volume reached 88.6, and then a scrubbing solution containing only Dy was fed into the column to promote the displacement of adsorbed Nd and the Dy in the scrubbing solution. Figure 10 shows the breakthrough and elution curves of the metals. The Nd adsorbed during the adsorption step was effectively scrubbed from the resin. The eluent contained 0.163 mmol/g of Dy and 9.15×10^{-4} mmol/g of Nd, indicating that the purity of Dy was improved to 99.4%.

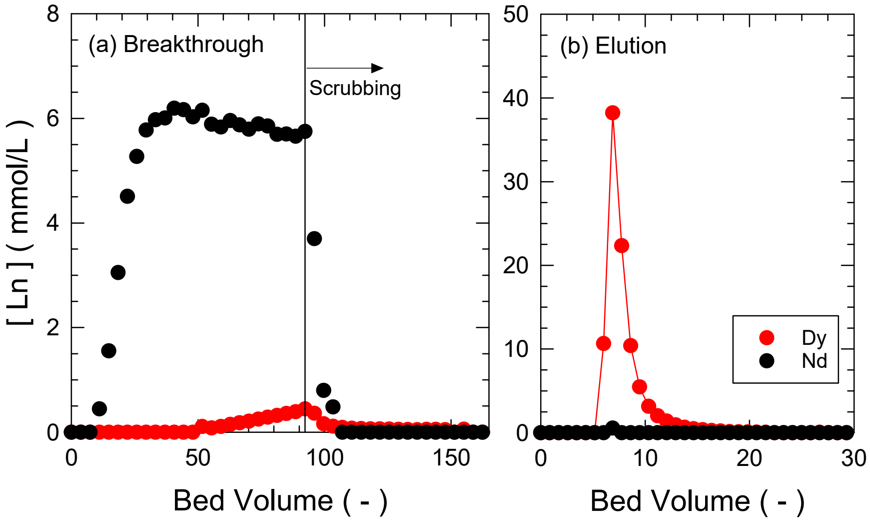

Figure 10. (a) Breakthrough and (b) elution curves of Dy and Nd from the simulated leaching solution of waste Nd magnet. Scrubbing was performed from a bed volume of 88.6. $[Dy]_{feed}$ = 0.997 mmol/L, $[Nd]_{feed}$ = 4.76 mmol/L, pH_{feed} = 1.45, $[Dy]_{scrubbing,feed}$ = 0.0551 mmol/L, $pH_{scrubbing,feed}$ = 1.46, and S.V. = 7.38 /h.

4. Conclusion

Novel phosphoric and phosphonic acid type ion exchange resins were prepared, and the separation of rare earth metals was investigated, with the following results.

(1) The impregnation type resins (KH001, KH002) were synthesized using PC-88A as a porogen during the synthesis of polymer beads, while the surface functional group type resins (KH003 – KH006) were synthesized by immobilizing the functional groups on the polymer beads.

(2) The adsorption kinetics of Dy were pseudo-second order for all ion exchange resins, including SIR. The rate constants of the surface functional group type resins were higher than those of the impregnation type resins. KH001 exhibited superior kinetics to SIR for the adsorption of rare earth metals.

(3) The adsorption isotherms of Dy followed the Langmuir mechanism. The saturated adsorption was greatest for KH003, with the other resins showing comparable values.

(4) The impregnation type resins (KH001, KH002) had separation ability for the rare earth metals, while almost no separation ability was observed for the surface functional group type resins (KH003, KH004, KH006).

(5) KH001 can be applied in column operations for the separation of rare earth metals. Dy was separated from the simulated leaching solution of waste Nd magnet by incorporating a scrubbing method.

Declaration

The authors declare that they have no conflict of interest.

References

1) S. Sharifian, N.-H. L. Wang, *J. Environ. Chem. Eng.*, **12**, 112402 (31 pages) (2024).

2) B. N. Kumar, S. Radhika, B. R. Reddy, *Chem. Eng. J.*, **160**, 138-144 (2010).
3) C. F. Croft, E. A. Nagul, M. I. G. S. Almeida, S. D. Kolev, *ACS Omega*, **9**, 40315-40328 (2024).
4) M. Hermassi, M. Granados, C. Valderrama, N. Skoglund, C. Ayora, J. L. Cortina, *J. Cleaner Prod.*, **379**, 134742 (13 pages) (2022).
5) S. Nishihama, K. Kohata, K. Yoshizuka, *Sep. Purif. Technol.*, **118**, 511-518 (2013).
6) E. Yamada, H. Murakami, S. Nishihama, K. Yoshizuka, *Sep. Purif. Technol.*, **192**, 62-68 (2018).
7) Y. S. Ho, *J. Hazard. Mater.*, **136**, 681-689 (2006).
8) A. Hino, T. Hirai, I. Komasawa, *J. Chem. Eng. Jpn.*, **29**, 1041-1044 (1996).
9) C. A. Morais, V. S. T. Ciminelli, *Hydrometallurgy*, **73**, 237-244 (2004).
10) H. Singh, S. L. Mishra, R. Vijayalakshmi, *Hydrometallurgy*, **73**, 63-70 (2004).