Diglycolamic Acid–Grafted Film-Type Adsorbent for Selective Recovery of Rare Earth Elements

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Previously, we investigated bead-type silica gel adsorbents bearing immobilized diglycolamic acid ligands for the recovery of rare earth elements (REEs). Although the ligand-bearing silica gel selectively adsorbs REEs, the ligand loading is limited by the specific surface area of the silica gel. To increase the ligand loading, we have prepared a film-type adsorbent by immobilizing diglycolamic acid ligands on a nonwoven poly(vinyl alcohol) fabric by means of grafting polymerization. Compared with the silica gel adsorbent, the film-type adsorbent showed similar selectivity for a heavy REE, but the adsorption capacity of the film-type adsorbent was 3–4 times that of the silica gel adsorbent because the ligand loading on the former was 3.81 times that on the latter.

1. Introduction

Recently, there has been increasing interest in the development of methods for recovering rare earth elements (REEs) from underutilized resources including low-grade ores [1–4] and REE-containing end-of-life products [5,6]. In any method developed to recover REEs from solution, hydrometallurgical processes, such as precipitation, solvent extraction, and adsorption, can be expected to play major roles. Precipitation and solvent extraction are well-established techniques that are particularly useful for solutions containing high concentrations of the target metal ions, and adsorption can be used to recover metal ions even from low-concentration sources. Many adsorbents for REEs have been studied [7–17]; however, none is in practical use, and the adsorption of dilute REE ions from solutions containing high concentrations of base metal ions is particularly difficult with the adsorbents reported to date.

In previous work, we developed a novel silica gel–based adsorbent bearing diglycolamic acid ligands for the selective adsorption of REEs [18–20]. This adsorbent selectively adsorbs REE ions from solutions containing high concentrations of base metal ions, and its adsorption capabilities for heavy REE ions are higher than those for light REE ions. The diglycolamic acid ligands are immobilized on the silica gel by means of a chemical reaction between the ligand functional groups and the silanol groups on the surface of the silica gel. The adsorption capacity of the adsorbent increases with increasing ligand loading on the
support, but ligand loading is limited by the number of silanol groups on the silica gel surface (that is, by the specific surface area of the gel). The specific surface area in turn decreases with increasing average pore size, but because decreasing the pore size reduces the adsorption rate, simultaneously improving both the adsorption capacity and the adsorption rate is difficult. Therefore, we focused on graft polymerization as a method for introducing a ligand to the support to improve its adsorption capacity. Graft polymerization has been used to introduce ligands to various forms of trunk polymers [21], and this method is expected to be useful for increasing ligand loading without reducing adsorption rate. The trunk polymers that were subjected to graft polymerization were in film form instead of in bead form. Conventional adsorbents are also commonly in bead form, which is suitable for column-based adsorption processes. However, for solutions that contain large amounts of suspended solids or deposited salts, column-based processes are not applicable. Film adsorbents are superior for systems in which liquid and solid coexist.

In the present study, we prepared a novel film-type adsorbent with immobilized diglycolamic acid ligands by using graft polymerization to improve the adsorption capacity. First, we synthesized polymerizable ligands bearing diglycolamic acid groups and then immobilized the ligands on the film by means of graft polymerization. For comparison, we also synthesized an adsorbent consisting of silica gel modified with diglycolamic acid groups. The adsorption behaviors, REE selectivities, and adsorption capacities of the two types of adsorbents were evaluated.

2. Experimental

2.1 Materials

We used a nonwoven poly(vinyl alcohol) fabric with a thickness of 160 μm and a weight of 50 g/m² as the support for the film-type adsorbent. 3-Aminopropyl silica gel (spherical particles with a diameter of 0.1 mm, Fuji Silysia, Japan) was used as a starting material for the silica gel adsorbent. Stock solutions of metal ions were prepared from neodymium(III) chloride hexahydrate, dysprosium(III) chloride hexahydrate, iron(III) chloride hexahydrate, copper(II) chloride dihydrate, and zinc(II) chloride (Wako Pure Chemical Industries, Japan). All chemicals and solvents used for the synthesis of the adsorbents were used as received from the suppliers. Deionized and distilled water was used in all the procedures.

2.2 Preparation of the polymerizable ligand

The synthetic procedure for the diglycolamic acid–methacrylate polymerizable ligand is shown in Scheme 1. Triethylamine (15.2 g, 0.15 mol) was added to a solution of 2-aminoethyl methacrylate hydrochloride (16.5 g, 0.1 mol) in 120 mL of tetrahydrofuran (THF) cooled in an ice bath, and then diglycolic anhydride (11.6 g, 0.1 mol) in 80 mL of THF was added while the reaction temperature was maintained at ≤283 K. The reaction mixture was allowed to cool to room temperature and was then stirred for 12 h. After filtration, the filtrate was purified by column chromatography on silica gel using THF as eluent, and the purified product was recrystallized from toluene to afford a white powder (11.24 g, 45.7% yield); 1H NMR (CDCl₃, 300 MHz, 295 K) δ 6.14 (s, 1H, =C₃H₂), 5.61 (s, 1H, =C₃H₂), 4.29 (t, 2H, O-C₃H₂-CH₂-N), 4.22 (s, 2H, O-C₃H₂-COOH), 4.14 (s, 2H, N-CO-C₃H₂-O), 3.65 (m, 2H, O-C₃H₂-CH₂-NH), 1.95 (s, 3H, CH₂=C=CH₃).
2.3 Preparation of the film-type adsorbent

A nonwoven fabric made from poly(vinyl alcohol) was irradiated with an electron beam in a nitrogen atmosphere at ambient temperature. The accelerating voltage was 250 kV, and the dose was 90 kGy. The irradiated fabric was immersed for 15 min at 323 K in a 50 wt% diglycolamic acid–methacrylate aqueous solution from which dissolved oxygen had been removed by nitrogen gas bubbling. After the reaction, the fabric was washed with water and dried in air at 313 K.

2.4 Preparation of the silica gel adsorbent

For comparison, we synthesized an adsorbent consisting of silica gel particles modified with diglycolamic acid groups (Scheme 2). Diglycolic anhydride (0.4887 g, 0.004 mol) and 3-aminopropyl silica gel (1 g) were added to 5 mL of dichloromethane. After reaction at 298 K for 3 days, the silica gel particles were filtered off, washed with dichloromethane and ethanol to remove any unreacted starting materials, and rinsed with water. The particles were dried in vacuo at 333 K.

2.5 Procedure for the adsorption experiments

In a typical adsorption experiment, the adsorbent was added to 5 mL of a solution containing metal ions, and the mixture was shaken at 298 K for 1 day. After filtration, the concentration of each metal ion in the filtrate was determined with an inductively coupled plasma spectrometer (Shimadzu, Japan, ICPE-9000), and the adsorbed amount of each metal ion was calculated.

3. Results and Discussion

3.1 Characterization of the adsorbents

We investigated the loading of diglycolamic acid ligands on the two adsorbents. For the film-type adsorbent, the degree of grafting ($d_g$, %), which is defined as

$$d_g = 100\left[\frac{W_1 - W_0}{W_0}\right]$$  (1)
where $W_0$ and $W_1$ are, respectively, the masses of the original and grafted films and $d_g$ was 136%. Therefore, the loading of diglycolamic acid ligands on the film-type adsorbent was 2.35 mmol/g-adsorbent. To estimate the loading of ligands on the silica gel adsorbent, we carried out elemental analyses of 3-aminopropyl silica gel (N 0.735, C 2.01) and the prepared silica gel adsorbent (N 0.898, C 6.35). From the C/N molar ratio, we estimated that the loading of diglycolamic acid ligands was 0.616 mmol/g-adsorbent. This value indicates that almost all the amino groups of the aminosilica gel were modified with diglycolamic acid groups. Our results indicate that loading of diglycolamic acid ligands on the film-type adsorbent was 3.81 times that on the silica gel adsorbent.

### 3.2 REE adsorption properties of adsorbents

To investigate the ability of the two adsorbents to adsorb REE ions (dysprosium and neodymium) and base metal ions (copper, iron(III), and zinc), we carried out adsorption experiments at an initial pH of 1.0; the initial concentration of each metal ion was 1 mmol/L. The two adsorbents showed similar adsorption behavior (Figure 1). Only small amounts of the base metal ions were adsorbed; that is, REE ions were adsorbed selectively. Moreover, the adsorbed amount of dysprosium (a heavy REE) was higher than that of neodymium (a light REE). The film-type adsorbent showed heavy-REE selectivity similar to that of the silica gel adsorbent.

![Figure 1. Amounts of metals adsorbed on the film-type and silica gel adsorbents. Initial concentration of each metal ion, 1 mmol/L; initial pH, 1.0 (adjusted with HCl); solution volume, 5 mL; amount of adsorbent, ca. 30 mg (2 pieces of film-type adsorbent, 1 x 1 cm each) or 50 mg (silica gel adsorbent).](image)

The isotherms for dysprosium adsorption at 298 K at the initial pH values of 1.0 and 3.0 were measured and analyzed by means of the Langmuir equation, which is commonly used to describe adsorption isotherms:

$$Q = \frac{K_L Q_m C_{eq}}{1 + K_L C_{eq}}$$  \hspace{1cm} (2)

where $Q$ is the amount of adsorbed dysprosium ions at equilibrium; $K_L$ is the Langmuir constant; $Q_m$ is the
adsorption capacity of the adsorbent; and $C_{eq}$ is the equilibrium concentration of dysprosium ions in the solution. Equation (2) can be rewritten in a linearized form as

$$\frac{C_{eq}}{Q} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right) C_{eq} \quad (3)$$

We fitted Eq. (3) to plots of $C_{eq}/Q$ versus $C_{eq}$ to obtain the values of $K_L$ and $Q_m$ (Table 1). The adsorption isotherms are shown in Figure 2; the curves represent the fitted values. Although both adsorbents had the same ligand, the values of $K_L$, which is related to adsorption energy, differed for the two adsorbents. We suggest that the difference in the $K_L$ values was due to differences in the properties of the supports (especially the hydrophilicities of the support surfaces). Note that the $Q_m$ value of the film-type adsorbent was about 3–4 times that of the silica gel adsorbent because the ligand loading on the former was 3.81 times that on the latter.

Table 1. Langmuir constants ($K_L$) and adsorption capacities ($Q_m$) for dysprosium on film-type and silica gel adsorbents at 298 K.$^a$

<table>
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<th>pH 1.0</th>
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<th>pH 3.0</th>
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<tbody>
<tr>
<td></td>
<td>$K_L$</td>
<td>$Q_m$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>Film-type adsorbent</td>
<td>0.231</td>
<td>0.261</td>
<td>23.5</td>
</tr>
<tr>
<td>Silica gel adsorbent</td>
<td>1.03</td>
<td>0.0691</td>
<td>668</td>
</tr>
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$^a$ Experimental conditions: initial concentration of dysprosium ion, 0.2–7 mmol/L; initial pH, 1.0 or 3.0 (adjusted with HCl); solution volume, 5 mL; amount of adsorbent, ca. 16 mg (3 pieces of film-type adsorbent, 0.5 × 0.7 cm each) or 50 mg (silica gel adsorbent).

Figure 2. Isotherms for adsorption of dysprosium on film-type and silica gel adsorbents at 298 K. Initial pH, 1.0 or 3.0 (adjusted with HCl); solution volume, 5 mL; amount of adsorbent, ca. 16 mg (3 pieces of film-type adsorbent, 0.5 × 0.7 cm each) or 50 mg (silica gel adsorbent).
4. Conclusion

We synthesized a novel film-type adsorbent bearing diglycolamic acid ligands immobilized on a nonwoven poly(vinyl alcohol) fabric by means of grafting polymerization. Compared to our previously reported silica gel adsorbent, the film-type adsorbent showed similar selectivity for a heavy REE, but the adsorption capacity of the film-type adsorbent was 3–4 times that of the silica gel adsorbent because the ligand loading on the former was 3.81 times that on the latter.

References