# Adsorption behavior of rare earth elements on silica gel modified with diglycol amic acid

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## A B S T R A C T

For the recovery of rare earth elements, we previously synthesized an adsorbent consisting of silica gel particles modified with diglycol amic acid groups. In the present study, we optimized the amount of diglycolic anhydride used for the synthesis of the adsorbent and evaluated the utility of the adsorbent in terms of its selectivity for rare earth metal ions, the rate of metal ion adsorption, and the desorption behavior of the ions. We also analyzed the adsorption isotherms of the metal ions. The optimum amount of diglycolic anhydride was 4.0 mmol/gram of amino silica gel, and this amount resulted in the introduction of 1.04 mmol of diglycol amic acid groups per gram of adsorbent. The introduction of the diglycol amic acid groups had little effect on the specific surface area and average pore size of the silica gel particles, and we attributed the high adsorption rate to the large pore size. Acid concentration strongly influenced the adsorbability of rare earth metal ions, which were readily desorbed by 1 mol/L mineral acid. The adsorption isotherms for the lanthanoids at an initial pH of 1.0 were determined with the Langmuir equation. The adsorption capacities of the adsorbent for the heavy rare earth metal ions were higher than those for the light ones.

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## 1. Introduction

The rare earth elements—a group of seventeen elements consisting of scandium, yttrium, and the lanthanoids—are used in cutting-edge technologies such as electric cars, smart phones, and wind turbines. In 2013, about 90% of the global production of rare earth elements occurred in China (U.S. Geological Survey, 2014), and therefore the production of these elements in other countries is important from the viewpoint of resource management and security. Previously unused sources of these elements, such as low-grade ores (Habashi, 1985; Kato et al., 2011; Kon et al., 2014; Wang et al., 2010) and REE-containing End-of-Life products (Binnemans et al., 2013; Tanaka et al., 2013), have been receiving increasing attention.

The recovery of rare earth elements from ores and scraps requires selective separation of dilute rare earth metal ions from solutions that also contain high concentrations of base metal ions such as iron, copper, and zinc. Iron in particular is typically present in ores at high concentrations and often prevents the recovery of rare earth metal ions (Wang et al., 2010; Wu et al., 2013; Xie et al., 2014); commercial organophosphorus extractants (e.g., DEHPA and PC-88A) extract iron(III) ions more efficiently than they extract rare earth(III) ions.

Precipitation and solvent extraction are established techniques for metal recovery and are especially useful for large-scale operations at high metal ion concentrations. In contrast, adsorption can be used to recover metal ions even from low-concentration sources by means of relatively simple processes. Many adsorbents for rare earth elements have been studied (Alakhras et al., 2005; Araki et al., 2000; Bou-Maroun et al., 2006; Chen et al., 2012; Choi et al., 2003; Das and Das, 2013; Dupont et al., 2014; Jia et al., 2004; Ramakrishnan and Rao, 2006; Shibata et al., 2000; Wang et al., 2013; Wu et al., 2013); nevertheless, there are no adsorbents in practical use. The requirements for practical adsorbents include high selectivity for rare earth metal ions, adsorbability at low pH, easy desorption of the metal ions, high adsorption and desorption rates, high adsorption capacity, durability against repeated use, low cost, and high mechanical strength.

With the goal of designing a practical adsorbent, we considered ligands, supports, and methods for introducing ligands onto supports. In previous work (Ogata et al., 2014), we focused on molecules with a diglycol amic acid framework as ligands for selective adsorption of rare earth metal ions. We selected silica gel particles as a support, owing to their low cost, mechanical strength, and chemical stability. We expected the mechanical strength and the volume change of silica gel-based adsorbents to be on par with or better than those of the polymer resin adsorbents that are widely used in real-world plants. We also expected that chemical immobilization of diglycol amic acid ligands onto the surface of silica gel particles would allow for repeatable use of the adsorbent. We found that the adsorbent selectively adsorbs rare earth elements from a low-pH solution containing high concentrations of base metals. We attributed the high selectivity for the rare earth elements to chelation by the tridentate diglycol amic acid framework.

In the present study, we determined the optimum amount of diglycolic anhydride for the synthesis of the adsorbent and evaluated the practicality of the adsorbent in terms of selectivity for rare earth metal ions, adsorption rate, and desorption behavior. We also obtained and analyzed the adsorption isotherms of the rare earth metal ions by using the Langmuir equation.

## 2. Materials and methods

### 2.1. Materials

Diglycolic anhydride and 3-(ethylenediamino)propyl silica gel (EDASi) were purchased from Tokyo Chemical Industry. Stock solutions of metal ions were prepared from the following reagents as received from the specified suppliers: lanthanum(III) chloride heptahydrate, cerium(III) chloride heptahydrate, neodymium(III) chloride hexahydrate, samarium(III) chloride hexahydrate, gadolinium(III) chloride hexahydrate, terbium(III) chloride hexahydrate, dysprosium(III) chloride hexahydrate, holmium(III) chloride hexahydrate, erbium(III) chloride hexahydrate, ytterbium(III) chloride hexahydrate, iron(III) chloride hexahydrate, copper(II) chloride dihydrate, zinc(II) chloride (Wako Pure Chemical Industries), praseodymium(III) chloride heptahydrate, thulium(III) chloride hydrate, lutetium(III) chloride hexahydrate (Strem Chemicals), and europium(III) chloride hexahydrate (Tokyo Chemical Industry). All chemicals and solvents used for the synthesis of the adsorbent were used without further purification. Deionized and distilled water was used in all the procedures.

### 2.2. Preparation and characterization of adsorbents

Silica gel particles modified with diglycol amic acid were prepared as described in our previous paper (Ogata et al., 2014). Briefly, diglycolic anhydride and EDASi were added to dichloromethane and allowed to react at 298 K for 3 days, at which point the particles were filtered off, washed with dichloromethane and ethanol to remove unreacted starting materials, and rinsed again with water. The washed and rinsed particles were dried under vacuum; the resulting particles are referred to hereafter as EDASiDGA (Fig. 1). Elemental analyses for carbon, hydrogen, and nitrogen, of EDASi and EDASiDGA were carried out with an elemental analyzer (EA1110, CE Instruments). Nitrogen sorption by EDASi and EDASiDGA was measured with a NOVA-4200e surface area analyzer (Quantachrome) at 77 K. Prior to nitrogen physisorption, the samples were allowed to outgas for 360 min at 383 K under vacuum. The specific surface areas of the particles were calculated from the Brunauer–Emmett–Teller equation over the relative pressure range ($P/P_0$) of 0.05–0.3, over which a linear relationship was maintained.
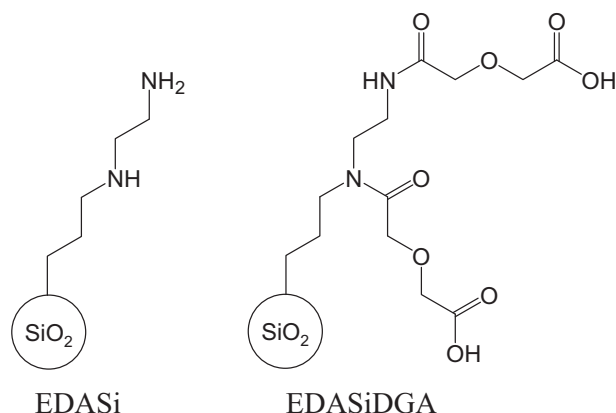
The average pore sizes and the pore volumes of the particles were calculated by means of the Barrett–Joyner–Halenda equation.

### 2.3. Procedure for adsorption and desorption experiments

Adsorption and desorption experiments for all rare earth metal ions were carried out in a batch system. A typical adsorption experimental procedure was as follows: the adsorbent (0.05 g, dry basis) was added to 5 mL of a solution containing metal ions, and the mixture was shaken at 298 K for at least 1 day (except the time course test). After filtration, the concentration of each metal ion, $C$, in the filtrate was determined with an inductively coupled plasma spectrometer (Shimadzu, ICPE-9000), and the adsorption ratio of each metal ion was calculated from the following equation:

$$\text{Adsorption ratio} = \frac{(C_0 - C)}{C_0} \times 100 \tag{1}$$

where $C_0$ is the initial concentration.

## 3. Results and discussion

### 3.1. Effect of the amount of diglycolic anhydride and characterization of the adsorbents

To determine the optimum amount of diglycolic anhydride for adsorbent synthesis, we carried out the synthesis with various amounts of anhydride (3, 4, and 6 mmol/g-EDASi). To estimate the amounts of amino groups and diglycol amic acid moieties on the silica gel, we conducted elemental analyses of EDASi and EDASiDGA (Table 1). From the mass percentage of nitrogen in EDASi, we calculated the amount of amino groups per gram of the EDASi particles to be 1.53 mmol. The yields and diglycol amic acid group contents were estimated from the C/N molar ratio (Table 1). We found that the amount of diglycol amic acid groups in EDASiDGA initially increased as the amount of diglycolic anhydride was increased but became saturated at 4 mmol/g-EDASi.

We conducted dysprosium adsorption tests in the initial pH range of 0.5 to 2.5 with adsorbents prepared with the diglycolic anhydride amounts listed in Table 1 (Fig. 2). The adsorption ability of EDASiDGA prepared with diglycolic anhydride at 4 mmol/g-EDASi was the same as that of the adsorbent prepared with 6 mmol/g-EDASi and was clearly higher than that of the adsorbent prepared with 3 mmol/g-EDASi. These results indicate that the optimum amount of anhydride was 4 mmol/g-EDASi, which was the amount that we used to prepare the adsorbents for the subsequent experiments.

The specific surface areas, average pore sizes, and pore volumes of EDASi and EDASiDGA were obtained from the nitrogen sorption measurements (Table 2). The values for EDASi were high enough to permit high mass transfer of metal ions to the silica gel support, and only slight decreases in these values were observed after the introduction of the diglycol amic acid groups. Therefore, we expected that EDASiDGA would also permit high mass transfer to the silica gel support.



Fig. 1. Chemical structures of EDASi and EDASiDGA.

**Table 1**
Elemental analyses of EDASi and of EDASiDGA prepared with various amounts of diglycolic anhydride.

| Adsorbent | Diglycolic anhydride amount (mmol/g-EDASi) | Mass percentage (mass %) | | C/N[a] | Yield (%) | Functional group content[b] (mmol/g-adsorbent) |
|---|---|---|---|---|---|---|
| | | C | N | | | |
| EDASi | – | 5.05 | 2.15 | 2.74 | – | 1.53 |
| EDASiDGA | 3 | 8.91 | 1.92 | 5.41 | 66.8 | 0.967 |
| EDASiDGA | 4 | 8.99 | 1.86 | 5.63 | 72.2 | 1.04 |
| EDASiDGA | 6 | 9.26 | 1.93 | 5.61 | 71.8 | 1.04 |

[a] Molar ratio.
[b] Amino groups in EDASi; diglycol amic acid groups in EDASiDGA.