



Adsorption mechanism of rare earth elements by adsorbents with diglycolamic acid ligands



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ABSTRACT

Previously, we investigated silica gel adsorbents bearing immobilized diglycolamic acid ligands (designated EDASiDGA) for the selective recovery of rare earth elements (REEs) from acidic solution, but the details of the adsorption mechanism remained to be elucidated. In this study, to clarify the adsorption mechanism, we prepared some derivatives of EDASiDGA and investigated the differences in their adsorption behaviors with respect to REE ions. On the basis of our results, we concluded that adsorbents with diglycolamic acid ligands adsorb REE ions via three oxygen atoms (that is, the ether, amide, and carboxylic acid oxygen atoms of the diglycolamic acid ligands) and that this tridentate chelation confers high selectivity for REE ions.

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1. Introduction

Rare earth elements (REEs) are used in clean energy technologies: for example, neodymium, and dysprosium for magnets in wind turbines and electric vehicles and lanthanum, cerium, europium, terbium and yttrium for phosphors in energy efficient lights. According to the U.S. Department of Energy, in the medium term (2015–2025), the heavy REE dysprosium is the most critical REE for the deployment of clean energy technologies (U.S. Department of Energy, 2011). The demand for heavy REEs is increasing, but most heavy REEs are produced from ion-adsorption-type ores in a single location, southern China (Roskill, 2015). Therefore, the development of new sources of heavy REEs is important to ensure a secure supply of these elements. Recently, there has been increasing interest in recovering them from underutilized low-grade ores including apatite (Emsbo et al., 2015; Ogata et al., 2016), as well as from deep-sea mud (Kato et al., 2011; Kon et al., 2014). Hydrometallurgical processes, such as precipitation, solvent extraction, and adsorption, can be expected to play major roles in any process developed to recover heavy REEs from solution. 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 (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); however, none are 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.

With the goal of designing a practical adsorbent, we investigated various ligands, supports, and methods for introducing ligands onto supports and eventually focused on diglycolamides (which contain ether linkages between two amide groups) as ligands for the selective adsorption of REE ions. Diglycolamide compounds have been studied as extractants for the separation of actinides from high-level nuclear waste (Ansari et al., 2012), and Narita and Tanaka (2013) synthesized *N,N'*-dimethyl-*N,N'*-dioctyldiglycolamide and found that it can be used for selective extraction of REE ions over base metal ions at relatively high concentrations in mineral acids. Naganawa et al. (2007) synthesized dioctyldiglycol amic acid, an analog of *N,N,N',N'*-tetraoctyldiglycolamide, and this analog has been used to extract REE ions from moderately acidic solution (pH 2–4) and separate REE ions from base metal ions (Baba et al., 2011). In our previous work (Ogata et al., 2014, 2015a, 2015b, 2016), we immobilized diglycolamic acid ligands on silica gel (designated EDASiDGA) in which we expected the mechanical strength and the volume change of the resulting silica gel-based adsorbent 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 the diglycolamic acid ligands on the surface of silica gel particles would allow for recycling of the adsorbent. As a result of the metal adsorption experiment, EDASiDGA was found to selectively adsorb REE ions from solutions containing

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high concentrations of base metal ions and have higher adsorption capabilities for heavy REE ions than those for light REE ions. Although the high REE selectivity seems to be attributed to chelation of the metal ions by the tridentate diglycolamic acid framework, the details of the adsorption mechanism remain to be elucidated.

In the present study, we prepared some derivatives of EDASiDGA and investigated the differences among their adsorption behaviors to clarify the REE ion adsorption mechanism. Specifically, nine adsorbents were synthesized from three types of amino-silica gels combined with three different cyclic anhydrides, which were allowed to react with the amino-silica gels to form amide compounds. The resulting adsorbents were used for REE ion adsorption tests, and their adsorption behaviors were evaluated.

2. Materials and methods

2.1. Materials

We used three kinds of amino-silica gels: 3-aminopropyl silica gel (NHSi), which contains a primary amine; 3-(methyleneamino)propyl silica gel (SNHSi), which contains a secondary amine; and 3-(ethylenediamino)propyl silica gel (EDASi), which contains primary and secondary amines. These amino-silica gels, which were purchased from Fuji Silysia, had approximately the same particle size (ca. 100 μm), pore size (ca. 10 nm), and specific surface area (ca. 300 m^2/g). To prepare amide compounds, we allowed these amino-silica gels to react with succinic anhydride (Wako Pure Chemical Industries), glutaric anhydride (Tokyo Chemical Industry). 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). All chemicals and solvents used for the synthesis of the adsorbents were used as obtained from the suppliers. Deionized, distilled water was used in all the procedures.

2.2. Preparation and characterization of adsorbents

Nine kinds of adsorbents were prepared by reactions of the three amino-silica gels with the three cyclic anhydrides (Fig. 1, schemes of synthesis of all adsorbents are shown in the supporting information). A typical procedure is as follows. A cyclic anhydride (0.004 mol) and an amino-silica gel (1 g) were added to 5 mL of dichloromethane and allowed to react at 298 K for 3 days. Then the silica gel particles were filtered off, washed with dichloromethane and ethanol to remove any unreacted substances, rinsed with water, and dried in vacuo at 333 K. The resulting succinamic acid, glutaramic acid, and diglycolamic acids are designated hereafter as SCA, GLA, and DGA, respectively. The attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra of the unmodified amino-silica gels and the synthesized adsorbents were measured with a Spectrum 100 spectrophotometer (Perkin Elmer). Elemental analyses of the unmodified amino-silica gels and the synthesized adsorbents were performed with a FLASH 2000 elemental analyzer (Thermo Scientific).

2.3. Procedure for adsorption experiments

The typical procedure for the adsorption experiments was as follows: an adsorbent (50 mg, dry basis) was added to 5 mL of a solution containing metal ions, and the mixture was shaken at 298 K for 3 days. After filtration of the mixture, the concentration of each metal ion (dysprosium, neodymium, copper, iron(III), and zinc) in the filtrate

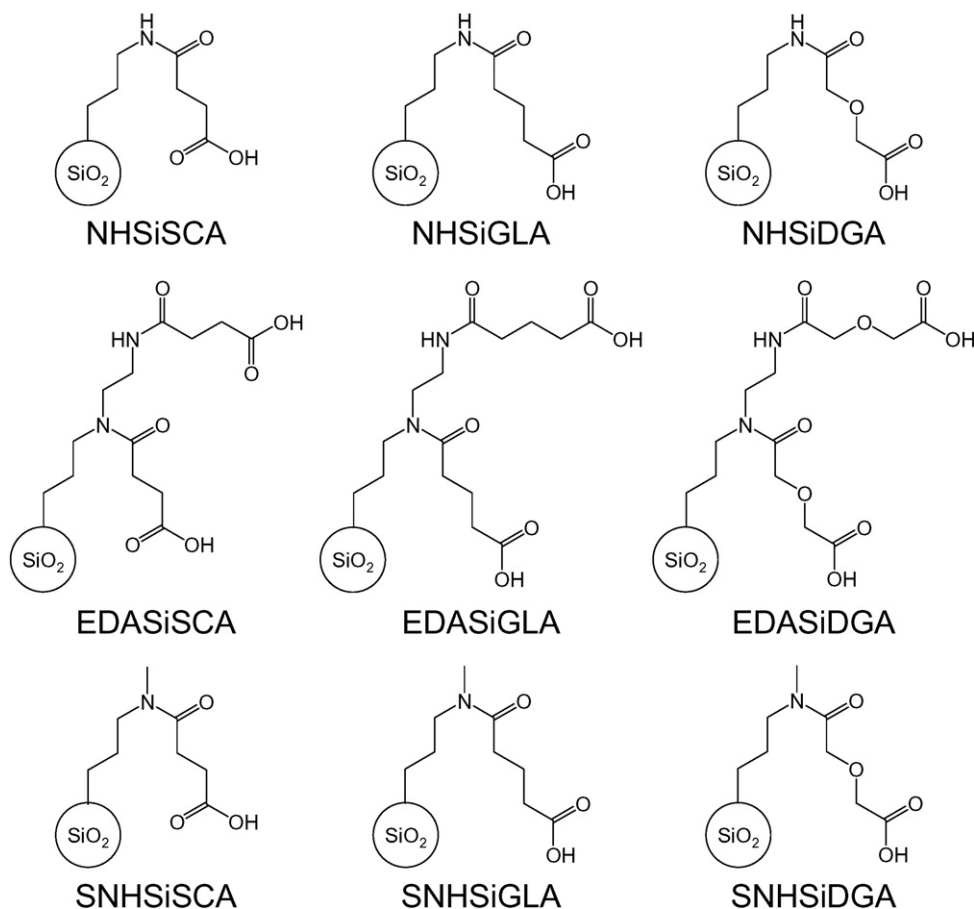


Fig. 1. Chemical structures of adsorbents.

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