Adsorbents for Selective Recovery of Heavy Rare Earth Elements

Takeshi Ogata, Hirokazu Narita and Mikiya Tanaka

Abstract There is an increasing attention to recover dilute rare earth elements (REEs) from acidic solutions in order to meet their demands and stabilize their supply chain. Adsorption is suitable for recovering target metal ions when their concentrations are low. Many adsorbents for REEs have been studied; nevertheless, there are no adsorbents in practical use. We have developed adsorbents consisting of silica gel particles modified with diglycolamic acid groups. The adsorbent has the ability to selectively adsorb RE ions from solutions containing high concentrations of base metal ions in a low pH region, and the adsorption capacities of the adsorbent for the heavy REEs were higher than those for the light ones. Moreover, this adsorbent meets the requirements for a practical adsorbent, such as high durability, easy desorption, and high adsorption rate. We therefore conclude that the adsorbent can contribute the production of heavy REEs from underutilized resources.

Keywords Rare earth · Adsorption · Separation · Recovery

Introduction

Rare earth elements (REEs)—a group of 17 elements consisting of scandium, yttrium, and the lanthanoids—are used in cutting-edge technologies such as electric cars, smart phones, and wind turbines. A U.S. Department of Energy report states that in the medium term (2015–2025), REEs such as yttrium, neodymium, europium, terbium, and dysprosium are important elements for the clean energy industry; and, except for Nd, all of these elements are middle and heavy REEs [1]. The demand for heavy REEs is increasing, but most heavy REEs are produced from

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ion-adsorption-type ores in a single location, southern China [2]. Therefore, the development of new sources of heavy REEs is important to ensure a secure supply of these elements.

We focus on underutilized resources of heavy REEs such as low-grade ores [3–6] and REE–containing End-of-Life products [7, 8]. Development risks can be avoided through recovery of REEs in the form of byproducts from the present industrial processes; furthermore, REEs can potentially be obtained at low cost. However, REEs only exist in low concentrations in such underutilized resources; what is more, base metals such as iron and aluminum coexist in high concentrations. Adsorption is an effective hydrometallurgical technology for recovering target metal ions when their concentrations are low. Many adsorbents for REEs have been studied, but none so far has been appropriate for practical use.

With the goal of designing a practical adsorbent, we considered (i) ligands that selectively adsorb REEs, (ii) supports to immobilize these ligands, and (iii) methods to introduce ligands onto supports. (i) We focused on diglycolamide compounds that are tridendate oxygen donor ligands as candidates with selectivity towards REEs. Diglycolamide compounds have been studied during nuclear energy research, where they are employed as extractants in solvent extraction processes; their application in the separation of actinides and lanthanoids has been investigated [9]. Narita and Tanaka, for example, synthesized *N,N′*-dimethyl-*N,N′*-di-*n*-octyl-diglycolamide as an extractant for separating REEs and base metals; they succeeded in the selective extraction of REEs at relatively high pH [10]. Further, rather than considering diamide compounds, Naganawa et al. synthesized dioctyldiglycol amic acid (DODGAA), as an analogue to *N,N,N′,N′*-tetraoctyl diglycolamide [11]; this extractant has selectivity for REEs in the relatively weak acid range of pH 2–4 [12]. Recovery of low concentrations of REEs is typically carried out in the dilute acid range (pH of ca. 1–2); for this reason, we selected diglycolamic acid as the adsorbent ligand. (ii) For supports on which to immobilize ligands, factors such as swelling, chemical and physical stability and cost need to be considered. Silica gel and zeolites are widely used as inorganic supports, while polystyrenes and polyacrylates are widely employed as organic supports. Adsorbents are generally spherical in shape. We used spherical silica gel particles with a low degree of swelling, and good chemical resistance, and mechanical strength. (iii) Broadly speaking, there are two methods employed for immobilizing ligands on supports: physical and chemical methods. The physical immobilization method imparts the ligands with a relatively high degree of freedom and for this reason, high selectivity on par with that of the solvent extraction method can be expected; however, physically immobilized ligands tend to leak out from their supports due to the physical nature of the bond and in many cases it is difficult to use such materials for an extended period of time. On the other hand, chemically immobilized ligands are chemically bonded to the support; therefore degradation is limited. We introduced the diglycolamic acid ligand to the surface of a silica gel support via chemical bonding (silane coupling). This method of introducing a ligand to a support is expected to facilitate rapid adsorption as well as extended utilization. The EDASiDGA (3-(ethylenediamino)propyl silica gel bearing

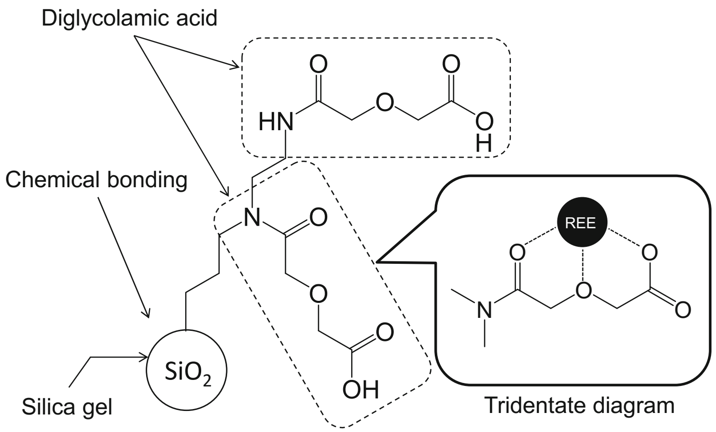

Fig. 1 Chemical structure of EDASiDGA adsorbent

immobilized diglycolamic acid ligands) adsorbent shown in Fig. 1 was developed based on such a guiding principle [13–16].

In the present study, we performed column experiments to clarify the feasibility of EDASiDGA for practical use. In addition, we evaluated the selective adsorption of heavy RE ions from a simulated solution containing dilute RE ions and high concentrations of base metal ions at low pH (pH 1.0).

Experimental

Silica gel particles modified with diglycolamic acid were prepared as described in our previous paper [13, 14]. Briefly, diglycolic anhydride and 3-(ethylenediamino) propyl silica gel 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.

Column adsorption experiments were carried out with the EDASiDGA adsorbent: An 8 mm internal diameter glass column was packed with 1.0 g of EDASiDGA (bed volume: 1.86 cm^3) that was then washed with a hydrochloric acid solution adjusted to pH 1.0. An appropriate quantity of adsorption test solution was then fed through the packed column and the effluent was collected. Then, a hydrochloric acid solution (pH 2.0) was fed as a cleaning solution, followed by a 1 M sulfuric acid solution as an eluent and the eluates were collected. Metal ion concentrations in each of the eluate fractions collected were measured using an inductively coupled plasma spectrometer (Shimadzu, ICPE-9000). All column experiments were conducted at room temperature (291 ± 2 K).

Results and Discussion

To investigate the adsorption and desorption rates of the EDASiDGA adsorbent, dysprosium recovery from 1 mM dysprosium chloride solution at pH 1.0 (adjusted by using HCl) was evaluated at various flow rates. We set the space velocity (*SV*) from 5 to 100 h^{-1}. Here, the *SV* is defined as the flow rate/the volume of the adsorbent bed in the column; *SV* indicates how many bed volumes of the test solution can be treated per hour. The results are shown in Fig. 2, in which the ratio of the concentration of dysprosium ion in the effluent (C) to its initial concentration (C_0) is plotted versus bed volumes. When the dysprosium solution was fed through the column as the adsorption test solution, the dysprosium concentration of the effluent was below the detection limit for all *SV* tested. After breakthrough, the concentration of dysprosium in the effluent rapidly increases and approaches the initial concentration. Furthermore, major differences in *SV* were not apparent for the breakthrough curve, and an acceptable breakthrough curve were obtained regardless of the *SV* values. When taking into consideration the fact that commercially available adsorbents are utilized at *SV*s of 5–40 h^{-1} [17], our results show that the adsorption rate of EDASiDGA is sufficiently high for practical application. The dysprosium that was adsorbed were quantitatively desorbed with ease using 1 M sulfuric acid solution and no tailing of the desorption curve was apparent. These findings clearly show that the adsorbed REEs are easily desorbed and recovered using relatively low concentrations of acid.

A test solution was prepared to simulate conditions of low concentrations of REEs and high concentrations of base metals in order to verify the practicality of the adsorbent. The simulated solution was adjusted to pH 1.0 using hydrochloric acid; each REEs concentration was 0.1 mM and each base metal concentration was 0.1 M (one-thousand times that of the REEs). After the test solution was fed, the base metals aluminum, calcium, iron (III), copper, and zinc did not interact with the

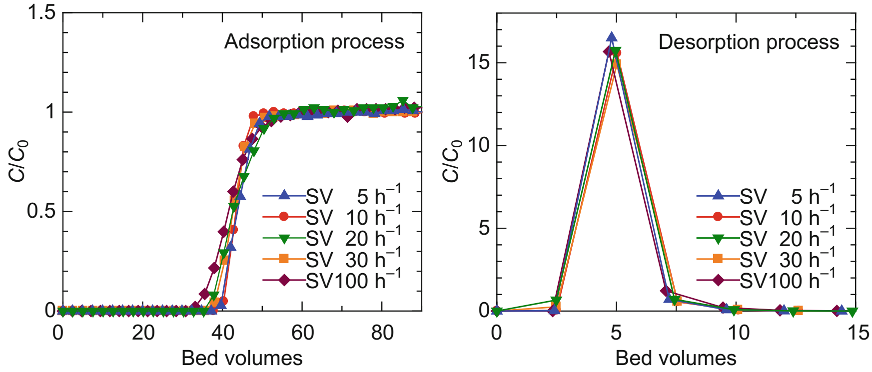

Fig. 2 Space velocity (*SV*) dependency of dysprosium on EDASiDGA. Adsorption solution: aqueous dysprosium solution (initial concentration: 1 mM, pH 1.0); washing solution: HCl (pH 2.0); eluent: H_2SO_4 (1 M)

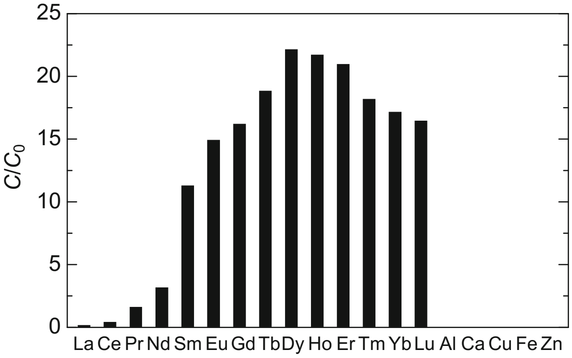

Fig. 3 Ratios of final effluent metal ion concentration (C) versus initial concentration (C_0)

adsorbent in the column and were discharged. Conversely, the rare earth elements were retained in the column. After a certain volume had passed through, rare earth elements started to break through in the order of atomic number (lanthanum, cerium, praseodymium…): this is thought to be due to displacement of light rare earth elements by heavy rare earth elements because of the higher adsorption capacity of the adsorbent for the latter. After heavy rare earth elements such as dysprosium, holmium, and erbium had broken through, the metal ions still adsorbed were desorbed using 1 M sulfuric acid solution. Figure 3 shows the ratio of the concentration of each metal ion in the effluent (C) to its initial concentration (C_0). The REEs alone were recovered, with almost no base metals such as aluminum, calcium, iron (III), copper, and zinc present in the effluent. The findings show that feeding an aqueous test solution to the packed column results in REEs being selectively retained in the column; these are then desorbed and recovered using acid solution of relatively low concentration. Furthermore, selectivity for medium and heavy REEs is higher than for light REEs; dysprosium can be concentrated to more than 20 times its initial concentration.

Conclusions

Targeting the recovery of REEs from underutilized resources such as low-grade ores and wastes, we developed a new adsorbent capable of selectively separating and recovering low concentrations of REEs from high concentrations of base metals. This adsorbent can selectively adsorb medium and heavy REEs, which can then be easily desorbed and recovered using relatively low concentrations of acid. Special mention should be made of the high adsorption capability for heavy REEs that are particularly valued as resources. Adsorption-desorption rates of the adsorbent are more than sufficient to be applied practically, while properties other than adsorption, such as physical stability, compare favorably with commercially available adsorbents. Thus, the absorbent has the potential to be applied commercially and may contribute to the recovery of REEs from underutilized resources.

References

1. *Critical Materials Strategy* (U.S. Department of Energy, 2011)
2. *Rare Earths: Market Outlook to 2020*, 15th edn. (Roskill, 2015)
3. F. Habashi, The recovery of the lanthanides from phosphate rock. J. Chem. Technol. Biotechnol. **35A**, 5–14 (1985)
4. Y. Kato et al., Deep-sea mud in the pacific ocean as a potential resource for rare-earth elements. Nat. Geosci. **4**, 535–539 (2011)
5. Y. Kon et al., Geochemical characteristics of apatite in heavy REE-rich deep-sea mud from Minami-Torishima area, southeastern Japan. Resour. Geol. **64**, 47–57 (2014)
6. T. Ogata et al., Selective recovery of heavy rare earth elements from apatite with an adsorbent bearing immobilized tridentate amido ligands. Sep. Purif. Technol. **159**, 157–160 (2016)
7. M. Tanaka et al., Recycling of rare earths from scrap, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. by J.C.G. Bünzli, V.K. Pecharsky, vol. 43 (Amsterdam, Elsevier, 2013), pp. 159–212
8. K. Binnemans et al., Recycling of rare earths: a critical review. J. Clean. Prod. **51**, 1–22 (2013)
9. S.A. Ansari et al., Chemistry of diglycolamides: promising extractants for actinide partitioning. Chem. Rev. **112**, 1751–1772 (2012)
10. H. Narita, M. Tanaka, Separation of rare earth elements from base metals in concentrated HNO_3, H_2SO_4 and HCl solutions with diglycolamide. Solvent Extr. Res. Dev. Jpn. **20**, 115–121 (2013)
11. H. Naganawa et al., A new “green” extractant of the diglycol amic acid type for lanthanides. Solvent Extr. Res. Dev. Jpn. **14**, 151–159 (2007)
12. Y. Baba et al., Selective recovery of dysprosium and neodymium ions by a supported liquid membrane based on ionic liquids. Solvent Extr. Res. Dev. Jpn. **18,** 193–198 (2011)
13. T. Ogata, H. Narita, M. Tanaka, Immobilization of diglycol amic acid on silica gel for selective recovery of rare earth elements. Chem. Lett. **43**, 1414–1416 (2014)
14. T. Ogata, H. Narita, M. Tanaka, Adsorption behavior of rare earth elements on silica gel modified with diglycol amic acid. Hydrometallurgy **152**, 178–182 (2015)
15. T. Ogata, H. Narita, M. Tanaka, Rapid and selective recovery of heavy rare earths by using an adsorbent with diglycol amic acid group. Hydrometallurgy **155**, 105–109 (2015)
16. T. Ogata, H. Narita, M. Tanaka, Adsorption mechanism of rare earth elements by adsorbents with diglycolamic acid ligands. Hydrometallurgy **163**, 156–160 (2016)
17. Dow Water & Process Solutions Home Page. Product Data Sheet. http://www.dowwaterandprocess.com/en/products/a/amberlite_ir120_h