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Rapid and selective recovery of heavy rare earths by using an adsorbent with diglycol amic acid group

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ABSTRACT

The recovery of rare earths from ores and scraps requires the selective separation of dilute rare earth ions from solutions containing high concentrations of base metal ions. Using column tests under conditions mimicking practical use, we investigated a novel adsorbent comprising silica gel particles modified with diglycol amic acid groups (EDASiDGA). We evaluated the influence of flow rate on dysprosium adsorption–desorption behavior and the selective adsorption of dysprosium ions from a simulated solution containing dilute rare earth ions and high concentrations of base metal ions at low pH (pH 1.0). The EDASiDGA-packed column had a high adsorption–desorption rate. Moreover, the EDASiDGA-packed column enriched middle and heavy rare earths more than 10- to 20-fold from even a dilute solution. In addition, the molar ratios of the rare earths to base metals in the solution after desorption were three to four orders of magnitude higher than the initial molar ratios.

1. Introduction

The rare earth elements comprise seventeen elements – scandium, yttrium, and the lanthanides – and are often divided into three groups: the light (La, Ce, Pr, and Nd), middle (Sm, Eu, Gd, Tb, and Dy), and heavy (Ho, Er, Tm, Yb, Lu, and Y) rare earths (Chi and Tian, 2008). Some rare earth elements are used in clean energy technologies, such as wind turbines and electric vehicles. According to the U.S. Department of Energy, five rare earth elements (Y, Nd, Eu, Tb, and Dy) are the most critical in the medium term (2015–2025) of clean energy technology deployment (U.S. Department of Energy, 2011); and, except for Nd, all of these elements are middle and heavy rare earths. In 2013, about 90% of the global production of rare earths occurred in China (U.S. Geological Survey, 2014). Rare earth resources have received increased attention worldwide in recent years, but almost all ores contain high concentrations of the light rare earths but only low quantities of the middle and heavy ones. Therefore, the production of middle and heavy rare earths from other countries is important from the viewpoint of resource management and security.

Underutilized resources of rare earths include low-grade ores (Habashi, 1985; Kato et al., 2011; Kon et al., 2014; Wang et al., 2010) and rare-earth-containing End-of-Life products (Binnemans et al., 2013; Tanaka et al., 2013). Typically, precipitation, solvent extraction, and adsorption are used to recover metal ions from low-grade resources. Precipitation and solvent extraction are established techniques for metal recovery and are useful particularly for solutions with high concentrations of the target metal ions. In contrast, adsorption is suitable for recovering target metal ions when their concentrations are low. Many adsorbents for rare earths 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), but none so far has been appropriate for practical use. In particular, adsorbing dilute rare earth ions from solutions containing high concentrations of base metal ions is prohibitively difficult with these previous adsorbents. For example, iron is typically present in ores and scraps at high concentrations and often prevents the recovery of rare earths (Wang et al., 2010; Wu et al., 2013; Xie et al., 2014); commercial organophosphorus extractants (e.g., bis(2-ethylhexyl)phosphoric acid and (2-ethylhexyl)phosphonic acid 2-ethylhexyl ester) extract iron(III) ions more efficiently than they do rare earth ions. Consequently, effective rare earth adsorbents require high selectivity over base metal ions. Additional characteristics of rare earth adsorbents for practical use include easy desorption of the metal ions, high adsorption and desorption rates, high adsorption capacity, durability against repeated use, low cost, and high mechanical strength.

Toward the goal of designing a practical adsorbent for the recovery of rare earths, we considered ligands, supports, and methods for introducing ligands onto supports. In our previous work (Ogata et al., 2014, 2015), we synthesized a novel adsorbent (that is, EDASiDGA), which comprises silica gel particles modified with diglycol amic acid groups,

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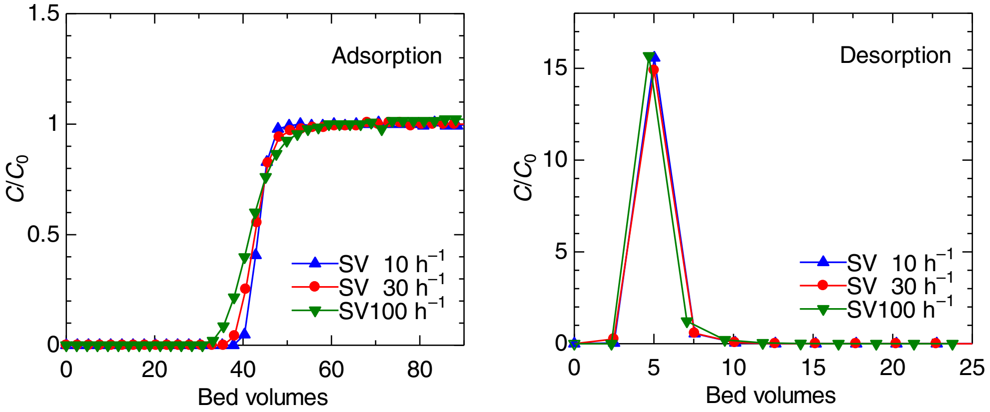

Fig. 1. Influence of flow rate on the dysprosium adsorption and desorption behaviors of the EDASiDGA-packed column. Conditions: flow rates, 0.313 mL/min (SV 10 h^{-1}), 0.931 mL/min (SV 30 h^{-1}), 2.95 mL/min (SV 100 h^{-1}); feed solution: dysprosium concentration, 1 mmol/L; pH, 1.0 (adjusted by using HCl); and eluent: 1 mol/L H_2SO_4.

and evaluated its utility. The results of batch experiments confirmed that the adsorbent had selectivity for middle and heavy rare earth ions (Ogata et al., 2014, 2015).

In the present study, we performed column experiments to clarify the feasibility of EDASiDGA for practical use. In addition, we evaluated the influence of flow rate on dysprosium adsorption–desorption behavior and the selective adsorption of dysprosium ions from a simulated solution containing dilute rare earth ions and high concentrations of base metal ions at low pH (pH 1.0). For comparison, we examined a commercially available, strongly acidic cation-exchange resin that can adsorb rare earths at low pH.

2. Materials and methods

2.1. Materials

The adsorbent was prepared as described in our previous paper (Ogata et al., 2014). Briefly, diglycolic anhydride and 3-(ethylenediamino)propyl silica gel were added to dichloromethane and allowed reacting at 298 K for 3 days, after which 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 a vacuum; hereafter the resulting particles are referred to as EDASiDGA (spherical particles, 0.1 mm in diameter). Amberlite™ IR120BNA (spherical particles, 0.5 mm in diameter) was washed with hydrochloric acid and dried under a vacuum (IR120B) before being used as a commercial strongly acidic cation-exchange resin. The reagents for preparation of stock solutions of metal ions and the adsorbent were listed in Supporting Information.

2.2. Procedure for recovery experiments

EDASiDGA or IR120B (1 g dry weight) was packed into a glass column (inner diameter, 8 mm) by the slurry method, and the volume of the adsorbent bed in the column was 1.86 and 2.11 cm^3, respectively. Both columns were conditioned by washing with 0.1 mol/L HCl. The adsorption solution containing metal ions was fed to the columns, which then were rinsed with 0.01 mol/L HCl in order to remove the residual adsorption solution. After rinsing, the adsorbed ions were eluted from the column by using 1 mol/L H_2SO_4. Each solution was fed upward by a double-acting plunger pump. The effluents from the column were collected continuously with 2.5-bed volume intervals by a fraction collector, and the concentration of each metal ion was determined by using an inductively coupled plasma spectrometer (Shimadzu, ICPE-9000). All column experiments were conducted at room temperature (291 ± 2 K).

3. Results and discussion

3.1. Influence of flow rates on the adsorption of rare earths

To investigate the adsorption and desorption rates of the EDASiDGA adsorbent, dysprosium recovery from 1 mmol/L dysprosium chloride

Table 1
BV when C/C_0 reached 0.1, the adsorbed dysprosium until C/C_0 reached 0.1 ($Q_{0.1}$), the total adsorbed dysprosium (Q), and the ratio of $Q_{0.1}$ to Q ($Q_{0.1}/Q$) at each SV.

SV (h^{-1})	BV	$Q_{0.1}$ (mg/g)	Q (mg/g)	$Q_{0.1}/Q$
10	42.8	10.8	11.0	0.988
30	40.6	10.1	10.6	0.956
100	38.0	9.26	10.1	0.920

Table 2
Amount of the dysprosium recovered from the fraction giving the maximal concentration (R_{max}), total recovered dysprosium (R), and the ratio of R_{max} to R (R_{max}/R) at each SV.

SV (h^{-1})	R_{max} (mg/g)	R (mg/g)	R_{max}/R
10	10.2	10.7	0.960
30	9.59	10.2	0.943
100	9.17	10.1	0.912

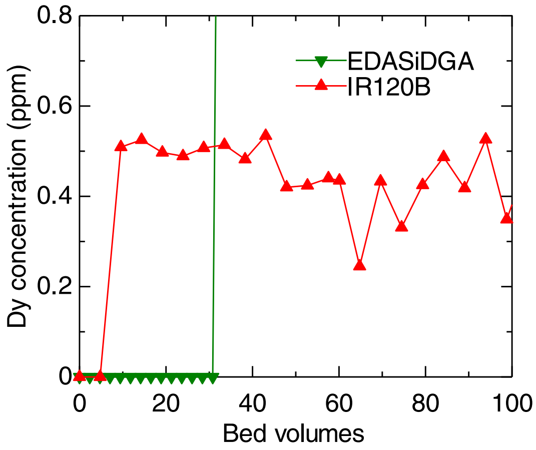

Fig. 2. Effluent concentrations of dysprosium ions from adsorbent-packed columns at SV 100 h^{-1}. Conditions: flow rates, 2.95 mL/min (EDASiDGA), 3.40 mL/min (IR120B); feed solution: dysprosium concentration, 1 mmol/L; and pH, 1.0 (adjusted by using HCl).