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Benzene triamido-tetraphosphonic acid immobilized on mesoporous silica for adsorption of Nd^{3+} ions in aqueous solution

Seenu Ravi [a], Yu-Ri Lee [a], Kwangsun Yu [a, b], Ji-Whan Ahn [b], Wha-Seung Ahn [a, *]

[a] Department of Chemistry and Chemical Engineering, Inha University, Incheon, South Korea
[b] Korea Institute of Geoscience and Mineral Resources (KIGAM), 124 Gwahang-no, Yuseong-gu, Daejeon, 305-350, South Korea

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ABSTRACT

Mesoporous silica SBA-15 grafted with benzene-1,3,5-triamido-tetraphosphonic acid (SBA-15-BTATPA) was synthesized. After detailed characterization of the material using various analytical instrumentation, it was applied for the recovery of Nd^{3+} as a function of the contact time, ion concentration, and pH. The adsorption equilibria and kinetics were also examined. Under the optimal conditions, adsorption equilibrium was reached within 60 min of contact time, and the adsorption capacity of Nd^{3+} at room temperature and pH 6 was 129.8 mg g^{-1}, which was higher than that by other rare earth element (REE) ions tested for comparison (Y^{3+}, La^{3+}, and Ce^{3+}). The adsorbent showed excellent distribution coefficient for Nd^{3+} greater than 1.0×10^5 mL/g. The preferential order of adsorption in the ion mixture with equal ion concentrations was $Y^{3+}>Nd^{3+}>Ce^{3+}>La^{3+}$, which followed the sequence of their decreasing atomic size and increasing stability constant. The competing adsorption by transition metal ions, such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}, on the REEs recovery was negligible (<2%). The observed adsorption isotherms could be fitted well to a Langmuir model (correlation factor $R^2 > 0.99$), whereas the adsorption kinetics could be described satisfactorily by a pseudo second order kinetic model. The material was reusable for up to 5 consecutive times with only a slight decrease in adsorption capacity.

1. Introduction

The increasing use of rare earth elements (REEs) produces aqueous solutions contaminated with rare earth metal ions that become an environmental burden. The broad and rapidly growing applications of REEs in the energy industry and their limited deposits on earth have also highlighted the necessity of separating and recycling REEs from various sources including industrial and urban waste [1,2]. Therefore, effective recovery of REEs from water is desirable for both the economy and environment.

The recovery of REEs have been conducted through various processes including solvent extraction [3,4], adsorption [5], biosorption [6], coprecipitation [7], hydrometallurgy [8], and ion exchange [9]. As adsorption processes employing an adsorbent with specific organic functionality have achieved selective metal separation on the small scale, a large number of studies have been reported recently for the adsorption of REEs in aqueous media using porous silica [10–14], carbons [15], metal oxides [16,17], metal organic frameworks [18,19], polymers [20], and biomaterials [6,21]. However, most of them showed poor adsorption capacity and/or reusability. The weak physicochemical stability of metal oxides and metal organic frameworks makes them less desirable for long term use in the separation of REEs. Carbon materials and resins, despite their stability, are difficult to functionalize with specific organic groups for the selective separation of REEs. Biomaterials show low chemical stability and poor mechanical properties. In contrast, porous silica materials tend to be more stable, eco-friendly, and possess a high population of surface hydroxyl groups that enable easy surface functionalization, and are widely used [22–27]. The high surface areas with uniform pore channel networks in mesoporous silica materials have great potential for REEs separation, in particular, for Nd^{3+} ions [28–31]. Roosen et al. reported a chitosan-supported hybrid silica material functionalized with ethylenediaminetetraacetic acid (EDTA)- and diethylenetriaminepentaacetic acid (DTPA), which exhibited a Nd^{3+} adsorption capacity of ca. 60 and 106 mg/g, respectively [28]. Melnyk et al. reported SiP-grafted silica adsorbent for REEs separation that exhibited 45 and 46 mg/g adsorption of Nd^{3+} and Dy^{3+}, respectively [29]. Legaria et al. functionalized iminodiacetic acid over Fe_3O_4/SiO_2 core shell

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* Corresponding author.
E-mail address: whasahn@inha.ac.kr (W.-S. Ahn).

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spherical particles that exhibited 27, 33 and 40 mg/g for La^{3+}, Nd^{3+} and Dy^{3+} ions, respectively [30]. These materials, despite their sufficient stability, showed rather low adsorption capacities for REE ions due most likely to the weakly binding functional groups on the silica surface. Thus, porous silica materials functionalized with stronger active sites, such as amide-based phosphonic acids, towards trivalent metal ions adsorption appear promising for effective adsorption of REE ions.

Herein, a benzene-1,3,5-triamido-tetraphosphonic acid (BTATPA) grafted on an acid-stable SBA-15 mesoporous silica (SBA-15-BTATPA) was proposed as a new adsorbent for the adsorption of Nd^{3+} ions. Adsorption of other REE ions such as La^{3+}, Ce^{3+}, and Y^{3+} were also examined for comparison. A systematic investigation on the adsorption equilibria and kinetics was made by examining the effect of the contact time, metal ion concentration, and pH of the system. In addition, REEs adsorption was carried out in the presence of potentially competing transition metal ions, and the recyclability of the adsorbent was examined.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123-EO/20:PO/70:EO/20), HCl, ethanol, N, N′–dimethylformamide (DMF), 1,3,5-benzenetricarbonyl trichloride, 3-aminopropyltriethoxysilane (APTES), iminodi(methylphosphonic acid) (IDMP), trimethylamine, and carbonyldiimidazole (CDI) were purchased from Sigma Aldrich. Aqueous rare-earth stock solutions for adsorption experiments were made from their corresponding REE salts such as $Y(NO_3)_3.6H_2O$ (99.9%), $La(NO_3)_3.6H_2O$ (99.9%), $Ce(NO_3)_3.6H_2O$ (99.9%), and $Nd(NO_3)_3.6H_2O$ (99.9%) supplied by Sigma-Aldrich. Transition metal nitrates $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.6H_2O$, and $Zn(NO_3)_2.6H_2O$, were also supplied by Sigma Aldrich. These chemicals were used as received.

2.2. Material synthesis

2.2.1. Preparation of SBA-15 and APTES-functionalized SBA-15 (SBA-15-NH_2)

The synthesis procedures of SBA-15 and APTES-functionalized SBA-15 mesoporous silica were reported elsewhere [32,33]. In a typical synthesis, Pluronic P123 (0.017 mol) was added in deionized water (193 mol) at 35 °C and stirred until fully dissolved, followed by addition of HCl (5.9 mol) solution. Once a clear solution was obtained, TEOS (1-x mole) was added to the reaction mixture and stirred for further 3 h. APTES (x mole, x = 0 and 0.1) was then added dropwise to the gel solution, and stirred for 24 h at 35 °C. The resulting gel solution was transferred to a sealed Teflon-lined stainless steel autoclave and heated to 100 °C for 24–36 h. The products were filtered, washed with ethanol and water and dried at 60 °C for 6 h in a vacuum oven. The as-synthesized SBA-15 was calcined at 550 °C for 6 h with a heating rate of 1 °C/min under air atmosphere. Besides, the APTES functionalized material i.e, SBA-15-NH_2 was solvent-extracted using an ethanol and HCl (36 wt %) (99:1) mixture, where 1 g of the as-synthesized material was dispersed in 300 mL of ethanol/HCl and heated under reflux for 12 h. The SBA-15-NH_2 was filtered and washed three to four times with hot ethanol, and finally dried at 55 °C for 4 h in a vacuum oven.

2.2.2. Preparation of amidotricarbonyl benzene-functionalized SBA-15 (SBA-15-NHTCB)

The prepared SBA-15-NH_2 (1 g) was treated with 1,3,5-benzenetricarbonyl trichloride (0.6 mmol) and triethylamine (0.06 mmol) in 100 mL of DMF. The solution was heated under reflux for 12 h, after which the material was filtered and washed with DMF and hot ethanol. The filtered material was vacuum-dried at 55 °C for 6 h. The resulting yellow colored material was designated as SBA-15-NHTCB (Fig. 1).

2.2.3. Preparation of benzene-1,3,5-triamido-tetraphosphonic acid (BTATPA)-incorporated SBA-15 (SBA-15-BTATPA)

The SBA-15-NHTCB (1 g) was treated with IDMP (1.2 mmol) in 100 mL DMF solvent, where 0.1 mmol of CDI was used to promote amide bond formation. The reaction mixture was heated refluxed for 20 h and filtered immediately under hot conditions, and washed with an ethanol and water mixture (1:1) to remove the unwanted residues from the material. The filtered material was dried at 55 °C for 6 h in a vacuum oven. The obtained material was called SBA-15-BTATPA (Fig. 1). The material was characterized and used as an adsorbent for the removal of REE ions.

2.3. Characterization

X-ray diffraction (XRD, Rigaku) patterns of the mesoporous silica products were recorded using CuKα ($\lambda = 1.54$ Å) radiation. The N_2 isotherms were measured using a BELsorpMax (BEL, Japan) at 77 K. The samples were degassed at 373 K for 12 h under high vacuum before the isotherms were measured. The surface areas were estimated using the Brunauer–Emmett–Teller (BET) method over the relative pressure (P/P_0) range of 0.0–0.2 The pore size distribution was calculated from the analysis of the isotherm desorption branch by the BJH (Barrett–Joyner–Halenda) method coupled with the apparatus software. The Fourier transform infrared (FT-IR, VERTEX 80 V FT-IR, Bruker, Germany) spectra were obtained at room temperature. KBr was used for preparing the pellet. The carbon, hydrogen, and nitrogen contents of the samples were measured using an elemental analyzer (EA, EA1112). The phosphorous content was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300DV) and Energy dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) was performed using a monochromatic Al Kα X-ray source (Thermo Scientific, USA) and a hemispherical analyzer. The morphologies were examined by field emission-scanning electron microscopy (FE-SEM, Hitachi S-4300).

2.4. Adsorption experiments

Batch adsorption experiments of REE ions over SBA-15-BTATPA were carried out and the adsorption under different conditions of the solution pH, contact time, and solution concentrations were investigated. The Nd^{3+} ion was used as model system for all rare earth ions (La^{3+}, Ce^{3+}, and Y^{3+}) in the optimization tests. The stock solutions of Nd^{3+} at specified concentrations were prepared. The pH of the solutions in the range of 3–9 was adjusted using either NaOH (0.01 M) or HNO_3 (0.01 M). All the adsorption tests were performed in a 10 mL aliquot of a suitably diluted stock solution. The adsorbent (10 mg) was added to the adsorbate vials and the solutions were equilibrated in a thermostatic water-bath shaker operated at 25° C and 200 rpm for a preset time period of 6 h. The amount of Nd^{3+} ions adsorbed onto SBA-15-BTATPA was calculated using equation (1).