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High-resolution separation of neodymium and dysprosium ions utilizing extractant-impregnated graft-type particles

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ABSTRACT

An efficient method for rare metal recovery from environmental water and urban mines is in high demand. Toward rapid and high-resolution rare metal ion separation, a novel bis(2-ethylhexyl) phosphate (HDEHP)-impregnated graft-type particle as a filler for a chromatography column is proposed. To achieve rapid and high-resolution separation, a convection-flow-aided elution mode is required. The combination of 35 μm non-porous particles and a polymer-brush-rich particle structure minimizes the distance from metal ion binding sites to the convection flow in the column, resulting in minimized diffusional mass transfer resistance and the convection-flow-aided elution mode. The HDEHP-impregnated graft-type non-porous-particle-packed cartridge developed in this study exhibited a higher separation performance for model rare metals, neodymium (III) and dysprosium (III) ions, and a narrower peak at a higher linear velocity, than those of previous HDEHP-impregnated fiber-packed and commercially available Lewatit[®] VP OC 1026-packed cartridges.

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1. Introduction

Progress in the high-tech industry increases the demand for rare metals. For instance, neodymium magnets, which are permanent magnets made from iron and rare metals neodymium (Nd) and dysprosium (Dy), are widely used for electronics such as magnetic resonance imaging (MRI) scanners and hybrid motor vehicles. However, the rare metals contained in neodymium magnets cannot be produced in Japan. Therefore, separation and recovery of rare metals from environmental water and urban mines, as well as from spent neodymium magnets, has attracted attention.

As methods for the separation and recovery of rare metal ions, liquid-liquid extraction [1,2] and solid-phase extraction [3–5] utilizing various extractants have been developed. Although liquid-liquid extraction is suitable for treatment of a large quantity of rare metal ions, separation and disposal of spent organic solvent after rare metal ion extraction is problematic. Solid-phase extraction solves the organic solvent problems. However, porous beads 100–1000 μm in diameter are generally used as a substrate for extractant impregnation. The extractant captures metal ions inside

the pores, and in the elution process, the long distance from the metal ion binding sites to the convection flow causes large diffusional mass transfer resistance. This resistance prevents rapid treatment of a large quantity of rare metals.

In our laboratory, for pretreatment for rare metal analysis, extractant-impregnated porous hollow fiber membranes [6,7] and porous sheets [8–10], which enable rapid treatment of rare metal ions without generating waste organic solvent, have been developed. To reduce the distance from metal ion binding sites to the convection flow, we selected porous materials with small pores, 0.3–1.2 μm in diameter, as a substrate. Utilizing electron-beam-induced graft polymerization (EIGP), a hydrophobic polymer brush was appended to the porous materials, and extractants were impregnated via hydrophobic interactions [6,10]. We selected EIGP from various chemical modification methods of porous materials because it easily provides stable covalent modification and functionalizable surfaces. Recently, for the separation of rare metal ions, we also developed an extractant-impregnated non-porous fiber [11]. The fiber was packed into an empty cylindrical cartridge and the cartridge was used as a chromatography column. However, the linear velocity for separation and separation performance were not sufficient.

In this study, we focused on non-porous particles as a substrate for extractant impregnation and as a filler for a chromatog-

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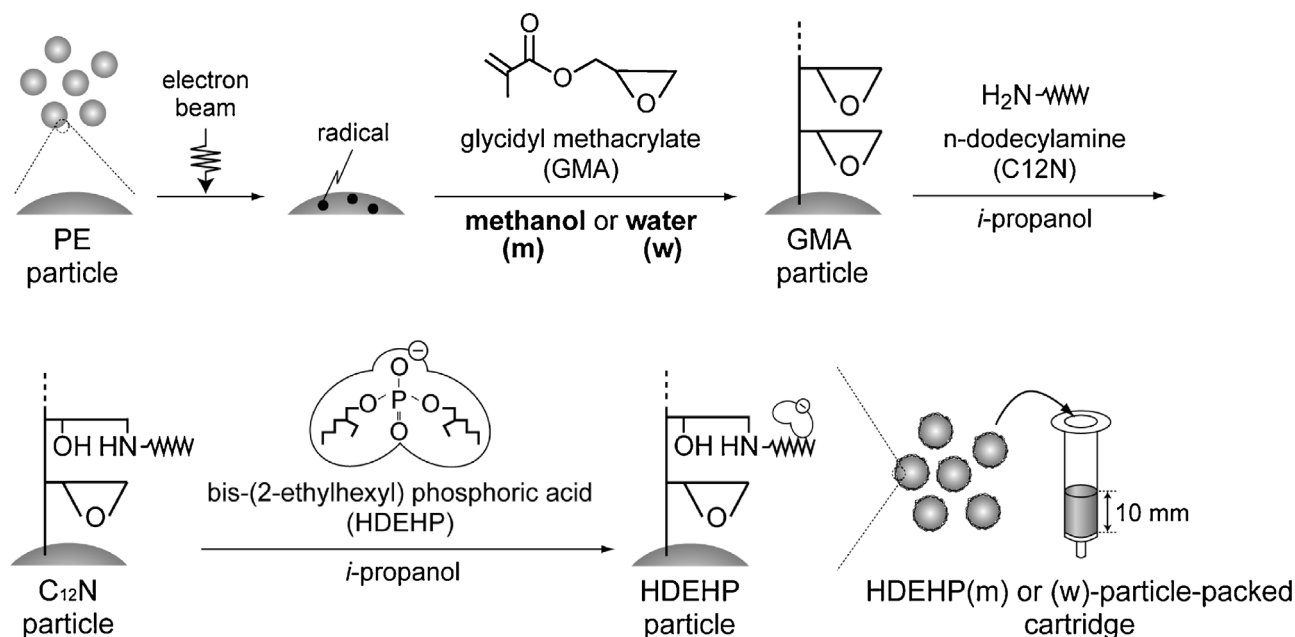


Fig. 1. Preparation scheme of HDEHP-impregnated graft-type non-porous-particle-packed cartridge.

raphy column. Compared to that of a non-porous-fiber-packed column, the packing density of the particle-packed column is expected to be higher, resulting in a shorter diffusional path from metal ion binding sites to the convection flow. Furthermore, to reduce the distance, a polymer-brush-rich particle structure is preferable. Recently, we also established polymer brush and root determination and the formation control method for rational design of graft-type functional materials prepared using radiation-beam-induced graft polymerization, which are detailed elsewhere [12,13]. The method was applied to the preparation of these extractant-impregnated graft-type particles. The combination of non-porous particles and the polymer-brush-rich particle structure minimizes the distance; in other words, it minimizes the diffusional mass transfer resistance of the column and enables rapid and high-resolution treatment of a large quantity of rare metals. The proposed separation method that utilizes the extractant-impregnated graft-type non-porous particles will contribute to rare metal separation and recovery applications.

2. Materials and methods

2.1. Materials

Non-porous polyethylene (PE) particles (Ticona Japan Ltd., Tokyo, Japan) were used as a starting substrate for grafting. The average particle diameter was 35 μm . An epoxy-group-containing vinyl monomer, glycidyl methacrylate (GMA, $\text{CH}_2 = \text{C}(\text{CH}_3)\text{COOCH}_2\text{CHOCH}_2$), was purchased from Nacalai Tesque Co. (Kyoto, Japan) and used without further purification. Bis(2-ethylhexyl) phosphate (HDEHP) was purchased from Tokyo Kasei Co. (Tokyo, Japan). Dodecylamine was purchased from Wako Chemicals Co. (Tokyo, Japan). Other reagents were of analytical grade or higher.

2.2. Preparation of extractant-impregnated graft-type non-porous particles

The preparation scheme of the extractant-impregnated non-porous-particle-packed cartridge is shown in Fig. 1. First, the non-porous PE particles were packed in a gas-barrier bag (Lamizip,

AS ONE Corp., Tokyo, Japan) with an oxygen scavenger (Ageless[®], Mitsubishi Gas Chemical Co., Tokyo, Japan). Then, the particles were irradiated with a 20 kGy electron beam, at an energy of 2.0 MeV and a current of 20 mA, using an accelerator (Dynamitron, Radiation Dynamics, Ltd.). Second, the irradiated particles were immersed in 2–5% (v/v) GMA/water or GMA/methanol solutions at 277 K, and poly(glycidyl methacrylate) (PGMA), which contains an epoxy group, was grafted onto the particle surface. The degree of PGMA grafting was calculated from the mass gain of the particles using the following equation:

$$\text{degree of PGMA grafting (\%)} = 100(W_1 - W_0)/W_0. \quad (1)$$

Where, W_0 and W_1 are the masses of the substrate and GMA-grafted particles, respectively. The resulting PGMA-grafted particles will be referred to as the GMA particles. Third, the GMA particles were immersed in a 40% (v/v) dodecylamine/isopropanol solution at 343 K for 12 h, and a dodecylamine (C_{12}N) group was introduced to the grafted PGMA via an epoxy ring opening reaction. The molar conversion of the epoxy group into a C_{12}N group was calculated using the following equation:

$$\text{molar conversion (\%)} = 100[(W_2 - W_1)/185]/[(W_1 - W_0)/142]. \quad (2)$$

Where, W_2 is the mass of C_{12}N -group-introduced particles. The numbers 185 and 142 are the molecular masses of dodecylamine and GMA, respectively. The resulting particles will be referred to as the C_{12}N particles. In this study, the molar conversion was set at 50%. Finally, the resulting C_{12}N particles were immersed in a 10% (v/v) HDEHP/isopropanol solution at 313 K for 3 h, and HDEHP was impregnated to the particles. The particles were washed with a 0.01–1.0 mol/L HCl solution. The amount of HDEHP impregnated was calculated using the following equation:

$$\text{amount of HDEHP impregnated (mol/kg-HDEHP particle)} = [(W_3 - W_2)/322]/W_3. \quad (3)$$

Where, W_3 is the mass of the HDEHP-impregnated particle. The number 322 is the molecular mass of HDEHP. The resulting extractant-impregnated graft-type particles will be referred to as the HDEHP(m) or HDEHP(w) particles. Here, the m and w in the

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