Article

Preparation of Extractant-impregnated Porous Sheets for High-speed Separation of Radionuclides

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Abstract
A novel method of preparing for an extractant-impregnated porous sheet with high values of adsorption rate and capacity for metal ions is described. First, an epoxy-group-containing polymer chain was appended onto a commercially available porous sheet by radiation-induced graft polymerization of glycidyl methacrylate (GMA). Second, n-octadecylamine was introduced into the graft chain via an epoxy-ring opening reaction. Third, bis(2-ethylhexyl)phosphate (HDEHP) was impregnated onto the n-octadecylamino group. An yttrium solution was forced to permeate through the pores of the HDEHP-impregnated porous sheet. The higher permeation rate of the yttrium solution led to the higher adsorption rate of yttrium ions because of a negligible diffusional mass-transfer resistance of the metal ions to the HDEHP impregnated.

Keywords: extractant, HDEHP, impregnation, porous sheet, yttrium ion, solid phase extraction

1 Introduction
Solid-phase extraction (SPE) has an extensive range of applications because of the ease with which various samples can be handled and the minimal use of organic solvents. Modified polymer and silica beads are packed into columns designed for SPE [1, 2]. A tradeoff between the mass-transfer and flow resistances exists in SPE operation; a higher adsorption rate that can be achieved by the beads with a smaller size causes a higher operational pressure.

Convection-aided separation using functional porous materials is effective in overcoming this drawback of SPE using the functional beads. High-performance membrane and perfusion chromatographies are ascribed to modified membranes [3] and beads [4] with “throughpores” through which the sample solutions are permeated,
respectively. By using radiation-induced graft polymerization, we have to date modified the microfiltration membranes to append various moieties [5], e.g., ion-exchange groups, and hydrophobic and affinity ligands, onto the pore surface. Recently, extractants designed for the solvent extraction of radionuclides have been impregnated onto the pore surface of a porous hollow-fiber membrane to shorten the processing time of the analysis of radionuclides [6, 7].

In this study, we prepared a novel SPE cartridge loaded with an extractant-impregnated porous sheet and demonstrated a high-rate collection of metal ions using the cartridge. Bis(2-ethylhexyl)phosphate (HDEHP) and yttrium ions were adopted as extractant and metal ions, respectively. HDEHP is representative of acidic extractants. The collection of yttrium ions (\(^{90}\text{Y}\)) is useful for the determination of radioactivity of strontium ions (\(^{90}\text{Sr}\)).

2 Experimental
2.1 Preparation of extractant-impregnated porous sheet

A porous sheet made of polyethylene, supplied by INOAC Co., was used as a base polymer for grafting. This porous sheet had a thickness of 2.0 mm with a porosity of 75% and an average pore diameter of 1.4 \(\mu\)m. An epoxy-group-containing vinyl monomer, glycidyl methacrylate (GMA, \(\text{CH}=\text{CCH}_3\text{COOCH}_2\text{CHOCH}_2\)), was purchased from Nakalai Tesque and used without further purification. An empty cylindrical cartridge with an inner diameter of 13 mm and a length of 65 mm was acquired from Varian.

A scheme for the impregnation of HDEHP onto the pore surface of the porous sheet is shown in Fig. 1. This scheme consists of the following four steps. (1) Electron beam irradiation to the starting porous sheet to produce radicals. The porous sheet was irradiated with an electron beam from an accelerator (Dynamitron model IEA 3000-25-2, Radiation Dynamics Inc.) at ambient temperature under a nitrogen atmosphere. The dose was 200 kGy. (2) Graft polymerization of GMA. The irradiated porous sheet was immersed in a 20 (v/v)% GMA/methanol solution at 313 K for 5 min. The degree of GMA grafting, defined as the weight increase, in percentage, of the porous sheet, was set at 120%. The resultant porous sheet was referred to as the GMA sheet. (3) Introduction of an octadecylamino group as a hydrophobic ligand into the graft chain. The GMA sheet was immersed in \(n\)-octadecylamine (\(\text{C}_{18}\text{H}_{37}\text{NH}_2\)) at 353 K. The molar conversion of the epoxy group into an octadecylamino (\(\text{C}_{18}\text{NH}\)) group was calculated as

\[
\text{Molar conversion} \ [%] = 100 \left[\frac{(W_2 - W_1)}{270}\right]/\left[\frac{(W_1 - W_0)}{142}\right]
\]

(1)

\[\text{OH} \quad \text{HN} \quad \text{HDEHP} \quad \text{sheet}\]

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Fig. 1 Preparation of HDEHP-impregnated porous sheet.
C_{18}H_{37}NH group density [mol / kg-GMA sheet] = \frac{(W_2 - W_1)/270}{W_1} \tag{2}

where \(W_0, W_1, \) and \(W_2\) are the masses of starting, GMA, and C_{18}NH-group-introduced porous sheets, respectively. The figures 270 and 142 are the molecular masses of C_{18}H_{37}NH_2 and GMA, respectively. The resultant C_{18}NH-group-introduced porous sheet was referred to as the C_{18}NH(x) sheet, where \(x\) designates the molar conversion. (4) Impregnation of HDEHP onto the C_{18}NH group of the graft chain. The C_{18}NH(x) sheet was immersed in a 50 (v/v)% HDEHP/ethanol solution at 313 K for 2 h. The sheet was vacuum-dried at 313 K for 12 h and weighed. The amount of HDEHP impregnated was evaluated as

\[
\text{Amount of HDEHP impregnated [mol/kg-GMA sheet]} = 1000 \frac{(W_3 - W_2)/322}{W_1} \tag{3}
\]

where \(W_3\) is the mass of the HDEHP-impregnated porous sheet. The figure 322 is the molecular mass of HDEHP. The HDEHP-impregnated porous sheet was referred to as the HDEHP (x, y) sheet, where \(y\) designates the amount of HDEHP impregnated.

2.2 Determination of liquid flux and metal ion binding capacity

An experimental apparatus for the determination of flux or liquid permeability is shown in Fig. 2. The HDEHP-impregnated porous sheet was cut into disks 13 mm in diameter and packed into the empty cylindrical cartridge with frit and an O-ring. The resultant disk and cartridge were referred to as the HDEHP(x, y) disk and cartridge, respectively. The cartridge was connected to a syringe pump. The flux for 0.01 M HNO_3 was evaluated by dividing the permeation rate of 0.01 M HNO_3 at 0.1 MPa and 298 K by the cross-sectional area of the HDEHP(x, y) disk.

A 50 mg-Y/L yttrium nitrate solution as a feed, dissolved with 0.01 M HNO_3, was made to flow through the HDEHP(16, 3.4)-disk-packed cartridge at constant flow rates of 200 and 2000 mL/h. The flow rate was converted into the residence time of the solution across the sheet from the following

\[
\text{Residence time [s]} = \frac{\text{porosity of the sheet) (volume of the HDEHP sheet)}}{\text{flow rate}} \tag{4}
\]

The effluent was continuously sampled with fraction vials until the yttrium concentration of the effluent reached that of the feed. The yttrium concentration in the effluent was determined from the measurement of VIS absorbance at 660 nm with Arsenazo III. The dynamic and equilibrium binding capacities of the HDEHP(x, y) sheet for yttrium ions were calculated as follows:

\[
\text{Dynamic binding capacity [mol / kg-HDEHP sheet]} = \int_{0}^{V_b} (C_0 - C) \, dV / W_3 \tag{5}
\]

\[
\text{Equilibrium binding capacity [mol / kg-HDEHP sheet]} = \int_{0}^{V_e} (C_0 - C) \, dV / W_3 \tag{6}
\]

where \(C_0\) and \(C\) are the yttrium concentrations of the feed and the effluent, respectively. \(V\) is the effluent volume. \(V_b\) and \(V_e\) are the effluent volumes when \(C\) reaches 0.1 \(C_0\) and \(C_0\), respectively.
3 Results and Discussion

3.1 Properties of HDEPE-impregnated porous sheet

n-Octadecylamine was reacted with the epoxy group of the GMA-grafted porous sheet with a degree of GMA grafting of 120%. The reaction time of 10 min at 353 K provided a molar conversion of 16%, i.e., a density of the octadecylamino (C_{18}NH) group of 0.62 mol/kg of the GMA sheet, as shown in Fig. 3. This molar conversion of 16% was adopted for the adsorption and elution experiments described below from the viewpoint of the mechanical strength of the sheet.
The extractant HDEHP was impregnated on the basis of the hydrophobic interaction between the hydrophobic part of HDEHP and the octadecyl part of the C$_{18}$NH group. The density of impregnated HDEHP was 3.4 mol/kg of the GMA sheet, which was comparable to that of the ion-exchange group of conventional ion-exchange resins. The HDEHP(16, 3.4) sheet with a thickness of 3.2 mm exhibited a flux for 0.01 M HNO$_3$ of 46 m/h at a permeation pressure of 0.1 MPa and 298 K, which was 1.2-fold that of the base sheet. A SEM image of the cross-sectional area of the HDEHP(16, 3.4) sheet is shown in Fig. 4. The porous structure of the sheet was retained after the graft polymerization of GMA, the reaction with n-octadecylamine, and the impregnation of HDEHP. The specific surface area of the GMA sheet was determined as 2.0 m$^2$/g by the nitrogen adsorption method.

3.2 Yttrium ion collection by HDEHP-impregnated-porous-disk-packed cartridge

Breakthrough curves of the HDEHP cartridge for the yttrium solution, i.e., dimensionless effluent concentration vs effluent volume, are shown in Fig. 5. Here, the ordinate is expressed as the ratio of the yttrium concentration of the effluent to that of the feed. The breakthrough curves overlapped irrespective of the flow rates, 200 and 2000 mL/h, of the solution through the pores, i.e., the residence times of the solution across the disk, 7.7 and 0.77 sec: the overall adsorption rate of yttrium ions onto the HDEHP(16, 3.4) sheet increased with an increase in the flow rate of the solution. This is due to the fact that the diffusional mass-transfer resistances in the solution and into the graft chain are negligible in the overall binding process of yttrium ions to the extractant HDEHP impregnated onto the graft chain and that the chelate formation of HDEHP with yttrium ions is instantaneous. These characteristics are desirable for the analysis of radionuclides in that the control of the flow rates of sample solutions is not required. The dynamic and equilibrium binding capacities of the HDEHP(16, 3.4) sheet evaluated by Eqs. (5) and (6) were 0.21 and 0.34 mol-Y/kg of the sheet, i.e., 0.093 and 0.15 mol-Y/L, respectively. This equilibrium binding capacity was equivalent to the equilibrium binding capacity of 0.15 mol-Nd/L of a commercially available HDEHP-impregnated resin (Ln Resin, Eichrom Co.) [8].

Fig. 5 Breakthrough curves of HDEHP-impregnated-porous-disk cartridge for yttrium
Acknowledgments

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References

8) http://www.eichrom.com/products/extraction.cfm