High-speed recovery of germanium in a convection-aided mode using functional porous hollow-fiber membranes

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Abstract

A porous hollow-fiber membrane capable of recovery of germanium from a liquid stream was prepared by radiation-induced graft polymerization of an epoxy-group-containing vinyl monomer, glycidyl methacrylate, and subsequent functionalization with 2,2′-iminodiethanol, di-2-propanolamine, *N*-methylglucamine, and 3-amino-1,2-propanediol. The functional group density was as high as 1.4 mol per kg of the resultant hollow fiber. The polymer chains containing functional groups surrounding the pores enabled a high-speed recovery of germanium during permeation of a germanium oxide (GeO_2) solution through the pores of the hollow fiber. Because of a negligible diffusional mass-transfer resistance, germanium concentration changes with the effluent volume, i.e., breakthrough curves, overlapped irrespective of the residence time of the solution, which ranged from 0.37 to 3.7 s across the hollow fiber. After repeated use of adsorption and elution, the adsorption capacity did not deteriorate. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Germanium is a useful element in pharmaceuticals [1,2] and catalysts [3,4]. Although the exhaust of germanium remains unregulated, a recovery system for germanium should be established from an environmental point of view. Preparation of polymeric adsorbents specific for germanium has been reported: Yasuda and coworkers [5–7] prepared 1,2-diol-group-containing beads based on a styrene-divinylbenzene copolymer matrix. Inukai et al. [8–10]

introduced *N*-2,3-dihydroxypropyl groups into chitosan beads cross-linked with ethylene glycol diglycidyl ethyl for selective adsorption of germanium and demonstrated a flow-through recovery of germanium across the bead-packed bed.

To achieve an efficient recovery of germanium from a liquid stream, a novel method must be designed. We have thus far proposed a convection-aided recovery system for metal ions using chelating porous membranes [11–14]. A high-density chelate-forming group was introduced into the polymer chains uniformly grafted onto the pore surface of the porous hollow-fiber membrane that was about 1 mm thick and 0.1 μm in diameter with 70% porosity. A

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metal solution was forced to permeate through the pores surrounded by the chelating polymer chains. During the transmembrane-pressure-driven permeation, a high-speed recovery of the metal ion was achieved because the time required for the diffusion of the metal ion to the chelating group is much shorter than the residence time of the solution across the membrane.

In this study, we prepared new porous hollow-fiber membranes containing various functional groups, and demonstrated a highly efficient recovery of germanium from a germanium oxide solution during permeation through the functional hollow fibers.

2. Experimental

2.1. Materials

A commercially available porous hollow-fiber membrane made of polyethylene (PE) and manufac-

tured by Asahi Chemical Industry Co., Ltd., Japan, was used as a trunk polymer for grafting. This hollow fiber had an inner and outer diameter of 2 and 3 mm, respectively, with an average pore diameter of 0.2 μm and a porosity of 70%. Glycidyl methacrylate ($CH_2=CCH_3COOCH_2CHOCH_2$, GMA) was purchased from Tokyo Kasei Co. (Tokyo, Japan) and used without further purification. Germanium oxide (GeO_2) solutions were purchased from Wako Pure Chemicals Co. (Tokyo, Japan). Other chemicals were of analytical grade or higher.

2.2. Preparation of functional porous hollow-fiber membranes

A reaction scheme for the introduction of various functional moieties into porous membranes is shown in Fig. 1. First, the PE hollow fiber was irradiated with an electron beam using a cascade-type accelerator to produce radicals throughout the trunk polymer [15]. Second, GMA was graft-polymerized to the hollow fiber to append the epoxy-group-con-
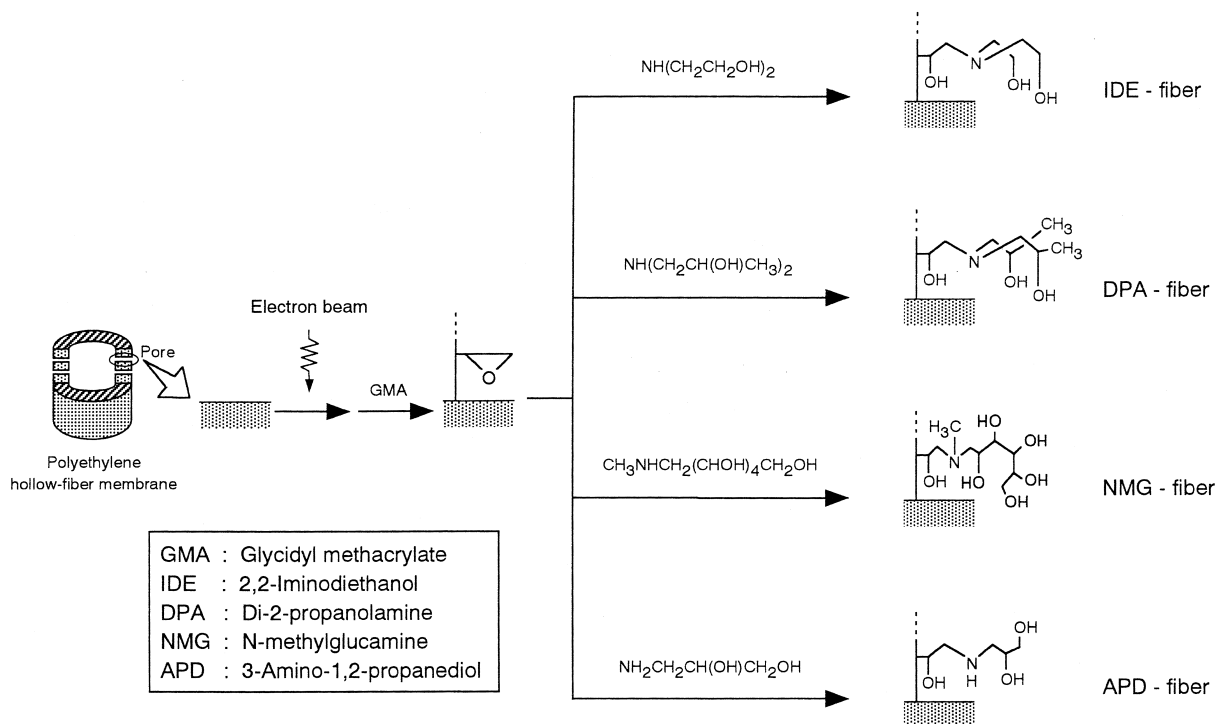

Fig. 1. A reaction scheme for the introduction of various functional groups into porous hollow-fiber membranes.

taining polymer chains [16]. The electron-beam-ir-radiated hollow fiber was immersed in a GMA monomer which had been previously deaerated by bubbling with nitrogen gas. After a prescribed time, the hollow fiber was removed and washed thoroughly with *N,N*-dimethylformamide. After the hollow fiber was dried in reduced pressure, it was weighed. The degree of GMA grafting defined below was evaluated from the weight gain:

dg (%)

$= 100$ (mass of graft chain)/(mass of trunk polymer)

(1)

Third, the epoxy group was converted to four kinds of functional groups:

(a) $-N(CH_2CH_2OH)_2$,
(b) $-N[CH_2CH(OH)CH_3]_2$,
(c) $-NCH_3CH_2(CHOH)_4CH_2OH$, and
(d) $-NHCH_2CH(OH)CH_2OH$.

The reaction conditions for the introduction of the functional groups are summarized in Table 1. The molar conversion of the epoxy group to the functional group was defined as follows:

Conversion (%)

$= 100$ (moles of functional group introduced)/

(moles of epoxy group before functionalization)   (2)

The conversions were calculated from the gain in mass of the hollow fiber. The resultant hollow fibers were referred to as the IDE, DPA, NMG, and APD fibers with reference to the reactants 2,2′-im-inodiethanol (diethanolamine), di-2-propanolamine (diisopropanolamine), *N*-methylglucamine, and 3-amino-1,2-propanediol, respectively.
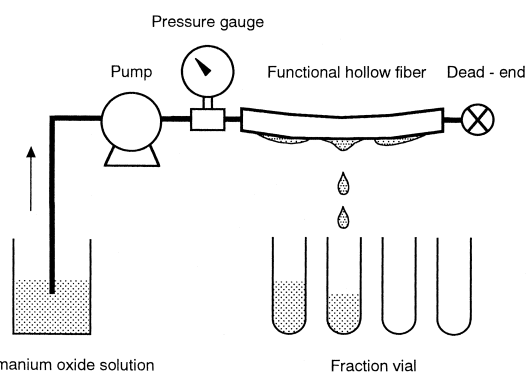

Fig. 2. Experimental apparatus for germanium recovery using the functional porous hollow-fiber membrane.

2.3. Germanium recovery during permeation through hollow fibers

A functional hollow fiber about 5 cm long was positioned in a configuration, as illustrated in Fig. 2. The germanium oxide (GeO_2) solution was forced to permeate radially outward from the inside to the outside surface of the hollow fiber at a constant flow-rate ranging from 5 to 50 ml/min. The Ge concentration of the feed solution was set at 0.10 g-GeO_2/L. The initial pH of the feed solution was adjusted from 3 to 12 with HCl and NaOH. Germanium of the effluent penetrating the outside surface of the hollow fiber was determined using phenylfluorone. The amount of Ge adsorbed onto the hollow fiber in equilibrium with C_0, i.e., the equilibrium adsorption capacity, q_e, was calculated from the following integration:

$$q_e = \int_0^{V_e} (C_0 - C)\, \mathrm{d}V/W \qquad (3)$$

Table 1
Preparation conditions for the introduction of various functional groups into porous hollow-fiber membrane

	IDE fiber	DPA fiber	NMG fiber	APD fiber
Reactant	2,2′-iminodiethanol	di-2-propanolamine	*N*-methylglucamine	3-amino-1,2-propanediol
Concentration	50 vol%	1.0 M	0.50 M	1.0 M
Solvent	water	water	50 (v/v)dioxane–water	50 (v/v) dioxane–water
Temp. (°C)	65	65	80	80
Time (h)	8	19	8	8

where C_0 and C are the Ge concentrations of the feed and effluent, respectively. The terms V, V_e, and W are the effluent volume, the effluent volume when C reached C_0, and the mass of the hollow fiber, respectively.

After the Ge concentration of the effluent reached that of the feed, the feed was switched to deionized water to wash the pores of the hollow fiber. Subsequently, 1 M HCl was permeated to elute the Ge adsorbed onto the hollow fiber. The elution percentage was defined as:

Elution percentage (%) =

$\quad$ 100 (amount of Ge eluted)/[(amount of Ge adsorbed)

$\quad$ − (amount of Ge washed)] $\hfill$ (4)

All experiments were performed at ambient temperature.

3. Results and discussion

3.1. Introduction of various functional groups

Time courses of the conversions in the reactions of the GMA-grafted hollow fiber with a dg of 120% with four reactants, 2,2′-iminodiethanol, di-2-propanolamine, *N*-methylglucamine, and 3-amino-1,2-propanediol, are shown in Fig. 3. Final conversions of the epoxy group to four kinds of functional groups ranged from 62 to 95%. Properties of the functional hollow fibers used below are summarized in Table 2. For example, the functional group density of the IDE fiber was 1.3 mole per kg of the dry product. This value was comparable to or higher than that of a commercially available functional bead containing a polyol group [17].

3.2. pH dependence of germanium recovery

To select a functional group favourable for germanium oxide (GeO_2) recovery, a GeO_2 solution, the initial pH of which was adjusted to 4.6, was forced to permeate through the pores across the functional hollow fiber. The amounts of Ge adsorbed on the four kinds of functional hollow fibers with almost identical functional group densities are compared in Fig. 4 as a function of dimensionless
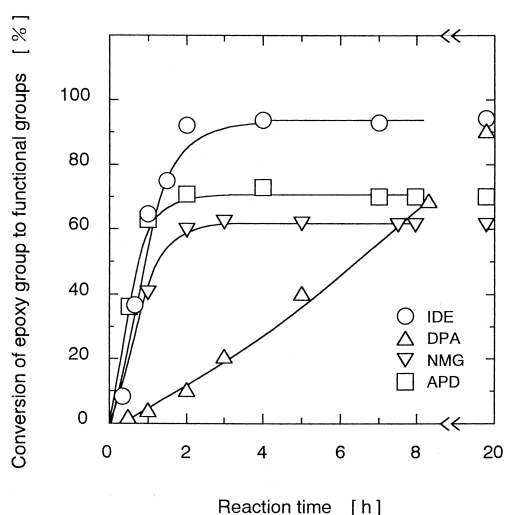

Fig. 3. Time courses of conversions of the epoxy group to various functional groups.

effluent volume, defined as the ratio of the effluent volume to the membrane volume, excluding the lumen. The equilibrium adsorption capacities of Ge for the 0.10 g-GeO_2/L solution can be evaluated according to Eq. (3) and are summarized in Table 2. The hollow fiber containing either an IDE or a DPA group as a functional group was suitable for Ge recovery from the GeO_2 solution. The IDE fiber had an equilibrium adsorption capacity to functional group density ratio that was about 20% higher than that for the DPA fiber. In addition, the IDE fiber, prepared at a grafting degree of 210% and a conversion of 86%, exhibited a functional group density of 2.9 mol/kg.

The equilibrium adsorption capacity evaluated from the breakthrough curve and the molar ratio of the amount of adsorbed Ge to the IDE group density are shown in Fig. 5 as a function of pH. The equilibrium adsorption capacity of the IDE fiber had a maximum value of 87 g-Ge/kg of the product at a pH of about 8.

3.3. Flow rate dependence

The breakthrough curves for various flow-rates of the GeO_2 solution through the IDE fiber are shown in Fig. 6. The flow-rate ranged from 5 to 50 ml/min.

Table 2
Properties of functional hollow-fiber membranes

	IDE fiber		DPA fiber	NMG fiber	APD fiber
dg (%)	120	210	120	120	120
Conversion (%)	40	86	43	41	42
Functional group					
density (mol/kg[a])	1.3	2.9	1.4	1.2	1.4
Size (mm)					
ID	2.4	2.7	2.3	2.3	2.4
OD	4.0	4.9	3.8	4.0	4.1
Flux of pure water[b] (m/h)	0.37	0.40	0.33	0.06	0.45
Equilibrium adsorption					
capacity at pH 4.6 (mol/kg[a])	1.1	2.7[c]	1.0	0.59	0.63

[a] Grams of dry state of the hollow fiber.
[b] $\Delta P = 0.03$ MPa, Temp.$= 297$ K.
[c] pH$= 7.8$.

The residence time, t_r, calculated below, was varied from 0.37 to 3.7 seconds:

$$t_r = \pi\epsilon(d_o^2 - d_i^2)L/4 \text{ (flow-rate)} \qquad (5)$$

where ϵ, d_i, d_o, and L are the porosity, inner and outer diameter, and length of the hollow fiber, respectively. The curves overlapped irrespective of the flow-rate, i.e., residence time. This demonstrates that a negligible diffusional mass-transfer resistance of the Ge species to the IDE group of the polymer

chain grafted onto the pore of the hollow-fiber membrane was achieved by the convective flow of the solution through the hollow-fiber membrane. In other words, a higher flow-rate of the GeO_2 solution led to a higher recovery rate of Ge onto the hollow fiber.

The breakthrough and elution curves of the IDE fiber, prepared at a degree of grafting of 120% and a conversion of 40%, are shown in Fig. 7 for $C_0 = 0.10$ g-GeO_2/L and pH$= 6.3$. The favourable characteristics of negligible diffusional mass-transfer resistance help reduce the tailing of the elution curves, resulting in a higher elution peak. This is a definite advantage
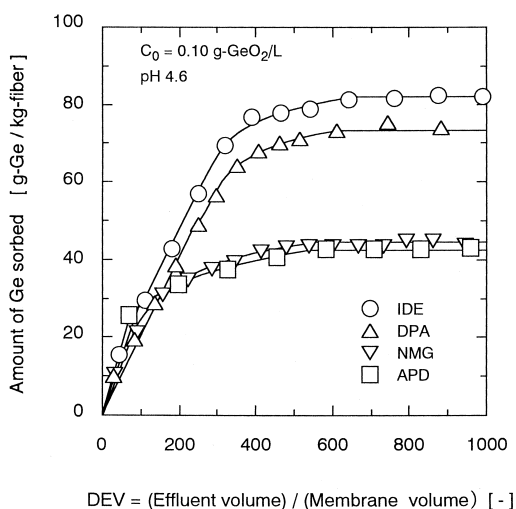

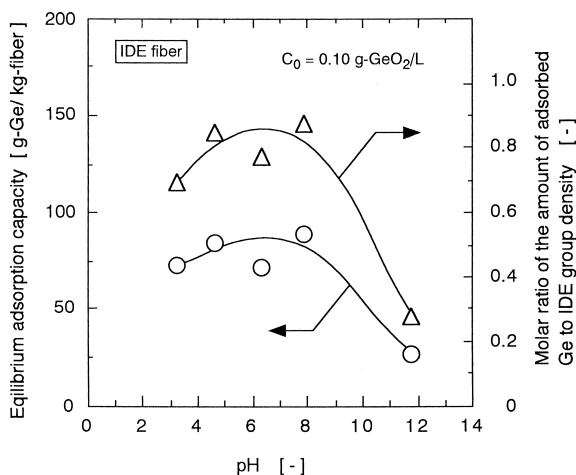Fig. 4. The amount of germanium adsorbed onto various functional hollow-fiber membranes.

Fig. 5. Equilibrium adsorption capacity of the IDE fiber for germanium vs. pH of the germanium oxide solution.
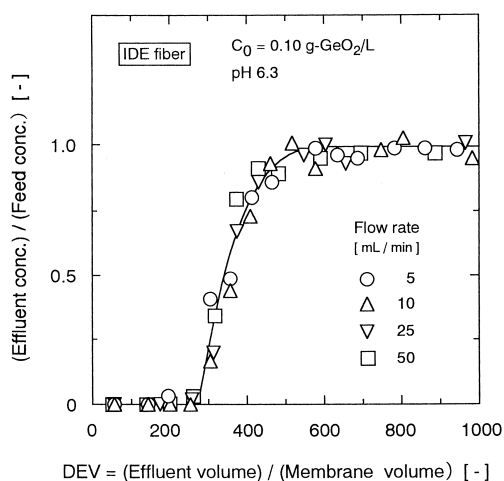
Fig. 6. Dependence of breakthrough curves on the flow-rate of the germanium oxide solution.

of the functional porous membranes in metal and protein purification over a bed charged with functional beads.

3.4. Repeated use of the hollow fiber

The Ge adsorbed onto the IDE fiber was quantitatively eluted by permeating 1 M HCl through the hollow fiber. During three cycles of adsorption and
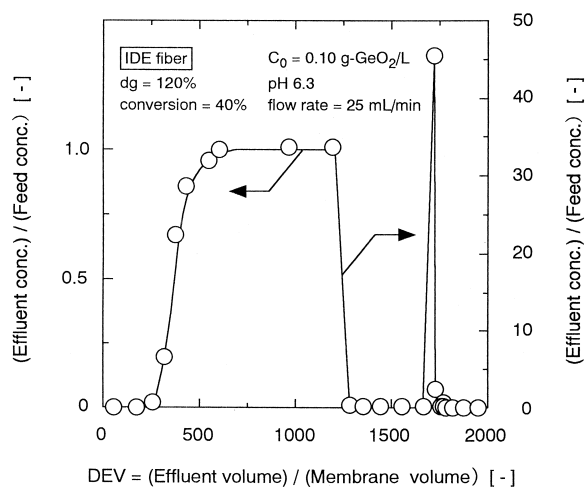
elution, the amount of Ge adsorbed and the elution percentage remained constant at 1.2 mol-Ge/kg for pH=6.3 and 100%, respectively. The functional group introduced via ring-opening of the epoxy group of the poly-GMA chain, $-N(CH_2CH_2OH)_2$, was stable for repeated use.

4. Conclusion

Various functional groups to selectively capture germanium from a germanium oxide (GeO_2) solution were appended onto a polyethylene porous hollow-fiber membrane by radiation-induced graft polymerization and subsequent chemical modifications. A high-speed recovery of germanium was achieved at a high capacity using the hollow-fiber membrane immobilizing the functional-group-containing polymer chains along the pores across the membrane thickness. Convective flow of the GeO_2 solution minimized the diffusion path of the germanium species to the functional group, resulting in an ideal recovery: the higher the flow-rate of the GeO_2 solution, the higher the recovery rate of Ge. A hollow-fiber membrane module [18] manufactured by bundling the functional hollow fibers is applicable to the large-scale recovery of Ge.

5. Nomenclature

C	Concentration of germanium in the effluent (g/L)
C_0	Concentration of germanium in the feed (g/L)
d_i	Inner diameter of the hollow fiber (mm)
d_o	Outer diameter of the hollow fiber (mm)
dg	Degree of grafting (%)
L	Length of the hollow fiber (mm)
q_e	Equilibrium adsorption capacity with C_0 (g/g)
t_r	Residence time (s)
V	Effluent volume (L)
V_e	Effluent volume where C reaches C_0 (L)
W	Mass of the hollow fiber (g)
ϵ	Porosity of the hollow fiber

Fig. 7. An example of breakthrough and elution curves for the IDE fiber.

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