Convection-aided collection of metal ions using chelating porous flat-sheet membranes

Kaori Saito[a], Kyoichi Saito[a,*], Kazuyuki Sugita[a], Masao Tamada[b], Takanobu Sugo[b]

[a]*Department of Materials Technology, Faculty of Engineering, Chiba University, Inage, Chiba 263-8522, Japan*
[b]*Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370-1292, Japan*

Abstract

Chelating porous membranes were prepared by radiation-induced graft polymerization of an epoxy-group-containing monomer onto a polyethylene flat sheet and subsequent conversion of the epoxy group to an iminodiacetate group as a chelate-forming group. The chelating group density on the resultant porous flat-sheet membrane of 1.0 mol/kg was comparable to that of commercially available chelating beads. The pure water permeability of the membrane was 40% that of the trunk porous membrane, which was used for microfiltration. During the permeation of a copper chloride solution through the membrane, diffusional mass-transfer resistance of copper ion was negligible, since the ion was transported by convective flow through the pore. The tensile strength and elongation at break of the membranes were measured as a function of dose of electron-beam irradiation, the degree of grafting, and the chelating group density to determine an applicable range for practical use.   © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Forced transport of ions and molecules driven by convection will exhibit much a higher rate of mass transfer than their diffusive transport driven by a concentration gradient. Both membrane chromatography using porous membranes [1–3] and perfusion chromatography using porous beads [4–6] are based upon convection-aided transport of ions and molecules. Brandt et al. [1] prepared affinity porous membranes and purified biomolecules. Afeyan et al. [4] prepared perfusion beads with various functionalities, which consisted of a bidispersive structure of throughpores and diffusive pores, for high-throughput protein purification.

Thus far, we have modified a porous hollow-fiber membrane to append ion-exchange groups [7,8], hydrophobic ligands [9], and affinity ligands [10], by applying the radiation-induced graft polymerization. Yamagishi et al. [11] removed cobalt ions from pure water using chelating porous hollow-fiber membranes and demonstrated an efficient removal of cobalt ions during the permeation of the solution through the pores of the membrane. Palladium ions [12] and germanium oxide [13] were recovered from the effluents produced by processing spent catalysts and the production of polyethylene terephthalate, respectively, using the chelating porous hollow-fiber membranes. Furthermore, bovine serum albumin [14]

*Corresponding author. Tel./fax: +81-43-290-3439.
E-mail address: marukyo@xtal.tf.chiba-u.ac.jp (K. Saito).

and hen-egg lysozyme [8] were adsorbed in multi-layers using ion-exchange porous hollow-fiber membranes.

Microfiltration (MF) membranes are the candidate substrates for preparing functionalized porous membranes. The shape of the MF membranes is classified into hollow fiber and flat sheet. The flat-sheet membrane has an advantage over the hollow-fiber membrane in that both the membrane sheet and the membrane module are produced more cost-effectively. Modification of a flat-sheet MF membrane into a flat-sheet functionalized membrane is required to satisfy the requirements of ion collection performance and mechanical strength, using the preirradiation technique of grafting and subsequent reactions.

The objective of this study was twofold: (1) to prepare a porous flat-sheet membrane containing a chelate-forming group by radiation-induced graft polymerization of an epoxy-group-containing vinyl monomer onto the membrane and subsequent conversion of the epoxy group into an iminodiacetate (IDA) group, and (2) to optimize the degree of grafting and the conversion to maintain mechanical strength of the membrane applicable for practical use.

2. Experimental

2.1. Materials

A porous flat-sheet membrane of polyethylene was used as a trunk membrane for grafting. The membrane, supplied by Asahi Kasei, was 0.10 mm thick with a nominal pore size of 0.24 μm and a porosity of 67%. Glycidyl methacrylate (GMA, $CH_2=CCH_3COOCH_2CHOCH_2$) was purchased from Tokyo Kasei, and used without further purification. Other reagents were of analytical grade or higher.

2.2. Preparation of chelating porous membranes

A scheme for preparing chelating porous flat-sheet membranes is shown in Fig. 1. (1) Electron beam (EB) irradiation: the membrane in the form of a flat-sheet was irradiated to produce a starting site of polymerization of the vinyl monomer with an electron beam accelerator (Radiation Dynamics, Model IEA 3000-25-2) in a nitrogen atmosphere at ambient temperature. The dose was set at 50 kGy. (2) GMA grafting: the EB-irradiated membrane was immersed in 5% (v/v) GMA-methanol solution at 313 K to graft-polymerize GMA. Reaction times ranged from 10 to 60 min. The degree of GMA grafting, dg, was defined as:

$$dg = 100 \cdot (W_1 - W_0)/(W_0) \tag{1}$$

where W_0 and W_1 are the masses of the trunk polymer and the GMA grafted polymer, respectively. The resulting porous flat-sheet membrane was referred to as a GMA(dg)-FS membrane. (3) Introduction of chelate-forming group: the GMA-grafted membrane was immersed in a 0.425 M disodium iminodiacetate solution at 353 K to convert the epoxy group into an IDA group [$-N(CH_2COOH)_2$] as a chelate-forming group. The conversion of the epoxy group, x, into the IDA group was defined as:

$$x = 100$$
$$\cdot \{142(W_2 - W_0)/[W_1 - W_0 - (142 + 18)]\}$$
$$/(133 - 18) \tag{2}$$

where W_2 is the mass of the resulting IDA membrane of the H type. The values 142, 133, and 18 are the molecular masses of GMA, iminodiacetic acid, and water, respectively. (4) Hydrophilization of the pore surface: the membrane was reacted with 0.5 M H_2SO_4 for 2 h at 353 K. The remaining epoxy groups were hydrolyzed to form a diol group to render the pore surface hydrophilic [15]. The resultant chelating porous flat-sheet membrane is referred to as an IDA(dg, x)-FS membrane.

2.3. Measurement of tensile strength and elongation of the chelating membranes

The flat-sheet membrane in a dry or wet state was cut into a dumbbell-shaped test piece 120 mm long and 25 mm wide with a neck 10 mm wide. The initial membrane thickness was measured with a thickness tester (Ono Sokki, ST-110). Both ends of the test piece were stretched at a rate of 50 mm/min to reach the breaking point at ambient temperature. The measurement was performed using a Shimadzu AGS-5D tester. The tensile strength is defined as the force per unit area of the original cross-section.
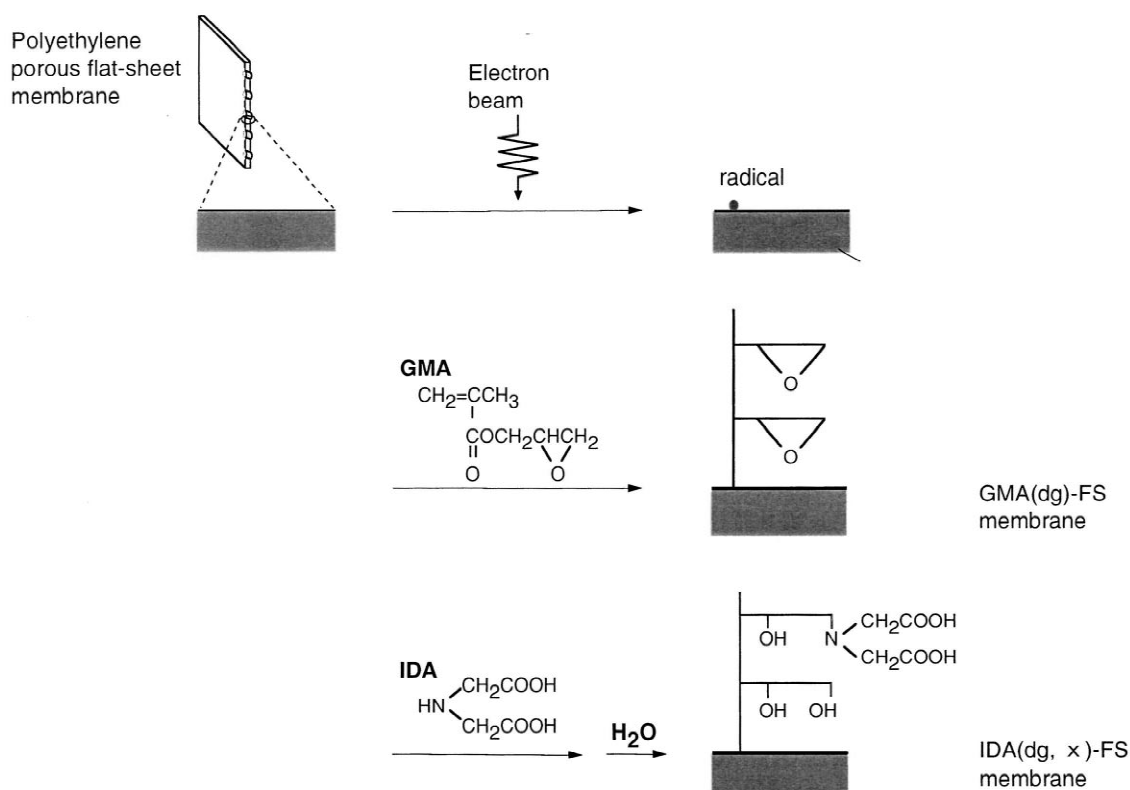
Fig. 1. Preparation of chelating porous flat-sheet membranes.

2.4. Collection of metal ion in a permeation mode

The IDA(110, 75)-FS membrane was sandwiched between two sheets of nonwoven fabric made of polyethylene to rectify the liquid flow. Then this set was inserted into a cartridge holder [purchased from Advantec (PP-25)], as shown in Fig. 2. The effective area of the membrane was 350 mm^2. Copper chloride (CuCl$_2$) solution, the feed concentration of which was 100 mg/l (pH 5.0), was forced to permeate from one side of the membrane at various permeation rates ranging from 30 to 120 ml/min at ambient temperature. The effluent penetrating the other side of the membrane was continuously sampled and the concentration of copper was determined by chelatometric titration with EDTA using 4-(2-thizolylazo)resorcinol as an indicator. After equilibration, i.e., when the effluent concentration of the metal attained the feed concentration, pure water was allowed to permeate to wash the pores. Sub-sequently, 1 M HCl was used to elute the adsorbed metal ion. The amount of metal adsorbed at equilibrium with a feed concentration was evaluated from the following:
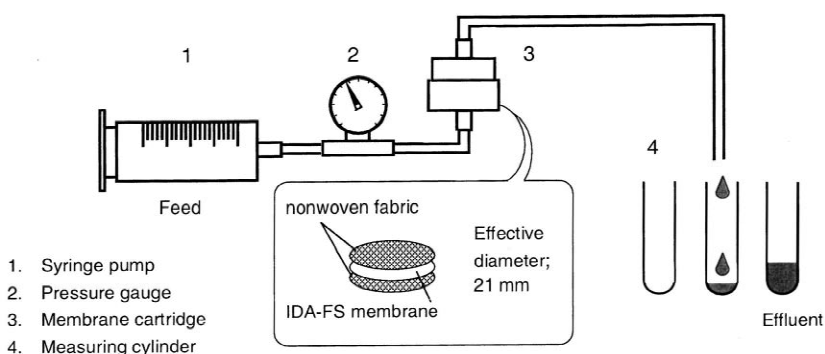
$$q = \int_0^{V_e} (C_0 - C) \cdot dV / W \qquad (3)$$

where C_0 and C are the metal ion concentrations of the feed and effluent, respectively. The terms V, V_e, and W are the effluent volume, the effluent volume where C reaches C_0, and the mass of the membrane, respectively.
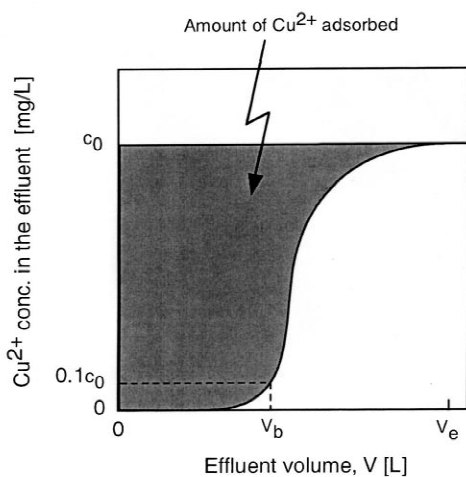
3. Results and discussion

3.1. Tensile strength and elongation of the membranes

Chelating porous membranes of a flat-sheet form

Fig. 2. Collection of copper ions through the chelating porous flat-sheet membrane.

were prepared using the pre-irradiation technique for grafting GMA and subsequent chemical modification of the introduced epoxy group to an IDA group. Tensile strength and elongation of the electron-beam-irradiated trunk polyethylene (PE) membranes are shown in Fig. 3a as a function of dose. 80% of the tensile strength of the starting PE membrane was maintained at 50 kGy. Then, the GMA-grafted membrane, GMA(dg)-FS membrane, exhibited a sharp decrease in elongation with increasing dg but a slightly linear increase in the tensile strength (Fig. 3b). The mechanical strength of the porous flat-sheet membranes containing the iminodiacetate group, i.e., IDA(150, x)-FS membranes, was measured for various conversions in a wet state (Fig. 4). The tensile

strength was almost constant irrespective of the conversion from 0 to 90% for the GMA(150)-FS membrane, whereas the elongation increased with increasing conversion.

To improve the adsorption capacity of the chelating porous membrane for the metal ions, the higher dg and conversion to IDA group are favorable; however, this means reduced elongation. The dg should be selected according to the strength required in practical uses. Here, a dg of 110% was employed where module fabrication is possible.

3.2. Collection of metal ions during permeation

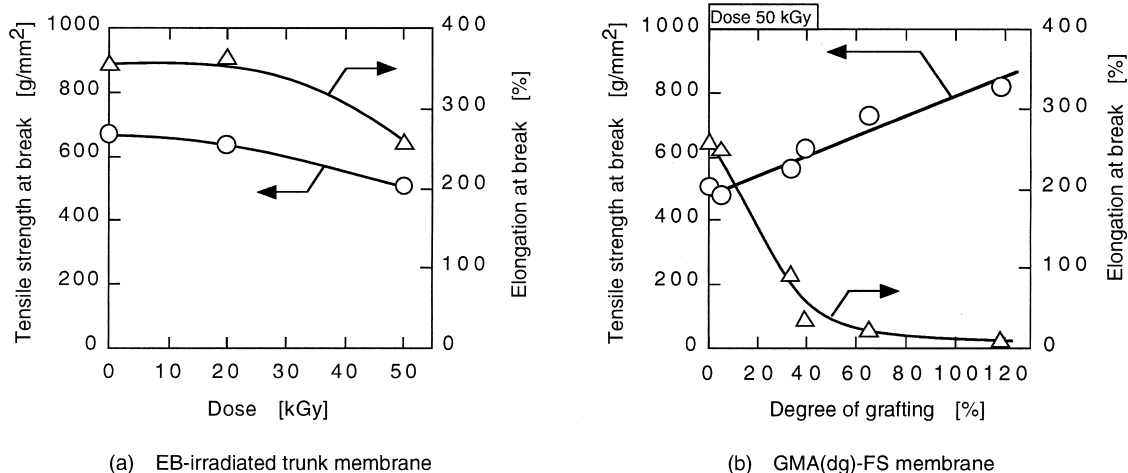The changes in the copper ion concentration of the

Fig. 3. Tensile strength and elongation at break.

(a) EB-irradiated trunk membrane

(b) GMA(dg)-FS membrane

effluent of the IDA(110, 75)-FS membrane with effluent volume, i.e., the breakthrough curves, are shown in Fig. 5. The abscissa is the dimensionless effluent volume (DEV) defined as the ratio of the effluent volume to the membrane volume, and the ordinate is the relative copper concentration of the effluent to the feed. The breakthrough curves overlapped irrespective of the permeation rate of the solution. Collection of the metal ion during the permeation of the metal-ion-containing solution through the pores rimmed by the polymer chains

containing the IDA group was effective because the diffusional path of the metal ion from the pore interior to the chelate-forming group can be minimized by convection. This advantage of porous membranes functionalized with grafted polymer chains over functionalized beads has been demonstrated for various target ions [16] and proteins [7,17–20].

Results of previous studies on convection-aided collection of metal ions or proteins using functionalized porous membranes are summarized in Table 1.
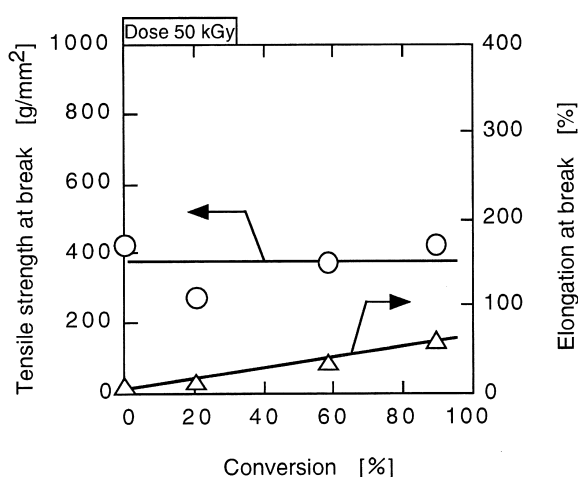

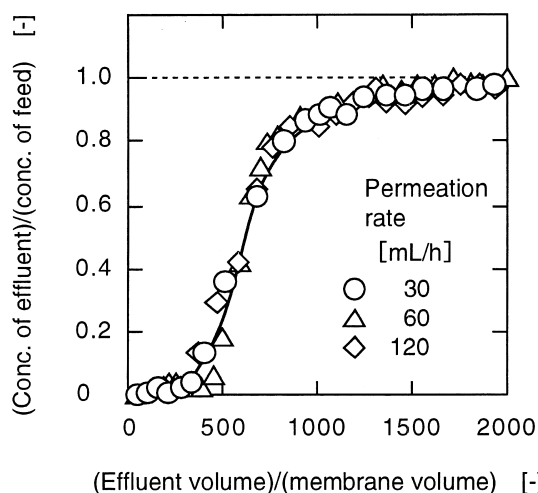Fig. 4. Tensile strength and elongation at break of IDA(150, x)-FS membrane.

Fig. 5. Effect of permeation rate on breakthrough curves of IDA(110, 75)-FS membrane.

Table 1
Previous studies on metal ion and protein collection using functionalized porous membranes

Ref.	Target	Diffusion coefficient (10^{-11} m^2/s)	Shape of porous membrane[a]	Pore diameter (μm)	Membrane thickness (mm)	Residence time (t_r[b], s)	t_D[c] (s)	Diffusional mass-transfer resistance
[7]	Albumin	6.7	HF	0.3	0.53	33–165	$4.3\cdot10^{-4}$	Negligible
[17]	Albumin	6.7	HF	0.2	0.36	1.2–12	$1.5\cdot10^{-4}$	Negligible
[16]	Co^{2+}	66	HF	0.4	0.85	0.86–3.5	$6.1\cdot10^{-5}$	Negligible
[18]	Albumin	6	FS	0.4	3	2.8	$6.7\cdot10^{-4}$	Negligible
[19]	Albumin	6.7	FS	150		120–2400	84	Definite
[20]	Lysozyme	11	FS[d]	40	0.35	4.3–65	3.6	Definite
This study	Cu^{2+}	72	FS	0.36	0.13	1.4–5.4	$4.5\cdot10^{-5}$	Negligible

[a] HF, Hollow fiber; FS, flat sheet.
[b] t_r = (pore volume)/(permeation rate).
[c] t_D = [(pore diameter)/2]^2/(diffusion coefficient).
[d] Nonwoven fabric.

The shapes of the membranes include flat sheets and hollow fibers. Favorable performance for practical applications, i.e., negligible diffusional mass-transfer resistance of the target ions or proteins to the functional groups immobilized onto the membrane, is realized when the time required for the diffusion process is much shorter than the residence time of the liquid across the membrane. We evaluated the Peclet number as follows:

Peclet number

$$= [(\text{pore diameter})^2/D]/(\text{residence time}) \qquad (4)$$

where D is the diffusion coefficient of the metal ions or proteins, and the residence time is calculated by:

residence time

$$= (\text{pore volume})/(\text{permeation rate}) \qquad (5)$$

The Peclet numbers are listed in order in Fig. 6. Two extremes of pore diameter, i.e., less than 1 μm and 40 or 150 μm, exhibited clear differences in mass-transfer performance: the functionalized porous membranes with pore sizes as small as one micron are appropriate due to a lower Peclet number when an intrinsic interaction such as ion-exchange, chelation, and hydrophobic interaction is extremely fast.

4. Conclusions

A flat-sheet form of a porous membrane made of polyethylene was modified into a chelating porous membrane by radiation-induced graft polymerization of an epoxy-group-containing vinyl monomer (GMA) and subsequent addition of iminodiacetic acid. The mechanical strength, i.e., tensile strength and elongation at break, of the resultant chelating porous membranes was measured before determining the adsorption kinetics of copper ion during the permeation of a copper chloride solution through the pores rimmed by the iminodiacetate group-immobilized graft chains. Mechanical strength was mainly governed by EB dose and the degree of GMA grafting and not by the conversion of the epoxy group to the iminodiacetate group. A degree of GMA grafting of 110% onto a 50 kGy-electron beam-
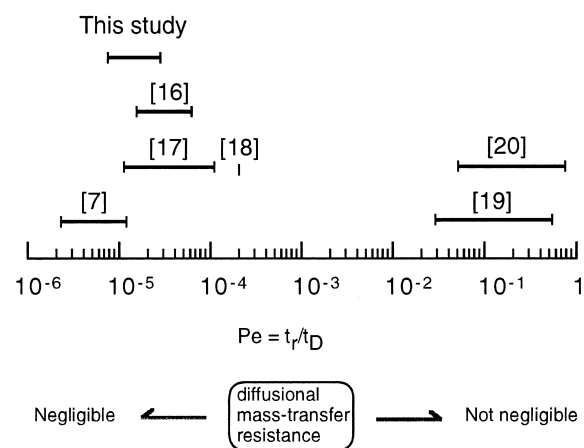

Fig. 6. Peclet numbers in previous studies of metal ion or protein collection using functionalized porous membranes. Reference numbers in the figure correspond to those listed in Table 1.

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irradiated membrane and a conversion of 75% produced a chelating porous membrane applicable for practical uses.

A negligible diffusional mass-transfer resistance of copper ion to the graft chain was experimentally verified using the flat-sheet form of a chelating porous membrane. The chelating porous flat-sheet membrane is a promising candidate for the low-cost removal of heavy metal ions from ultrapure water because of the favorable kinetics of adsorption and easy assembly of a membrane module.

Acknowledgements

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