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Removal of Antimony (III) Using Polyol-Ligand-Containing Porous Hollow-Fiber Membranes

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ABSTRACT

A polyol-ligand-containing porous hollow-fiber membrane capable of removing antimony (III) from a liquid stream was prepared by radiation-induced graft polymerization of an epoxy-group-containing vinyl monomer, glycidyl methacrylate (GMA), and subsequent

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functionalization with *N*-methylglucamine (NMG) and 3-amino-1,2-propanediol (APD). The resultant chelate-forming group density was 1.6 mol per kg of the NMG-group-containing porous hollow-fiber membrane. An antimony (III) oxide solution (10 mg per L, pH 3.6–13) was forced to permeate through the submicron-diameter pores of the chelating porous hollow-fiber membrane. The antimony concentration of the effluent penetrating the outside surface of the hollow fiber was determined as a function of the effluent volume. The breakthrough or dynamic adsorption capacity for antimony was 54 g of Sb per kg of membrane at pH 11. Because of negligible diffusional mass-transfer resistance, the breakthrough curves overlapped irrespective of the permeation rate of the antimony solution across the chelating porous hollow-fiber membranes.

Key Words: Antimony (III) oxide; Polyol ligand; Chelating porous hollow-fiber membrane; Radiation-induced graft polymerization.

INTRODUCTION

Water easily can be polluted by metal ions as a result of their release from industrial plants. For example, when polyester is produced by a reaction of ethylene glycol with terephthalic acid, antimony (III) oxide is used as a homogeneous catalyst of polymerization; therefore, some of the catalyst is contained in the effluent of the polyester production plant. The LD_{50} as a measure of antimony toxicity is 100 and 150 mg per kg of intraperitoneal rats and guinea pigs, respectively.[1] The World Health Organizations guideline for drinking water quality with regard to antimony is 0.005 mg of Sb per L.[2]

Various kinds of adsorption treatments have been investigated to remove poisonous metal ions from water in the environments. Previous publications[3–9] on the adsorption treatments of antimony are intended for the removal of antimony from a copper electrolyte, the pH of which is around 1. Argekar and Manjrekar[9] used cation-exchange resin to adsorb antimony diluted with 6 M HCl in a column mode.

We have thus far proposed a permeation-aided removal of metal ions using chelating porous hollow-fiber membranes.[10–14] A high-density chelate-forming group, capable of specifically capturing metal ions, was introduced into the polymer chains grafted onto the pore surface of the porous hollow-fiber membrane. A metal-ion-containing solution was forced to permeate through the submicron-diameter pores rimmed by the chelating polymer chains across the membrane thickness of 1 mm. During the trans-membrane-pressure-driven permeation, the high-speed removal of the metal ion was achieved because the time required for the diffusion of the metal ion from the solution to the chelating group is much shorter than the residence time of the solution across the membrane.[13,14]

The objective of our study was to prepare porous hollow-fiber membranes containing polyol ligands as a chelate-forming group and to demonstrate the high-speed removal of antimony (III) species in the permeation mode.

EXPERIMENTAL

Materials

A commercially available porous hollow-fiber membrane made of polyethylene, supplied by Asahi Kasei Corporation (Tokyo, Japan), was used as the trunk polymer for grafting. This hollow fiber had inner and outer diameters of 2 and 3 mm, respectively, with a pore diameter of 0.4 μm and a porosity of 70%. Glycidyl methacrylate (GMA, $CH_2{=}CCH_3$-$COOCH_2CHOCH_2$) was purchased from Tokyo Kasei (Tokyo, Japan), and used without further purification. *N*-methylglucamine (NMG, $CH_3NHCH_2(CHOH)_4CH_2OH$,) and 3-amino-1,2-propanediol (APD, $NH_2CH_2CH(OH)CH_2OH$) were purchased from Wako Pure Chemical Industries (Osaka, Japan) and Sigma-Aldrich Co. (St. Louis, MO, USA), respectively, and used without further purification. Other chemicals were of analytical grade or higher.

Antimony (III) oxide (Sb_2O_3) was dissolved in 1 M sodium hydroxide to yield 100 mg of Sb per L of antimony solution. The pH of 10 mg of Sb per L of Sb_2O_3 solution was adjusted from 3.6 to 13 with sulfuric acid.

Preparation of Polyol-Ligand-Containing Porous Hollow-Fiber Membranes

The introduction scheme of two kinds of polyol ligands as the chelate-forming group into the porous hollow-fiber membranes is shown in Fig. 1. First, the porous hollow-fiber membrane was irradiated with an electron beam using a cascade-type accelerator to produce radicals throughout the trunk polymer.[15] Second, the electron-beam-irradiated hollow fiber was immersed in a 10 (v/v)% GMA/methanol solution at 313 K, which had been previously deaerated by bubbling with nitrogen gas. After a reaction time of 11 min, the hollow fiber was removed and washed thoroughly with

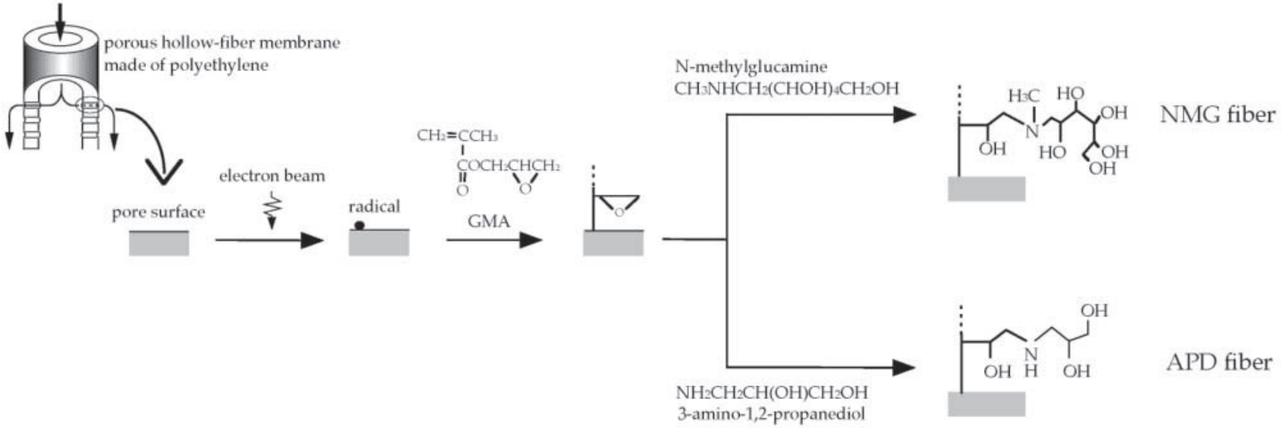

Figure 1. A reaction scheme for the introduction of two kinds of chelate-forming groups into a porous hollow-fiber membrane.

N, N-dimethylformamide. The hollow fiber was dried in a reduced pressure and weighed. The degree of GMA grafting, defined below, was evaluated from the weight gain.

$$\mathrm{dg}\,(\%) = \frac{100\ (\text{mass of poly-GMA chain})}{(\text{mass of trunk polymer})} \tag{1}$$

The degree of GMA grafting was set at 140%. Third, the epoxy group of the poly-GMA chain was converted into two kinds of polyol ligand: $-NCH_3CH_2(CHOH)_4CH_2OH$ (NMG group) and $-NHCH_2CH(OH)CH_2OH$ (APD group). The reaction conditions for the introduction of the chelate-forming groups are summarized in Table 1. The molar conversion of the epoxy group to the polyol ligand was defined as follows:

$$\text{Molar conversion}\,(\%) = \frac{100\ (\text{moles of polyol ligand introduced})}{(\text{moles of epoxy group before functionalization})} \tag{2}$$

The molar conversion was evaluated from the weight gain in a dry state. The resultant hollow fibers were referred to as the NMG and APD fibers corresponding to the reactants of *N*-methylglucamine and 3-amino-1,2-propanediol, respectively.

Antimony Removal During Permeation Across Chelating Porous Hollow-Fiber Membranes

A chelating porous hollow-fiber membrane with an effective length of 2.4 cm was positioned in the configuration, as shown in Fig. 2. The antimony trioxide solution (10 mg of Sb per L) as a feed was forced to permeate radially outward from the inside surface of the hollow fiber to the outside surface at a constant permeation rate using a pump. The permeation rate ranging from 40 to 150 mL per hour was converted to space velocity (SV) defined by dividing

Table 1. Preparation conditions for the introduction of chelate-forming groups into a porous hollow-fiber membrane.

	APD fiber	NMG fiber
Reactant	3-amino-1,2-propanediol	*N*-methylglucamine
Concentration (M)	1.0	0.50
Solvent	50 (v/v) dioxane/water	50 (v/v) dioxane/water
Temp. (°C)	80	80

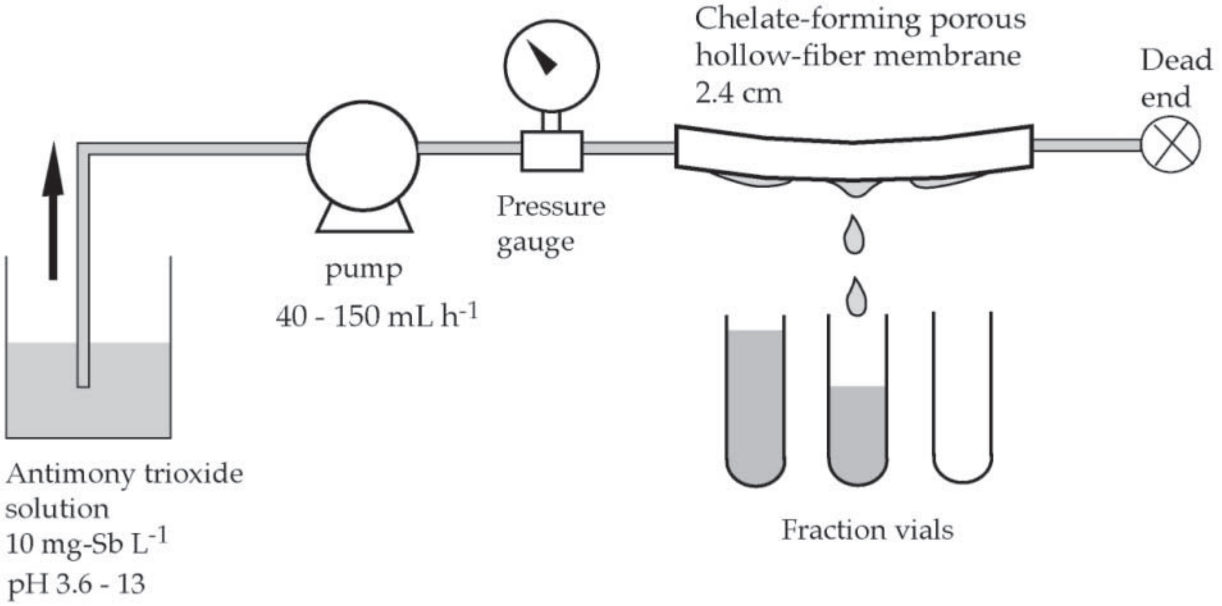

Figure 2. Experimental apparatus for antimony removal using chelate-forming porous hollow-fiber membranes.

the permeation rate by the membrane volume excluding the lumen part. The effluent penetrating the outside surface of the hollow fiber was continuously sampled and its antimony concentration was determined by atomic absorption spectrophotometry (Hitachi A-2000) to yield a breakthrough curve, namely, the time course of the antimony concentration of the effluent with the effluent volume.

The dynamic adsorption capacity of the chelating porous hollow-fiber membrane for antimony was evaluated from the following integration.

$$q_B = \int_0^{v_B} \frac{(C_0 - C)\mathrm{d}V}{W} \tag{3}$$

where C_0 and C are the antimony concentrations of the feed and effluent, respectively. W is the mass of the chelating porous hollow-fiber membrane. V and V_B are the effluent volume and the effluent volume when C reached 10% of C_0, respectively.

Elution of Antimony with Hydrochloric Acid

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

$$\text{Elution percentage}\,(\%) = \frac{100\ (\text{amount of Sb eluted})}{(\text{amount of Sb adsorbed}) - (\text{amount of Sb washed})} \tag{4}$$

All experiments were performed at ambient temperature.

RESULTS AND DISCUSSION

Polyol Group Density of the Porous Hollow-Fiber Membranes

The time courses of the molar conversions of the epoxy group into the NMG and APD groups are shown in Fig. 3. Molar conversions increased with an increasing reaction time. Molar conversions of the epoxy group to the NMG and APD groups of 56% and 53% at a reaction time of 4 hr were equivalent to chelating group densities of the NMG and APD fibers of 1.6 and 1.8 mol per kg of the dry membrane, respectively.

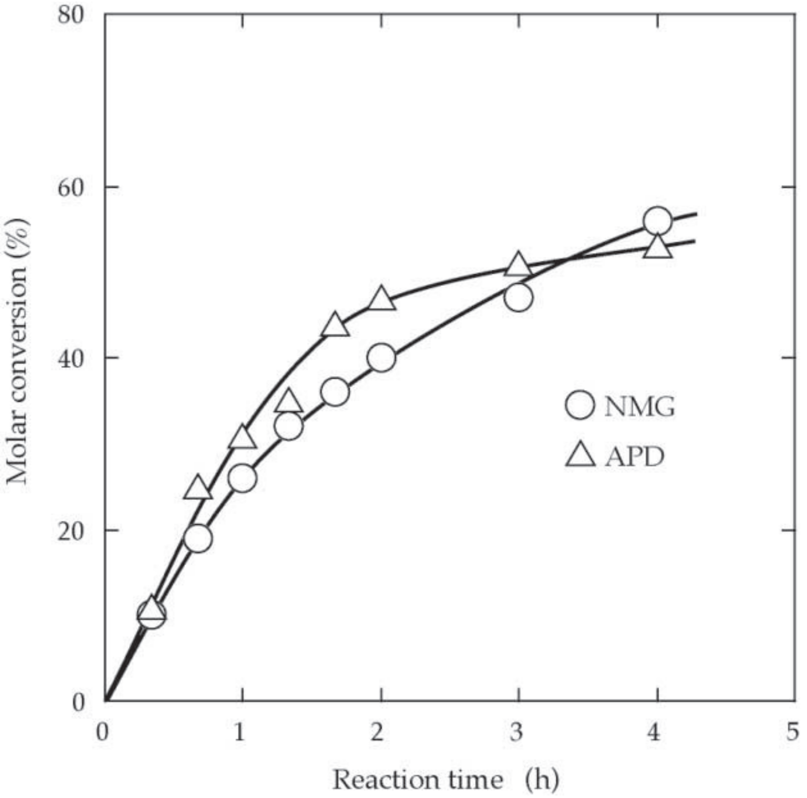

Figure 3. Time courses of molar conversions of the epoxy group to chelate-forming groups.

Antimony Removal During Permeation Across the Chelating Membranes

The breakthrough curves for various SVs of the antimony (III) oxide solution (pH 11) through the pores of the NMG fiber prepared at a molar conversion of 26% are shown in Fig. 4. The residence time, calculated below, ranged from 4.1 to 16 sec.

$$\text{Residence time} = \frac{\varepsilon\pi(d_o^2 - d_i^2)L}{[4(\text{permeation rate})]} \tag{5}$$

where ε, d_i, d_o, and L are the porosity, inner and outer diameters, and effective length of the hollow fiber, respectively. The breakthrough curves overlapped

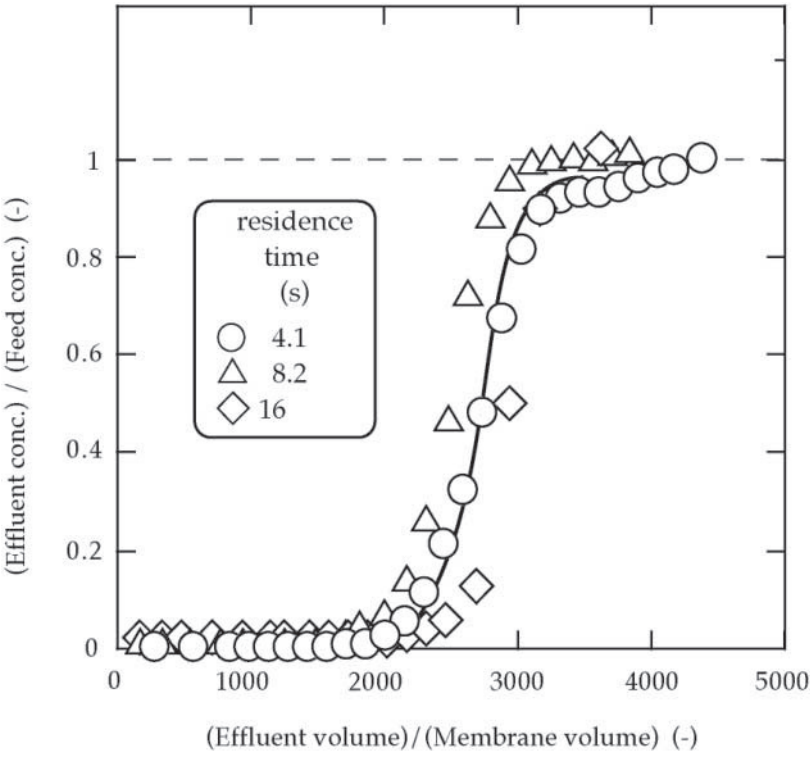

Figure 4. Breakthrough curves for various residence times of the Sb_2O_3 solution through the pores of the NMG fiber.

irrespective of the residence time of the antimony solution. This demonstrates that diffusional mass-transfer resistance of the antimony species to the NMG group of the polymer chains grafted onto the pores of the hollow fiber was negligible due to the permeation of the antimony solution through the pores of the NMG fiber. In other words, the higher permeation rate of the antimony (III) oxide solution led to a higher overall removal rate of antimony by the chelating porous hollow-fiber membrane.

pH Dependence of Antimony Adsorption

The dynamic adsorption capacities of the NMG and APD fibers for antimony are compared in Fig. 5 for various pHs of the antimony (III)

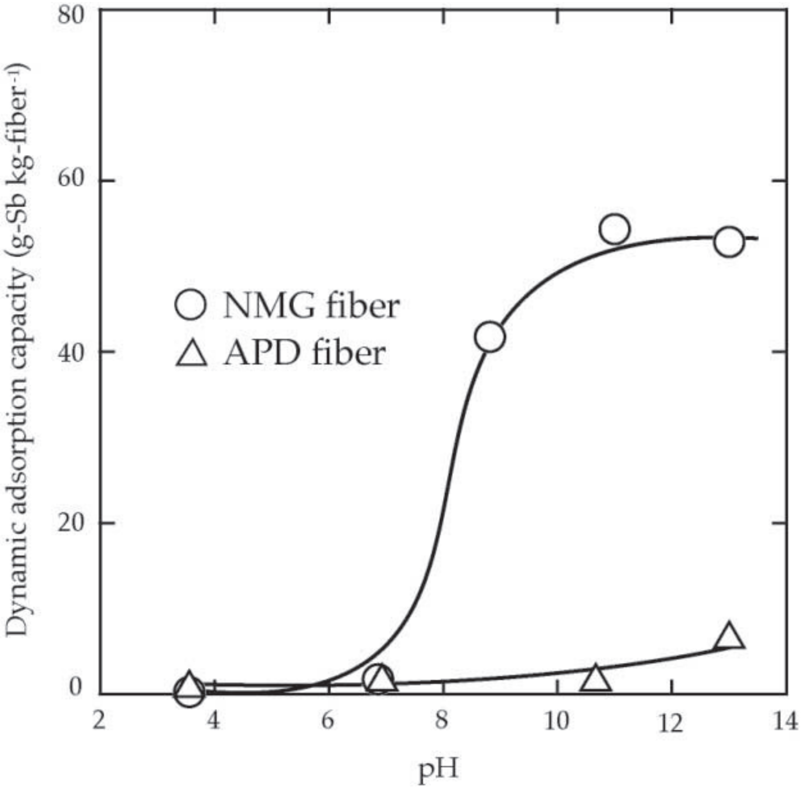

Figure 5. Dynamic adsorption capacity of the NMG and APD fibers for Sb(III) as a function of the pH of the Sb_2O_3 solution.

oxide solution. The dynamic adsorption capacity of the NMG fiber increased as the pH of the solution increased, whereas the APD fiber exhibited a lower dynamic adsorption capacity than the NMG fiber over the pH range of 3.6 to 13. The dynamic adsorption capacity of 54 g of Sb per kg of the NMG fiber at pH 11 was higher than that of a polyol-type adsorbent (22 g of Sb per kg of the adsorbent) which was synthesized by covalent binding of pyrogallol to a silica gel ceramic support.[8]

Elution of Antimony

The antimony adsorbed onto the NMG fiber was quantitatively eluted by permeating 1 M hydrochloric acid through the pores of the NMG fiber.

In addition, after three cycles of adsorption and elution, the amount of adsorbed antimony and the elution percentage remained constant at 45 g of Sb per kg of the NMG fiber (pH 11) and 100%, respectively: the chelating porous hollow-fiber membrane was stable for the repeated use of the NMG fiber for adsorption and elution.

CONCLUSIONS

Two kinds of polyol ligands were introduced into the polymer chains grafted onto a porous hollow-fiber membrane by radiation-induced graft polymerization of an epoxy-group-containing monomer and subsequent epoxy-ring opening with *N*-methylglucamine (NMG) and 3-amino-1,2-propanediol (APD). An antimony (III) oxide solution was permeated through the pores rimmed by the polymer chains containing the polyol ligand, and the high-speed removal of antimony was demonstrated because of negligible diffusional mass-transfer resistance of the antimony species to the polyol ligand. Over a pH range of 3.6 to 13, the porous hollow-fiber membrane prepared with a reactant of NMG exhibited higher adsorption capacity of antimony than that prepared with a reactant of APD. The antimony adsorbed onto the membrane was quantitatively eluted with 1 M hydrochloric acid.

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