Adsorption of Co²⁺ and Cs¹⁺ by Polyethylene Membrane with Iminodiacetic Acid and Sulfonic Acid Modified by Radiation-Induced Graft Copolymerization

SEONG-HO CHOI, YOUNG CHANG NHO

Isotope Radiation Application Team, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejon, 305-600 Korea

Received 11 March 1998; accepted 7 June 1998

ABSTRACT: Two modified hollow fiber membranes, the chelating hollow fiber membrane with iminodiacetic acid and the cation-exchange hollow fiber membrane with sulfonic acid group (—SO₃H), were prepared by radiation-induced grafting of glycidyl methacrylate onto polyethylene hollow fiber membrane and its subsequent iminodiacetation and sulfonation. The adsorption characteristics of Co^{2+} and Cs^{1+} for the 2 hollow fiber membranes were examined when the solutions of Co^{2+} and Cs^{1+} permeate across the 2 membranes, respectively. Without regard to the chelating membrane with iminodiacetic acid group and the cation-exchange membrane with sulfonic acid group (—SO₃H), 2 membranes were observed to adsorb Co^{2+} higher than Cs^{1+} . The adsorption curves of Co^{2+} by IDA group-chelating fiber membrane in the presence of Na^{1+} and Ca^{2+} showed that the chelating hollow was found to have a very high selectivity for Co^{2+} , even though there is a high concentration of Na^{1+} and Ca^{2+} in the inlet solution. (© 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 999–1006, 1999

Key words: chelating hollow fiber membrane; cation-exchange hollow fiber membrane; radiation-induced graft copolymerization; iminodiacetic acid; sodium sulfite; adsorption characteristics

INTRODUCTION

Reactor coolant in a nuclear power plant contains fission products and radioactive nuclides. The purification of reactor coolant is very important for the operation of the plant and reactor safety. In particular, the treatment of radioactive Co^{2+} and Cs^{1+} in reactor coolant and low level nuclear waste is essential in the nuclear industry.

Radiation-induced graft copolymerization is a good method for modification of chemical and physical properties on polymer materials because it can endow properties such as membrane quality,¹ ion exchange,^{2,3} blood compatibility,⁴ dyeability,⁵ protein adsorption,⁶ and immobilization of bioactive materials.⁷

A hollow fiber membrane is superior to a flat sheet membrane because of its high ratio of surface area to volume. A polymer with a functional group cannot be always processed into a porous hollow fiber membrane. Therefore, the chemical modification of the existing hollow fibers can be a effective method to add new properties, such as the collection of ions and nonfouling. Grafting is a useful method for modifying the existing polymers chemically. Initiation of graft polymerization is induced by the irradiation with high-energy radiation,^{8–13} ultraviolet (UV) radiation,¹⁴ and plasma treatment.¹⁵ In particular, as compared with others, radiation-induced graft poly-

Correspondence to: Y. C. Nho.

Journal of Applied Polymer Science, Vol. 71, 999-1006 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/060999-08





merization has an advantage to easily control the site of grafted polymer branches and the density of the functional groups.¹⁶

In a previous article,¹⁷ the adsorption characteristics of lead and palladium ions were examined when two ions were permeated across six types of the chelating hollow fiber membranes containing trimethylamine, dimethylamine, ethylenediamine, hexamethyldiamine, diethylenetriamine, and iminodiacetic acid, respectively. Subsequently, cation-exchange hollow fiber membrane was prepared by radiation-induced graft of styrene onto polyethylene hollow fiber membrane and its sulfonation, and the adsorption characteristics of Co^{2+} by the modified hollow fiber membrane were evaluated.¹⁸

In this study, two modified hollow fiber membranes were prepared by radiation-induced grafting of glycidyl methacrylate (GMA) onto polyethylene hollow fiber membrane and its subsequent chemical modification. When the cobalt and cesium ion were permeated across the two-type membranes, respectively, the adsorption characteristics of the chelating and the cation-exchange fiber membranes on Co^{2+} and Cs^{1+} were examined.

EXPERIMENTALS

Materials

A commercially available microfiltration polyethylene hollow fiber membrane (Asahi Chemical Industry Co., Ltd., Tokyo, Japan) was used as the trunk polymer for the grafting. The inner and outer diameter of the porous polyethylene (PE) hollow fiber were 1.95 and 3.01 mm, respectively. The hollow fiber had 0.34 μ m pore diameter and 71% porosity. Glycidyl methacrylate (CH_2 =CCH₃COOCH₂CHOCH₂; GMA) was used without further purification. Other chemicals were of reagent grade.

Grafting Procedures

Scheme 1 shows the procedures of radiation grafting of GMA onto PE hollow fiber and introduction of a functional group, such as iminodiacetic acid (IDA) and the sulfonic acid group, respectively. 10-cm hollow fiber was irradiated by γ -ray at a total dose 40 kGy from Co-60 under ambient temperature in an atmosphere. The irradiated hollow fiber was immersed in a 30% (v/v) GMA-methanol solution. Monomer and homopolymer after grafting were removed with tetrahydrofuran using a Soxhlet apparatus, and GMA-grafted membrane obtained by the grafting copolymerization was dried in vacuum at 60°C for 4 h. The degree of grafting (%) was determined by

Degree of grafting (%) =
$$\frac{(W_g - W_0)}{W_0} \times 100$$
 (1)

where W_g and W_0 are the weights of the grafted and the ungrafted polyethylene hollow fiber, respectively.

Preparation of the Chelating and Cation-Exchange Hollow Fiber

The GMA-grafted hollow fiber was immersed in 0.425M iminodiacetic acid $(NH(CH_2COOH)_2)$ dissolved by dimethyl sulfoxide (DMSO)-water. The volume ratio of DMSO to water was 1. The reaction was performed at 80°C for 48 h, which was sufficient to reach the final conversion.¹¹ The modifid hollow fiber was washed repeatedly with

deionized water and was dried under reduced pressure. IDA group content was measured as follows.

IDA group content (mmol/g)

$$=\frac{(W_s - W_g)}{W_s} \times \frac{1000}{133} \quad (2)$$

where W_g is the weight of grafted hollow fiber, and W_s is the weight of the PE hollow fiber membrane modified with the IDA group, and the factor of 133 corresponds to the molecular weights of the IDA group.

The epoxy group of GMA-grafted polyethylene membrane was converted into the $-SO_3Na$ group by immersing GMA-grafted membrane in sulfonating reagents. After sulfonation, the membrane was converted into H form by treating with 1.0*M* HCl. The sulfonic acid content (mmol/g) was determined as follows.

Sulfonic acid group content (mmol/g)

$$=\frac{(W_s - W_g)}{W_s} \times \frac{1000}{81} \quad (3)$$

where W_s is the weight of the sulfonated PE hollow fiber membrane, and the factor of 81 corresponds to the molecular weights of the $-SO_3H$ group. The $-SO_3H$ group content was also determined from the measurement of total ion exchange capacity by titration. The H-form membrane was immersed in 5% NaCl aqueous solution at a room temperature for 12 h, and then the hydrogen ion liberated from the membrane was titrated with 0.02M NaOH aqueous solution.

Breakthrough Curve

Scheme 2 shows the experimental apparatus for measuring flux and breakthrough curves. The inner and outer diameter and the length of hollow fiber membrane were measured in the wet state with a microscope, respectively. After the hollow fiber was dried under reduced pressures, the pore volume distribution was measured by mercury intrusion method. The flux, u_i , was determined by

$$u_i = (\text{volumetric flow rate}) / \pi D_i L$$
 (4)

where D_i is the inner diameter, and L is the length of the hollow fiber. The volumetric flow



rate of pure water was measured from the amount dropped from the outside of the membrane. The collection of Co^{2+} and Cs^{1+} during permeation of the solution across the membrane was carried out in measuring cylinder under a constant pressure of 1.0×10^5 Pa. The concentration of Co^{2+} ion permeation was determined by inductively coupled plasma atomic emission spectroscopy (ICP), while the concentration of Cs^{1+} was determined by ICP–mass spectroscopy (MS). Subsequently, the concentrations of Na^{1+} and Ca^{2+} were determined by an atomic absorption spectrophotometer (AA, model ANALAB-9100A). The concentration of permeation was determined as follows

$$C/C^0 \tag{5}$$

where C^0 is the initial concentration of Co^{2+} and Cs^{1+} ion, respectively, before permeation across PE hollow fiber membrane. *C* is the final concentration of Co^{2+} and Cs^{1+} ion after permeation across membrane. C^0 and *C* were determined by ICP and ICP-MS in this study, respectively. The permeation volume (*PV*) was determined by

$$PV = \pi D_i L u_i t \tag{6}$$

where t is the time of permeation.

RESULTS AND DISCUSSION

Properties of the Chelating Hollow Fiber

The properties of the chelating fiber membrane are shown in Table I. The IDA group density of the chelating fiber amounted to 1.29 mmol/g.

Property	Chelating Hollow Fiber	Starting Hollow Fiber
Degree of grafting (%)	100	_
IDA group density (mmol/g)	1.29	
Inner diameter (mm)	2.58	1.95
Outer diameter (nm)	4.83	3.01
Length (cm)	10	10
Porosity	60	71
Flux of pure water (m/h) ^a	0.3324	3.117
Pore volume $(cm/g)^{b}$	1.49	2.61

Table I	Properties	of Che	lating	Fiber
Membra	nes Modifie	d with	IDA G	roup

 $^{\mathrm{a}}$ 1.0 \times 10⁵ Pa.

^b By a mercury intrusion method.

Preparation and Properties of the Cation-Exchange Fiber Membrane

The solubility of sulfonating reagents in water was determined at 70°C in water, respectively. The solubility of NaHSO₃, Na₂SO₃, and Na₂S₂O₅ in water were about 5.0, 2.0, and 2.3 mol per liter (M), respectively.

The sulfonation reaction on 80% GMA-grafted hollow fiber was carried out with 2.0M sulfonating reagents at 80° C as a function of the reaction time (Fig. 1). The conversion yield of epoxy group



Figure 1 Sulfonation of 80% GMA-grafted PE hollow fiber with 2.0*M* sulfonating reagents at 80°C.



Figure 2 Sulfonation of 80% GMA-grafted PE hollow fiber with sulfonating reagents for 48 h; total concentration = 2.0M.

in GMA-grafted hollow fiber into sulfonic acid group was higher in Na₂SO₃ than in NaHSO₃ and Na₂S₂O₅ solution. 100% GMA-grafted hollow fiber reached a conversion yield of 1.49 mmol/g after 24 h by treating with Na₂SO₃. On the other hand, Na₂S₂O₅ induced a conversion yield of 1.0 mmol/g after reaction for 24 h. The low conversion of 0.35 mmol/g was obtained from NaHSO₃ solution. The content of sulfonation by sulfonating reagents was the following order: sodium sulfite (Na₂SO₃) > sodium metasulfite (Na₂S₂O₅) > sodium bisulfite (NaHSO₃).

In order to increase —SO₃H grup content, the mixed sulfonating reagents were used. The relationship between —SO₃H content and the compositions of NaHSO₃–Na₂SO₃ and NaHSO₃–Na₂SQ₅ is shown in Figure 2. The total concentration of NaHSO₃–Na₂SO₃ or NaHSO₃–Na₂SQ₅ was adjusted to 2.0*M*. In the case of NaHSO₃–Na₂SO₃ mixture, the increment in NaHSO₃ composition increased the sulfonation reaction up to 0.2 mmol of NaHSO₃ and then leveled off. On the other hand, the mixture reagents of NaHSO₃–Na₂SQ₅ did not show any synergistic effect.

The effect of reaction temperature on the sulfonation of 150% GMA-grafted PE hollow fiber using 2.0*M* NaHSO₃–Na₂SO₃ is shown in Figure 3. The sulfonation reaction of epoxy group was ended after 18 h at 80°C and after 72 h at 50°C. However, the sulfonation reaction was very slow



Figure 3 Sulfonation of 150% GMA-grafted PE hollow fiber with $NaHSO_3-Na_2SO_3$ (0.2/1.8, mmol/mmol) in water.

at 30°C and continued to proceed even after 100 h. GMA-grafted PE hollow fiber with different grafting yield was sulfonated with 2.0M NaHSO₃/Na₂SO₃ (Fig. 4). It was shown that the higher



Figure 4 Sulfonation of PE-g-GMA with Na₂SO₃-NaHSO₃ (0.2/1.8, mmol/mmol) at 80°C.

Table II	Comparison of -SO ₃ H Group by	
Weight Ga	ain, Titration, and EA Analysis	

No	Weight Gain (mmol/g)	Titration (mmol/g)	EA Analysis (mmol/g)
1	1.52	1.21	2.61
2	1.68	1.34	2.73
3	2.07	1.65	2.81
4	3.21	2.65	3.04
5	3.54	2.72	3.57

grafting yield exhibited the higher sulfonation.

The — SO_3H group content (mmol/g) determined with the weight gain, titration, and EA analysis was shown in Table II. — SO_3H group content (mmol/g) determined with the weight gain and EA analysis was higher than that of titration method. The reason why the titration method showed the low content of — SO_3H group can be attributable to the fact that the ion-exchange reaction by titration method may not be complete.

Adsorption of Co²⁺ and Cs¹⁺ Ion for the Chelating and Cation-Exchange Fiber Membranes

The breakthrough curves of Co^{2+} for the chelating fiber membrane as the function of the inlet concentration are shown in Figure 5. The inlet concentrations of Co^{2+} were 20, 50, and 100 mg per liter (ppm), respectively. In case of 20-ppm inlet concentration, C/C^0 remained zero until permeation volume (PV) value reached 0.48 L. After the point, C/C^0 rose gradually with increasing PV. A lower inlet concentration required a higher PV until $C/C^0 = 1$. At $C/C^0 = 1$, the amount of Co^{2+} adsorbed by the chelating fiber membrane with IDA functionality can be calculated from the area of PV times C, which is the upper portion above the breakthrough curves. The adsorbed amount of Co^{2+} was almost the same 20 g per kg for 20-, 50-, and 100-ppm inlet concentration. These results indicate that the amount of Co^{2+} adsorbed by IDA-chelating membrane is constant regardless of the inlet concentration.

The breakthrough curves of Co^{2+} for the IDAchelating fiber membrane as the function of the inlet pressure. The amount of Co^{2+} adsorbed by IDA-chelating membrane under 1.0×10^5 and 0.5×10^5 Pa were almost the same 20 g per kg. These results also indicate that the amount of Co^{2+} adsorbed by IDA-chelating membrane is constant



Figure 5 Breakthough curves of Co^{2+} ion to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.

regardless of the inlet preassure, as illustrated in Figure 6.

The desorption characteristic curves of Co²⁺ for IDA-chelating fiber membrane as a function of



Figure 6 Breakthough curves of Co^{2+} ion (20 ppm) to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.



Figure 7 Desorption characteristics of Co^{2+} ion to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.

the HCl concentration are shown in Figure 7. Co^{2+} desorbed from the chelating fiber membrane was calculated from the area of elimination curves. IDA-chelating fiber membrane was calculated from the area of elimination curves. IDA-chelating membrane having 1.29 mmol/g showed different elution curves according to HCl concentration. However, the amount of Co^{2+} desorbed from the chelating was approximately 20 g per kg equally, respectively. The final desorption quantity of Co^{2+} was the same regardless of 1.0*M* or 0.5*M* HCl. However, it was possible to desorb Co^{2+} in shorter time with 1.0*M* HCl compared to 0.5*M* HCl.

The breakthrough curves of readsorption for IDA-chelating fiber membrane, which was washed with HCl, are shown in Figure 8. The shape of the breakthrough curves for the regenerated membrane was the same with that of the original membrane. From the results, it was shown that the chelating fiber modified with IDA had a good regeneration property.

The adsorption curves of Co^{2+} by IDA-chelating fiber membrane in the presence or in the absence of Na¹⁺ and Ca²⁺ are shown in Figure 9. Co²⁺ concentration in the inlet solution was 50 ppm, with including 500-ppm Na¹⁺ and 500-ppm Ca²⁺ in the inlet solution. In case of inlet solution having only Co²⁺, C/C^0 remained zero up to PVvalue of 0.18 L. After the point, C/C^0 rose gradually with increasing PV. The adsorbed amounts of



Figure 8 Readsorption characteristics of Co^{2+} (20 ppm) to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.

 Co^{2+} by the chelating membrane in the absence of Na^{1+} and Ca^{2+} were approximately 20 g per kg, while the absorbed Co^{2+} in the presence of Na^{1+} and Ca^{2+} was approximately 17.0 g per kg. It was found that the chelating hollow fiber containing



Figure 9 Breakthough curves of Co^{2+} to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.



Figure 10 Breakthough curves of Co^{2+} and Cs^{1+} ion (20 ppm) to the PE hollow fiber membrane (dg = 100%) having an IDA group of 1.29 mmol/g.

IDA group was a very high selectivity for Co^{2+} , even though there is a high concentration of Na^{1+} and Ca^{2+} in the inlet solution. According to the analysis of Na^{1+} and Ca^{2+} by atomic adsorption spectrometer, it was found that only a extremely small quantity of Ca^{2+} was adsorbed by IDAchelating fiber membrane, while Na^{1+} was not almost adsorbed by IDA-chelating fiber membrane.

The breakthrough curves of Co^{2+} and Cs^{1+} by chelating fiber membrane modified with IDA group are shown in Figure 10. The inlet concentrations of Co^{2+} and Cs^{1+} were the same 20 ppm, respectively. C/C^0 remained zero until PV value reached 0.45 L in Co^{2+} and 0.07 L in Cs^{1+} , respectively. The adsorbed amounts of Co^{2+} and Cs^{1+} were approximately 20 and 2.34 g per kg, respectively. The chelating hollow fiber containing IDA group was found to have a higher adsorption capacity for Co^{2+} than Cs^{1+} .

The breakthrough curves of Co^{2+} and Cs^{1+} by the cation-exchange fiber membrane with —SO₃H of 4.87 mmol/g are shown in Figure 11. Inlet concentrations of Co^{2+} and Cs^{1+} were the same, 50 ppm, respectively. C/C^0 remained zero until PVvalue reached 0.34 liter in Co^{2+} , and 0.18 liter in Cs^{1+} . The adsorbed amounts of Co^{2+} and Cs^{1+} were approximately 28.3 and 15.0 g per kg, respectively. The cation-exchange fiber membrane containing —SO₃H group was also found to have a higher adsorption capacity for Co^{2+} than Cs^{1+} .



Figure 11 Breakthough curves of Co^{2+} and Cs^{1+} ion (50 ppm) to the PE hollow fiber membrane (dg = 150%) having a —SO₃H group of 4.87 mmol/g.

CONCLUSION

Two hollow fiber membranes, the chelating fiber with iminodiacetic acid group (IDA) and the cation-exchange fiber with sulfonic acid group (—SO₃H), were prepared by radiation-induced grafting of GMA onto a PE hollow fiber membrane and its subsequent iminodiacetation and sulfonation. The solutions of cobalt (Co²⁺) and cesium (Cs¹⁺) were forced to permeate across the chelating and the cation-exchange fiber membranes, respectively. Without regard to the chelating membrane with IDA group functionality and the cation-exchange membranes were observed to adsorb Co²⁺ higher than Cs¹⁺. The adsorption curves of Co²⁺ by the IDA group-chelating fiber membrane in the presence of Na¹⁺ and Ca²⁺ showed that the chelating hollow fiber containing IDA group was found to have a very high selectivity for Co²⁺, even though there is a high concentration of Na¹⁺ and Ca²⁺ in the inlet solution. According to the analysis of Na¹⁺ and Ca²⁺ by atomic adsorption spectrometer, it was found that only a extremely small quantity of Ca²⁺ was adsorbed by IDA group-chelating fiber membrane, while Na¹⁺ was not almost adsorbed by IDA group-chelating fiber membrane.

REFERENCES

- Hori, T.; Saito, K.; Frusaki, S.; Sugo, T.; Okamoto, J. Chem Soc Jpn 1986, 12, 1792.
- Kim, M.; Saito, K.; Frusaki, S.; Sato, T.; Sugo, T.; Ishigaki, I. J Chromatogr 1996, 586, 27.
- Yamagishi, H.; Saito, K.; Frusaki, S. Ind Eng Chem Res 1991, 30, 2234.
- 4. Andrade, J. D. Med Ist 1973, 7, 110.
- 5. Sugo, T.; Saito, K. Membrane 1992, 17, 58.
- Kim, M.; Saito, K.; Furusaki, S.; Sugo, T.; Okamoto, J. J Membr Sci 1991, 56, 289.
- Okamoto, J.; Sugo, T.; Katakai, A.; Omichi, H. J Appl Polym Sci 1985, 30, 2967.
- Nho, Y. C.; Park, J. S.; Jin, J. H. J Macromol Sci, Pure Appl Chem 1997, A34, 831.
- 9. Kaji, A. J Appl Polym Sci 1983, 28, 3767.
- Gupta, B. D.; Chapiro, A. Eur Polym J 1987, 24, 1137.
- Turmanova, S.; Dimitrova, A.; Kostov, G. Macromol Chem Phys 1996, 197, 2973.
- 12. Godjevargova, T. J Appl Polym Sci 1996, 61, 343.
- Omichi, H.; Katakai, A.; Okamoto, J. J Appl Polym Sci 1989, 37, 2429.
- Nho, Y. C.; Garnett, J. L.; Dworjanyn, P. A. J Polym Sci, Polym Chem Ed 1991, 31, 1621.
- Seguchi, T.; Tamura, N. J Polym Sci, Polym Chem Ed 1974, 12, 1671.
- Shinano, H.; Tsuneda, S.; Saito, K.; Frusaki, S.; Sugo, T. Biotechnol Prog 1993, 9, 193.
- 17. Choi, S. H.; Kim, G. T.; Nho, Y. C. J Appl Polym Sci in press.
- 18. Choi, S. H.; Nho, Y. C. J Appl Polym Sci in press.