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ADSORPTION OF UO_2^{2+} BY POLYETHYLENE HOLLOW FIBER MEMBRANE WITH AMIDOXIME GROUP

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Key Words: Polyethylene Membrane, Radiation-Induced Grafting, Acrylonitrile, Amidoxime Group, Adsorption Characteristics

ABSTRACT

The polyethylene (PE) membrane was prepared by the radiation-induced grafting of acrylonitrile (AN) onto PE hollow fiber and by the subsequent amidoximation of cyano groups in poly-AN graft chains. The adsorption characteristics of the chelating hollow fiber membrane was examined as the solution of UO_2^{2+} permeated across the chelating hollow fiber membrane. The inner and outer diameter increased with an increasing grafting yield, whereas, the pure water flux and pore diameter decreased with an increasing grafting yield. The adsorption of UO_2^{2+} by the chelating hollow fiber membranes increased with an increasing amidoxime group. The adsorbed amount of UO_2^{2+} in the uranyl acetate solution was higher than that in the uranyl nitrate solution. The adsorbed amount of UO_2^{2+} is higher than that of Cu^{2+} when the solution of UO_2^{2+} and Cu^{2+} permeated across the chelating membrane, respectively. The adsorption characteristics of UO_2^{2+} by the amidoxime group-chelating fiber membrane in the presence of Na^{1+} and Ca^{2+} showed a high selectivity for UO_2^{2+} even though there was a high concen-tration of Na^{1+} and Ca^{2+} in the inlet solution.

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INTRODUCTION

Uranium recovery from seawater is important for the security of a future energy supply. The main difficulty in the recovery process arises from the low concentration (~3 ppb) of the uranyl ion in seawater, whereas other metal ions are abundantly present. Thus, development of selective adsorbents with a high adsorption rate and a large adsorption capacity is essential for the economic recovery of the uranyl ion. The polymeric adsorbents containing the amidoxime group are mostly promising, but information on their adsorption characterization in the presence of other abundantly metal ions such as sodium, calcium, etc. is still insufficient [1-6].

A hollow fiber membrane has the advantage of a higher ratio of surface area to volume compared with a flat sheet membrane. A polymer with a functional group can not be easily molded into a porous hollow fiber membrane. Therefore, the chemical modification of existing hollow fibers is effective in adding new properties to collect protein [7] and metal ions [8-10].

In our previous studies [11], the graft copolymerization of acrylonitrile (AN), and mixtures of acrylic acid (AA) and acrylonitrile (AN) onto polypropylene film was carried out. We found that the extent of grafting was found to increase with an increasing radiation dose, reaction temperature, and composition of AA. We also reported on the graft copolymerization of AN/AA, methacrylic acid (MA)/AN, and glycidyl methacrylate (GMA)/AN onto pre-irradiated polyethylene film. In these cases, we found that the extent of grafting increased with an increasing AA and GMA component as hydrophilic monomers [12].

In this paper, the polyethylene (PE) membrane was prepared by the radiation-induced grafting of acrylonitrile onto PE hollow fiber and by the subsequent amidoximation of cyano groups of poly-AN graft chains. The adsorption characteristics of the uranyl ion (UO_2^{2+}) in the presence of other metals such as sodium and calcium ions by the PE membrane were examined.

EXPERIMENTAL

Materials

A commercially available microfiltration hollow fiber membrane (Ashahi Chemical Industry Co., Ltd.) was used as a trunk polymer for the grafting. The inner and outer diameters of the porous PE hollow fiber were 1.95 and

3.01 mm, respectively. The PE hollow fiber has a 0.34 μm pore diameter and 71% porosity. Acrylonitrile (AN, Junsei, Japan) was used without further purification. Uranyl acetate and uranyl nitrate were purchased from Merk (Germany).

Grafting Procedure

Scheme 1 shows the preparation procedure of the radiation grafting of AN onto PE hollow fiber. The PE hollow fiber was used as the base polymer for grafting polymerization. The PE hollow fiber was irradiated by γ-ray from Co-60 under atmospheric pressure and ambient temperatures, and then the irradiated PE hollow fiber was immediately grafted with monomer. In a previous paper [11], we described the grafting conditions such as pre-irradiation dose, reaction temperature, monomer concentration, additives *etc.*, on the individual grafting of acrylonitrile onto polyethylene film. In these experiments, 25%, 50%, 85%, and 100% AN-grafted PE hollow fiber membranes were obtained with an 15. 0 M monomer concentration in the presence of 0.2 M sulfuric acid and 2.5 × 10-3 M ferrous sulfate in MeOH by changing the reaction time. The unreacted monomer and homopolymers were removed with N,N-dimethylformamide after grafting using a Soxhlet apparatus, and the AN-grafted PE hollow fiber obtained by grafting copolymerization was dried in a vacuum oven at 50°C for 12 hours. For the studies of the effects of various parameters on the grafting copolym-erization, the degree of grafting was defined by the following equation:

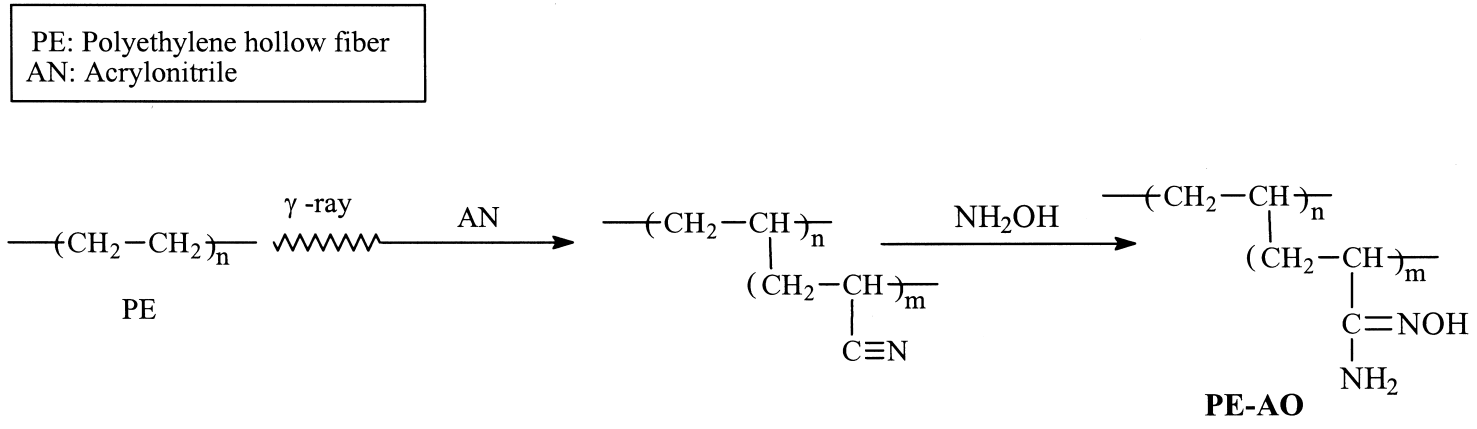
$$\text{Degree of grafting (\%)} = [(Wg - Wo) / Wo] \times 100 \quad (1)$$

where Wg and Wo denote the weights of the grafted and the ungrafted PE hollow fiber.

Amidoximation Procedure

The resultant cyano group was converted into an amidoxime (-CNH_2(=NOH)) group by immersing the AN-grafted PE hollow fiber in 6.5% (vol%) hydroxylamine (NH_2OH) solutions of H_2O and MeOH/H_2O [(1/1, vol%)] at 80°C for 3, 7, 10, 12, and 24 hours. Subsequently, the PE hollow fiber membrane was repeatedly washed with water. The amidoxime group (AO) content was determined by:

$$\text{AO content (mmol/g)} = [(Ws - Wg) / Ws] \times (1000 / 33) \quad (2)$$



Scheme 1. Preparation of Chelating Hollow Fiber Membrane (PE-AO).

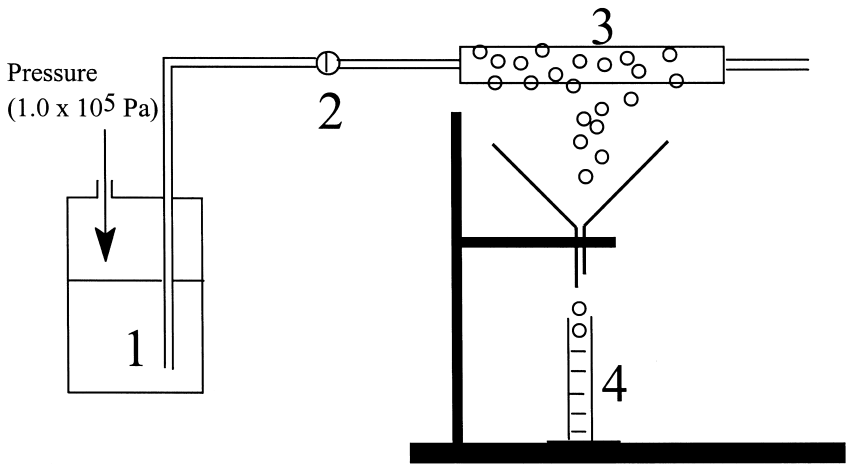
where Ws is the weight of the amidoximated PE hollow fiber, and the factor of 33 corresponds to the molecular weights of hydroxylamine.

Breakthrough Curves

Scheme 2 shows the experimental apparatus for measuring pure water flux and breakthrough curves. The inner and outer diameters and lengths of the PE hollow fiber were measured in the wet state with a microscope. After the PE hollow fiber was dried in a vacuum, the pore volume distribution was measured by mercury intrusion method. The flux, U_i, was determined by:

$$U_i = (\text{volumetric flow rate})/\pi D_i L \quad (3)$$

where D_i is the inner diameter, and L is the length of the PE hollow fiber (10 cm). The volume flow rate of the pure water was measured from the amount of dropping from the outside of the PE hollow fiber. The pressure inside the feed tank, shown in Scheme 2, was 1.0×10^5 Pa. The concentrations of UO_2^{2+} obtained during permeation were determined by inductively coupled plasma atomic emission spectroscopy (ICP). The concentration of Na^{1+} and Ca^{2+} were determined by an atomic absorption spectrometer (AA, model ANALAB-



1 Feed Tank 2 Flow Controller
3 PE Hollow Fiber Membrane 4 Measuring Cylinder

Scheme 2. Experimental Apparatus for Determining Flux and Breakthrough Curves.

9100A). The extent of adsorption was determined by a ratio of C to C^o, where C^o is the initial concentration of UO_2^{2+} before the permeation across the PE hollow fiber and C is its final concentration after the permeation. The per-meation volume (PV) was determined by:

$$PV = \pi D_i L U_i t \quad (4)$$

where t is the time of permeation.

RESULTS AND DISCUSSION

Preparation and Properties of PE Membrane with the Amidoxime Group

Figure 1 shows the diameter and pure water flux of the PE and AN-grafted PE hollow fiber. The inner and outer diameter increased due to the grafting, whereas the pure water flux decreased. This decrease in water flux is due to the growth of graft chains inside the polymer matrix pore.

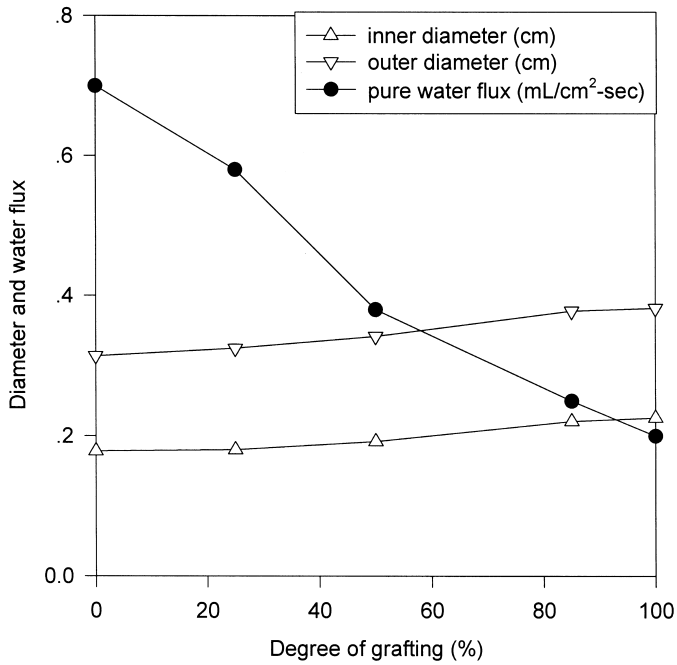


Figure 1. Diameter and Pure Water Flux of PE and AN-Grafted PE Hollow Fiber.

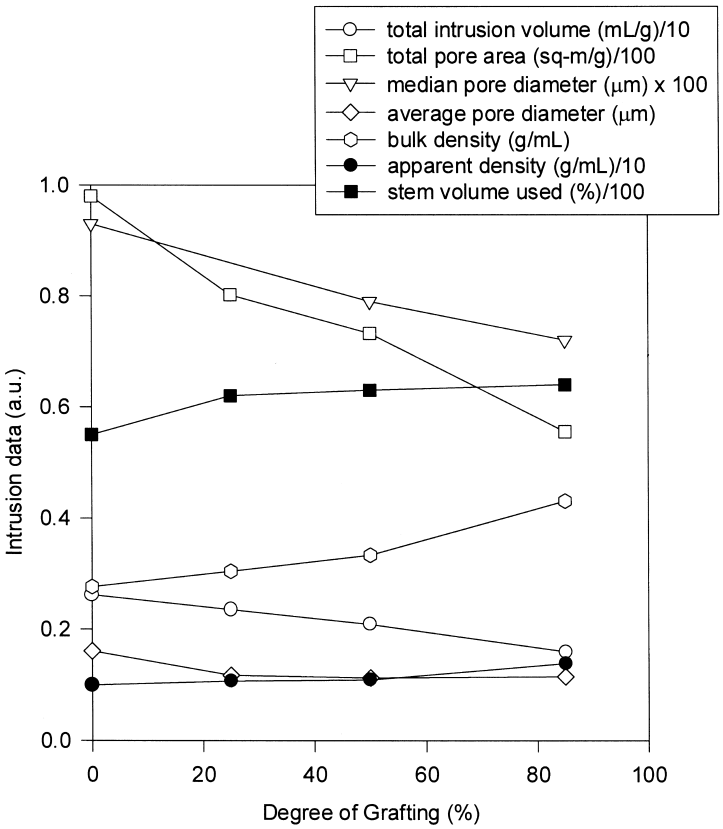


Figure 2. Intrustion Data of PE and AN-Grafted Hollow Fiber Membrane by Porosimeter.

Figure 2 shows the intrusion data of mercury to PE and AN-grafted PE hollow fiber membranes by porosimeter. The total pore area, median pore diameter, total intrusion, and average pore diameter decreased with an increasing grafting yield, whereas apparent density and steam volume increased with an increasing grafting yield. These results clearly indicate that the growth of graft chains occurs in the polymer matrix pore.

Figure 3 shows the relationship between the pore volume distribution and the grafting yield. The pore volume on a region ranging from 1 to 10^{-1} μm pore diameter was found to be large. The pore volume decreased with an increasing grafting yield. The pore volume of 2.6 L/kg of the PE hollow fiber was reduced to 2.3 L/kg with a 25% grafting yield, to 2.0 L/kg with a 50% and to 1.5L/kg with 85% grafting yield. The pore volume was approximately linearly proportional to the degree of grafting up to 85%.

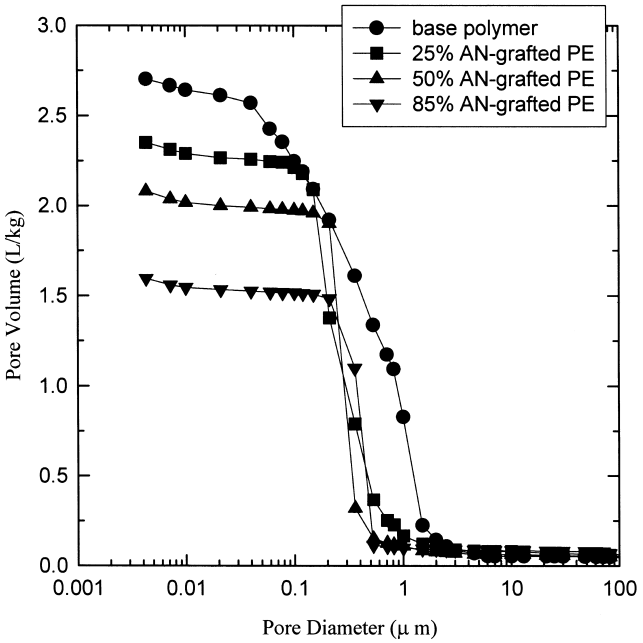


Figure 3. Pore Volume Distribution of PE and AN-Grafted PE Hollow Fiber Membranes.

Figure 4 shows the surface morphology of a base PE hollow fiber (a) and an 85% AN-grafted PE membrane (b). The pore size decreased with an increasing grafting yield. This decrease is attributable to the growth of graft chains inside the pore.

Figure 5 shows the effect of reaction time on the content of the amidoxime group. The amidoxime content increased until 7 hours, and then leveled off. The amidoxime content was higher in MeOH/H_2O (1/1, vol%) solution than H2O solution. It is assumed that this increase in MeOH/H2O may be attributable to the wettability onto its graft poly-AN.

Adsorption of UO_2^{2+} By PE Membrane with Amidoxime Group

Figure 6 shows the breakthrough curves of UO_2^{2+} (uranium nitrate) for the chelating hollow fiber membrane as the function of the amidoxime content. The inlet concentration of UO_2^{2+} was 30 ppm. In the case of amidoxime group of 3.57 mmol/g, C/C° remained zero until permeation volume value reached 0.18 liter. C/C° rose gradually with increasing permeation volume. A higher amidoxime group content required a higher permeation volume until $C/C^o = 1$.

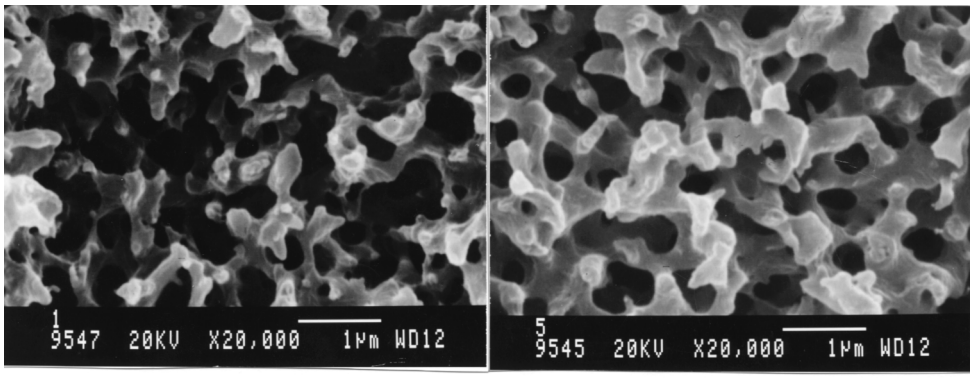


Figure 4. Surface Morphology of a Base PE Membrane and a 85% AN-Grafted PE Membrane: (a) Base PE Membrane, (b) 85% AN-Grafted PE Membrane.

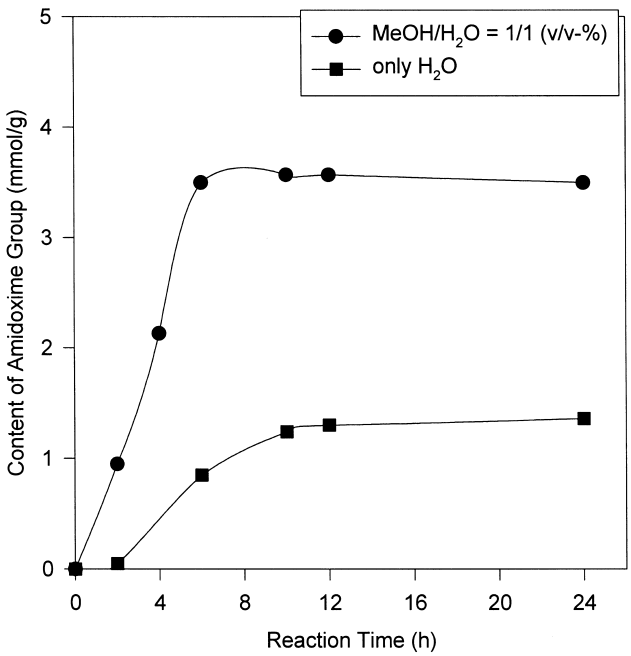


Figure 5. Extent of Amidoximation of AN-Grafted PE Hollow Fiber with 6.5% Hydroxyl Amine (vol%) at 80°C.

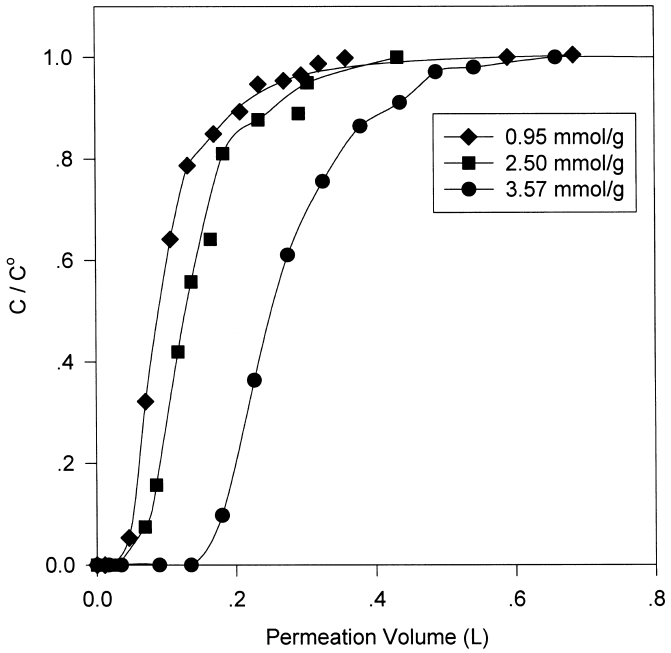


Figure 6. Breakthrough curves of UO_2^{2+} (Uranyl Nitrate) Ion to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Modified with Different Contents of Amidoxime Groups.

At C/C° =1, the amount of UO_2^{2+} adsorbed by the PE hollow fiber membrane with amidoxime group can be calculated from the area PV time C which is the upper portion above the breakthrough curves. The adsorbed amount of UO_2^{2+} was 12.6, 25.3, and 42.2 g per kg for amidoxime groups of 0.95, 2.50, and 3.57 mmol/g, respectively. A higher amidoxime group density resulted in higher amounts of adsorption.

Figure 7 shows the breakthrough curves of UO_2^{2+} for the PE hollow fiber membrane containing the amidoxime group of 0.95 mmol/g as a function of inlet uranyl salts. Uranyl salts from two different uranyl sources (such as uranyl nitrate and uranyl acetate) were selected to investigate the effects of counter ions of uranyl ions on the adsorption of uranyl ions by the amidoxime group. The adsorption of uranyl ion in the uranyl acetate solution is higher than that in the uranyl nitrate solution. pH of 30 ppm uranyl acetate solution and 30 ppm uranyl

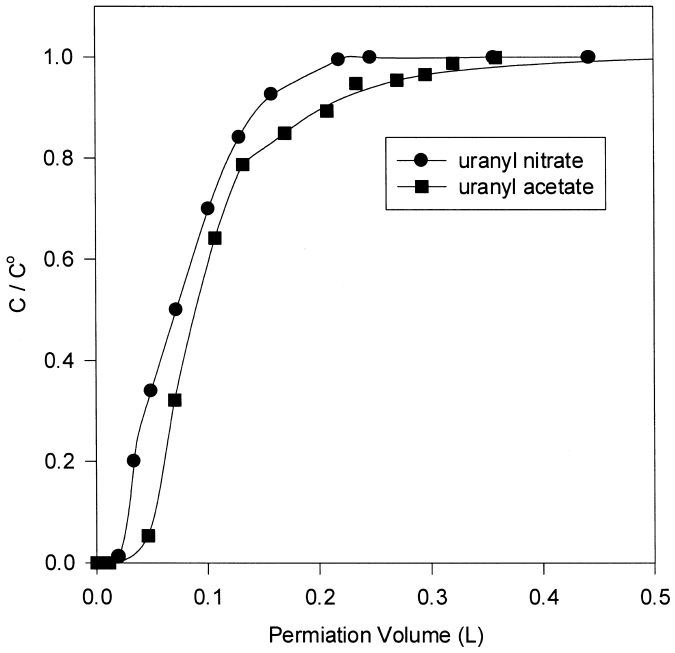


Figure 7. Breathrough Curves of UO_2^{2+} Ion to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Containing 0.95 mmol/g of Amidoxime Group.

nitrate solution was determined to be about 5.5 an 4.4, respectively. As the chelating hollow fiber memrane having amidoxime group adsorbs much more UO_2^{2+} in neutral solution than in acidic solution, the adsorption of UO_2^{2+} was larger in uranyl acetate solution than in the uranyl nitrate solution.

Figure 8 shows the breakthrough curves of UO_2^{2+} and Cu^{2+} by the PE hollow fiber membrane modified with the amidoxime group. The inlet concentration of UO_2^{2+} and Cu^{2+} were the same, 30 ppm, respectively. C/C^o remained zero until the PV value reached 0.18 liters in UO_2^{2+}. The PE hollow fiber membrane containing the amidoxime group was found to have a higher adsorption capacity for UO_2^{2+} than Cu^{2+}.

Figure 9 shows the adsorption curves of UO_2^{2+} by the PE hollow fiber membrane in the presence or in the absence of Na^{1+} and Ca^{2+}. UO_2^{2+} concentration in the inlet solution was 30 ppm, with including 300 ppm Na^{1+} and 300 ppm Ca^{2+} in the inlet solution. In the case of the inlet solution having only UO_2^{2+}, C/C^o remained zero up to a PV value of 0.18 liter. After that point, C/C^o rose

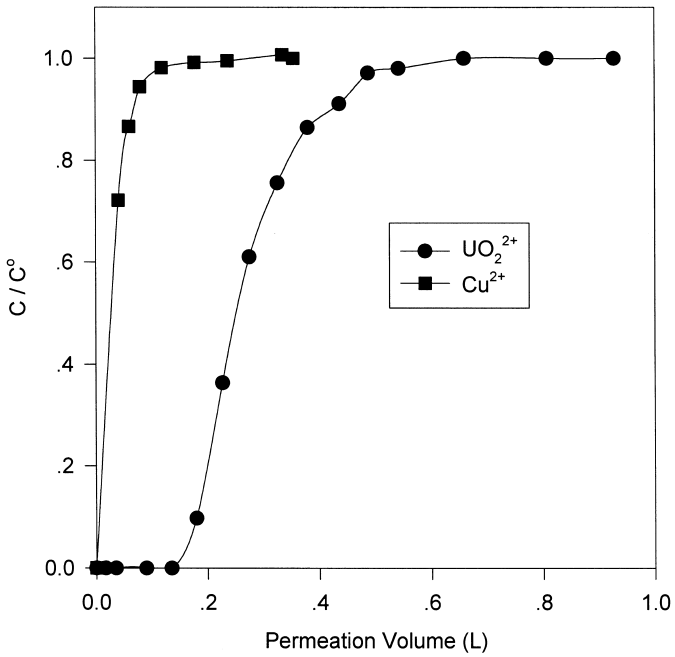


Figure 8. Breakthrough Curves of UO_2^{2+} (Uranyl Nitrate) and Cu^{2+} Ions to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Containing 3.57 mmol/g of Amidoxime Group.

gradually with an increasing PV. The adsorbed amounts of UO_2^{2+} by the PE-AO in the absence of Na^{1+} and Ca^{2+} was *ca.* 42.2 g per kg. The adsorbed amounts of UO_2^{2+} in the presence of Na^{1+} or Ca^{2+}, and both Na^{1+} and Ca^{2+} were *ca.* 43.6, 43.8, and 45.8 g per kg, respectively. It was found that the PE hollow fiber membrane containing the AO group has a strong selectivity for UO_2^{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 an atomic adsorption spectrometer, it was found that Na^{1+} and Ca^{2+} were not absorbed by the PE membrane modified with the AO group.

Figure 10 shows the desorption curves of UO_2^{2+} for the PE-AO as a function of the HCl concentration. UO_2^{2+} desorbed from the PE-AO was calculated from the area of elimination curves. PE-AO having an amidoxime group of 3.57 mmol/g showed different elution curves according to HCl concentration. However, the amount of UO_2^{2+} desorbed from the PE-AO was *ca.* 42 g per kg equally, respectively. The final quantity of UO_2^{2+} desorption was the same

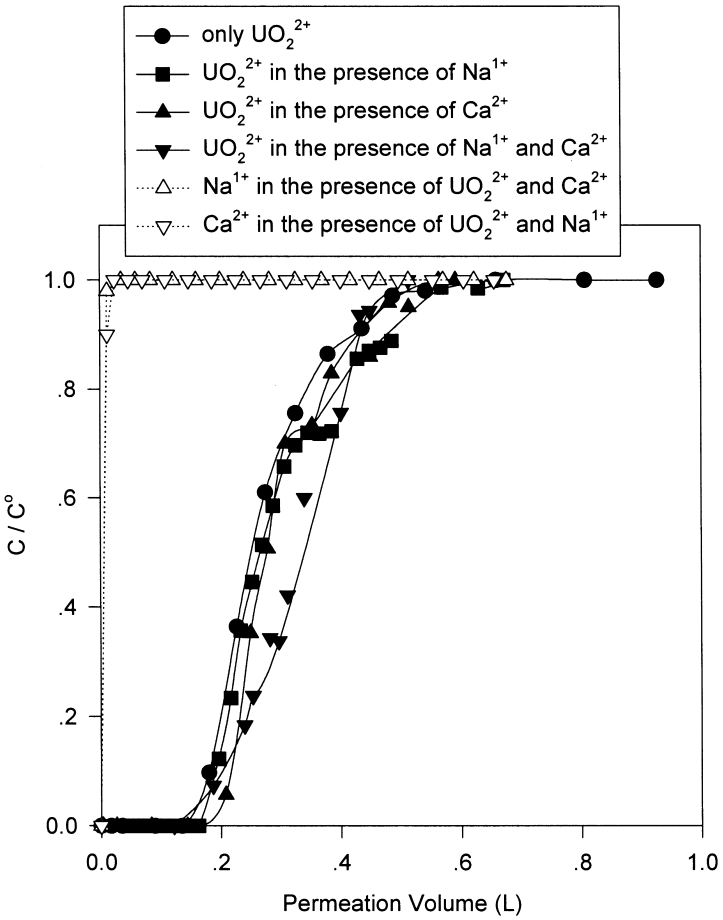


Figure 9. Breakthrough Curves of UO_2^{2+} (Uranyl Nitrate) Ion to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Containing 3.57 mmol/g of Amidoxime Group.

regardless of HCl concentration. However, it was possible to desorb UO_2^{2+} in shorter time with 1.0M HCl, compared with 0.5M HCl.

Figure 11 shows the breakthrough curves of readsorption for the PE-AO membrane which was washed with HCl. The shape of the breakthrough curves for the regenerated membrane was the same as that of the original membrane. From the results, it was shown that the chelating fiber modified with the amidoxime group showed a good regeneration property.

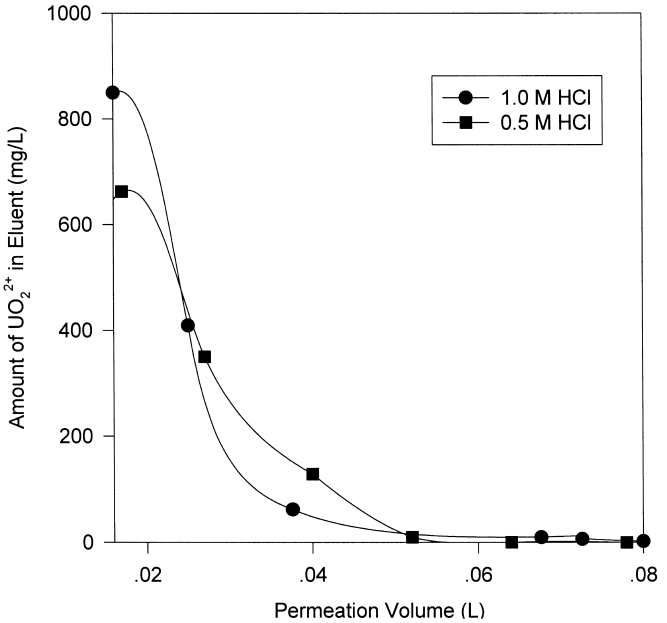


Figure 10. Desorption Characteristics of UO_2^{2+} (Uranyl Nitrate) Ion to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Containing 3.57 mmol/g of Amidoxime Group.

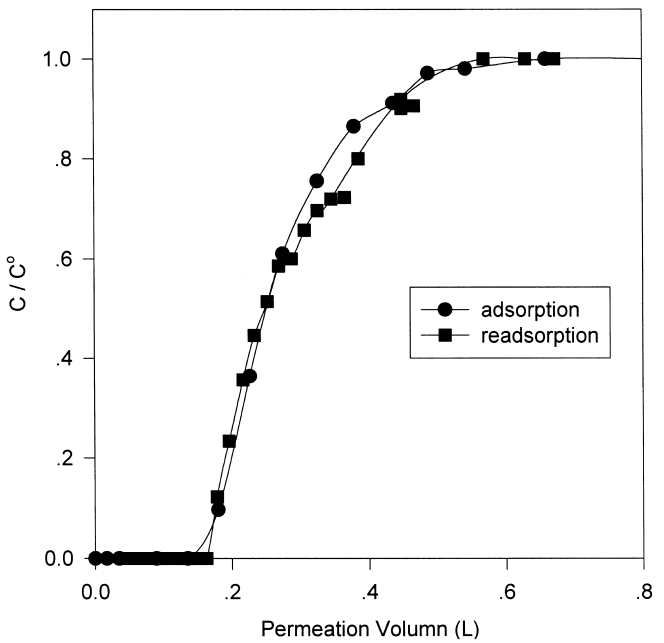


Figure 11. Breakthrough Curves of UO_2^{2+} (Uranyl Nitrate) Ion to AN-Grafted PE Hollow Fiber Membrane (d.g. = 85%) Containing 3.57 mmol/g of Amidoxime Group.

CONCLUSION

The polyethylene (PE) membranes were prepared by the radiation-induced grafting of acrylonitrile (AN) onto PE hollow fiber and by its subsequently amidoximation. The adsorption characteristics of the uranyl ion (UO_2^{2+}) were discussed.

The inner and outer diameter increased with an increasing grafting yield, whereas the pure water flux and pore diameter decreased with an increasing grafting yield.

The adsorption of UO_2^{2+} by the chelating hollow fiber membranes increased with an increasing amidoxime group.

The adsorbed amount of UO_2^{2+} in uranyl acetate solution was higher than that in the uranyl nitrite solution.

The adsorbed amount of UO_2^{2+} was higher than that of Cu^{2+} when the solution of UO_2^{2+} and Cu^{2+} permeated across the chelating membrane, respectively.

The adsorption characteristics of UO_2^{2+} by the amidoxime group-chelating fiber membrane in the presence of Na^{1+} and Ca^{2+} showed a high selectivity for UO_2^{2+}, even through there was a high concentration of Na^{1+} and Ca^{2+} in the inlet solution.

The chelating fiber modified with the amidoxime group was found to have a good regeneration property from a experimental result of desorption and readsorption.

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