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PREPARATION AND CHARACTERIZATION OF POLYSULFONE AND POLYETHERSULFONE MEMBRANES FOR CALCIUM (Ca^{2+}) AND MAGNESIUM (Mg^{2+}) SEPARATION BY COMPLEXATION ULTRAFILTRATION

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ABSTRACT

Asymmetric ultrafiltration membranes were synthesized from locally available polysulfone and polyethersulfone polymers using aprotic solvents and organic additives by the phase inversion method. The membranes were characterized in terms of pure water permeability, separation behavior with respect to polyethylene glycols of various molecular weights and electrolytes. The suitability of using polyethyleneimine (PEI) for selective removal of calcium and magnesium salts by an ultrafiltration process was studied in terms of optimum polymer loading at reasonable permeate flux, irreversible adsorptive fouling of the macromolecular ligand on the polymer as functions of solution pH and ionic strength, and metal ion separation as a function of concentration and pressure. Direct electron microscopic observation of fresh, as well as fouled, membranes are presented.

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Key Words: Ultrafiltration; Polyethyleneglycol; Polyethyleneimine; Separation; Polysulfone; Polyethersulfone

INTRODUCTION

Membrane separation processes are of major interest for water treatment owing to, among others, the simplicity of plant operating systems and their moderate energy consumption. They find important industrial applications for waste water purification, water reuse, and recovery of valuable materials.[1] Membrane processes have been shown to be applicable to the treatment of metal ion containing effluents like wastes from electroplating industries.[1] Ultrafiltration membranes work as a molecular size barrier, the pore size of which is too large to retain metal ions except in the colloidal form. Conversely, formation of high molecular weight species by complexation with water soluble macromolecular ligands leads to metal retention by ultrafiltration.[2] Water soluble polymer complexes for use in complexation ultrafiltration process have a unique advantage over insoluble chelating resins as the latter involves reaction in heterogeneous phase and larger contact times. The complexation ultrafiltration process for heavy metal removal is extensively reviewed in the literature.[3] For efficient removal of metal ions complete removal of macromolecular complex during ultrafiltration, high selectivity to the metal ion, and stability of the metal ion complex are desirable. Many investigations on the preparation and performance of water soluble macromolecular complexes for specific use in ultrafiltration systems are carried out and reported.[4–14] Metal ion selectivity and enhancement of selectivity by synergistic effect in the presence of specific additives are also reported.[15] Among the complexing macromolecules, polyethyleneimine (PEI), a polymeric amine, has been used in several studies as a complexing agent, as well as a chelating derivative. PEI exhibits a high content of functional groups, good water solubility at very high concentrations, and chemical stability. In addition, the branched structure of PEI provides better chelating properties in comparison to other linear complexing agents. Most of the reported work on the complexation ultrafiltration process involves the use of 1 to 10 wt% of the macromolecular solutions with commercially procured ultrafiltration membranes of low molecular weight cut off. Preparation of low molecular weight cut off ultrafiltration membranes, as well as the problems of severe fouling and water flux reduction associated with the use of high concentration of macromolecular ligands are not adequately addressed. The aromatic polysulfone family of polymers are extensively used for preparing ultrafiltration membranes, due to their wide temperature, pH, and chlorine tolerance. Preparation of ultrafiltration membranes from cellulose acetate butyrate, cellulose propionate, and polyethersulfone, and their characterization are reported from this laboratory.[16–18] This paper reports on the preparation of polysulfone and polyethersulfone ultrafiltration membranes of high water permeation rate and low molecular weight cut off, their fouling characteristics with respect to polyethyleneimine under low polymer loadings and as a function of pH and ionic strength, and the separation performance for calcium and magnesium salts.

EXPERIMENTAL

Materials

Polysulfone ($M_n = 80{,}000$, $M_w = 109{,}000$) and polyethersulfone ($M_n = 94{,}000$, $M_w = 132{,}000$) polymers were obtained in powder form from M/s. Gharda Chemical Company, India. The inherent viscosity (η_{inh}) of the polymers in N-methyl pyrrolidone solvent and the equilibrium moisture uptake at ambient conditions (82% RH and 26°C) are given in Table 1. N-methyl pyrrolidone was used as the solvent, and polyethylene glycol (PEG 6000) was used as the pore forming agent for membrane preparation. Polyethyleneimine (BDH make) was procured as a 50% aqueous solution. The average molecular mass of polyethyleneimine was 50,000. The weight percentage of primary, secondary, and tertiary amino groups were found to be 12.4%, 11.6%, and 10.8%, respectively.

Preparation of Membranes

In an airtight glass bottle, a specified quantity of polymer was taken, and a known quantity of the solvent was added. The solution was kept agitated for several hours for complete dissolution. A calculated quantity of the additive was subsequently added, and the solution was homogenized and kept for deaeration. The solution viscosity was measured using a standard Brookfield Viscometer.

The dope solution thus obtained was spread over a smooth glass plate with the help of a knife edge. The thickness of the membranes was controlled by varying the thickness of side runner tapes. The glass plate was kept in an environment of controlled temperature and humidity during membrane casting. No deliberate solvent evaporation period was allowed. The glass plate was

Table 1. Inherent Viscosity and Moisture Uptake Data of Polymer Samples

Polymer	Inherent Viscosity (dL/g)	Moisture Uptake (%)
Polysulfone	1.30	1.98
Polyethersulfone	1.27	2.07

subsequently immersed in a gelation bath, which is generally demineralized water maintained at a known temperature. Immediately, phase inversion started and after a few minutes a thin polymeric film separated out from the glass. It was repeatedly washed with demineralized water and wet stored. The actual thickness of the membranes was measured using a micrometer.

Characterization of Membranes

Membranes were characterized in terms of transmembrane flux and solute separation of different systems in a tangential flow type test cell offering a membrane area of 15.4 cm^2. The feed water was pumped across a given membrane specimen at a flow rate of 3 Lpm using a reciprocating pump. The experimental setup is described elsewhere.[19] A permeate flux was calculated by using the average of three readings taken at regular intervals by noting the time taken to collect 10 mL of permeate in each condition. Three sets of membrane samples were made for each casting condition specified in this paper, and the average flux and solute separation data are reported. An analytical method for the determination of polyethyleneglycols was given previously.[16] Surface structure morphology was obtained by scanning electron microscopy with coating the membrane with 40% gold and 60% palladium of the order of 60 nm.

RESULTS AND DISCUSSION

Effect of Casting Parameters on Membrane Performance

Three UF membrane samples, designated as PES, PES-1, and PES-2, were prepared from the polyethersulfone polymer, and three UF membrane samples, designated as PS, PS-1, and PS-2, were prepared from the polysulfone polymer. The composition of the casting solutions, solution viscosity, membrane coagulation time, final membrane thickness, and pure water permeability data measured at 340 kPa, are given in Table 2. UF membrane samples from both the polymer samples are prepared using the same solvent and additive under identical composition for the sake of comparison in their performances. The polyethersulfone polymer was found to dissolve faster in the chosen solvent, giving a slightly lower viscosity casting solution; whereas the polysulfone polymer was found to dissolve slowly, giving a slightly higher viscosity casting solution. Polyethersulfone UF membranes give lower pure water permeability as compared to polysulfone UF membranes under identical casting conditions. Pure water permeability data increases with an increase in the composition of the additive in both the polymer systems, although the extent of the increase in pure water permeability is significantly

Table 2. Casting Solution Composition

Membrane	Polymer (g)	Solvent (g)	Additive (g)	Viscosity (Centipoise)	Thickness (μm)	Coagulation Time (s)	Pure Water Permeability (L m^{-2} h^{-1})[a]
PES	1.5	8	Nil	13142	110	14	10
PES 1	1.5	8	0.45	14705	118	12	33
PES 2	1.5	8	0.75	16247	122	11	173
PS	1.5	8	Nil	15678	117	11	180
PS 1	1.5	8	0.45	16543	108	9	240
PS 2	1.5	8	0.75	17983	125	7	440

Humidity-41%, temperature 26°C,
[a] Measured at 340 kPa.

higher in the case of polyethersulfone. The coagulation time data reflects the time required for the membrane to become a completely opaque film subsequent to immersion in the gelling bath. The time was measured for a membrane specimen size of 10 cm × 10 cm × 150 μm. The higher solubility of polyethersulfone in the solvent is reflected in the lower viscosity, as well as in the slightly higher coagulation time in the case of polysulfone membranes. From the six UF membranes prepared, three membranes, namely PS, PS-1, and PES-2, were selected for further studies. These membranes were selected for their comparative water permeation characteristics.

Figure 1 gives the pure water permeability data of PS, PS-1, and PES-2 membranes as a function of pressure. The pure water permeability increases linearly with an increase in pressure for both the membranes, which is as expected. However, the pure water permeability does not increase in proportion to the increase in pressure. With a fourfold increase in pressure, the pure water permeability data increase by a factor of 1.83 for PS membrane, 1.33 for PS-1 membrane, and 2.54 for PES-2 membrane. This indicates the changes in the morphological characteristics of the UF membranes with an increase in pressure. By comparing the rate of increase in pure water permeability data with pressure for both the polymer systems, it appears that the morphological changes brought about at higher pressures are more significant for the PES-based membranes as compared to PS membranes.

Separation Data for Polyethylene Glycols

Table 3 gives the separation data of polyethylene glycol of PS, PS-1, and PES-2 membranes. It can be seen that polysulfone membranes give comparatively higher separation for polyethylene glycol solutes at comparative water permeation. PS membranes give progressively higher separation of

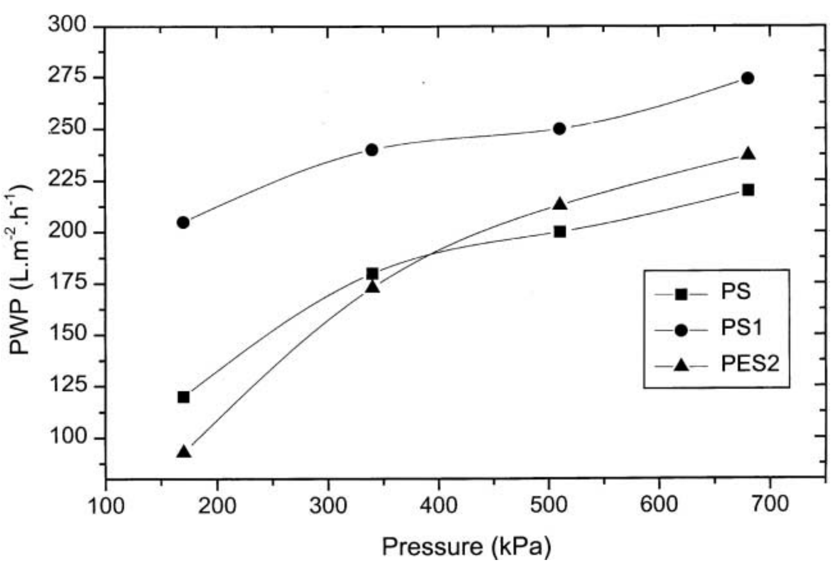

Figure 1. Variation of pure water permeability as a function of pressure.

polyethyleneglycol with increasing molecular weight, whereas PES-2 membrane shows almost the same rejection for the entire range of molecular weights, namely, 4000 to 20,000. The PS-1 membrane shows lower separation as compared to the PS membrane. This indicates that the addition of polyethylene glycol solute in the membrane casting solution affects the solute separation behavior of membranes much more than the water permeation characteristics.

Separation Data for Polyethyleneimine

Table 4 gives the separation data for polyethyleneimine solute of molecular weight 50,000 for the three UF membrane systems, namely, PS, PS-1,

Table 3. Separation Data for PEG Solutes

	PS		PS 1		PES 2	
Molecular Weight of PEG Solute	Flux (L m^{-2} h^{-1})	SR (%)	Flux (L m^{-2} h^{-1})	SR (%)	Flux (L m^{-2} h^{-1})	SR (%)
4000	180	12.1	238	10.3	170	10.2
8000	175	21.6	235	12.1	169	10.1
12,000	172	32.6	231	18.3	164	11.2
20,000	170	33.5	221	18.9	162	11.6

Conc. of feed = 100 ppm, pressure = 340 kPa.

Table 4. Separation Data for Polyethyleneimine

Membrane	Flux (L m^{-2} h^{-1})	SR (%)
PS	93	95.6
PS1	138	91.4
PES 2	114	87.9

Conc. of feed = 100 ppm, pressure = 340 kPa.

and PES-2. It can be seen that the UF membrane samples show a higher separation for polyethyleneimine solute as compared to polyethylene glycol solutes. This could be due to the higher molecular weight of the solute, as well as the polar nature of the solute, which could be adsorbed on the membrane surface leading to pore blockage. The permeate flow is also found to be lower as compared to what was observed for polyethylene glycol solutes under the same feed concentration. This suggests the onset of membrane fouling.

Effect of pH and Ionic Strength on Separation of Polyethyleneimine

The efficiency of the heavy metal ion removal by complexation ultrafiltration process depends on the extent of retention of polymeric ligand. The extent of retention of the polymeric ligand depends not only on the pore size and pore size distribution of the UF membranes, but also on the molecular weight distribution of the polymeric ligand itself. The polymeric ligands are known to undergo change in their size in solution, depending on the degree of ionization or the presence of salts in solution. The influence of solution pH and ionic strength on the extent of retention of polyethyleneimine was studied for the two membrane systems, and the data are presented in Tables 5 and 6, respectively. It can be seen from Table 5 that there is more separation of polyethyleneimine at higher pH. At lower pH, polyethyleneimine gets protonated through amine groups and becomes positively charged. As a result, it forms a gel layer adjacent to the membrane surface, which is slightly negatively charged. This gel layer formation and pore blockage could be the reason for lower flux at lower pH. The observed lower separation of polyethyleneimine at lower pH could be due to passage of low molecular weight oligomers of polyethyleneimine facilitated by the increased membrane-solute interaction. From Table 6 it can be seen that separation of polyethyleneimine reduces as the ionic strength of the feed solution increases. The hydrodynamic volume of polyethyleneimine is known to decrease with an increase in ionic strength of the solution,[20] which could account for the reduced separation observed. The extent of decrease in separation of polyethyleneimine is found to be relatively more in the case of the polysulfone

Table 5. Separation of Polyethyleneimine as a Function of pH

	Polysulfone (PS-1)		Polyethersulfone (PES-2)	
pH	Flux (L m^{-2} h^{-1})	SR (%)	Flux (L m^{-2} h^{-1})	SR (%)
2.5	81	71.4	73	67.2
4.5	97	79.7	85	74.9
5.5	124	86.2	109	82.3
9.1	138	91.5	114	87.9

Conc. of feed = 100 ppm, pressure = 340 kPa.

membrane, as compared to the polyethersulfone membrane. This could be due to possible changes in the morphology of the membrane surface at the solution interface because of the different extent of fouling. The fouling aspect of both the membrane systems are compared in subsequent sections.

Effect of Absorptive Fouling on Membrane Performance

Fouling of the membrane surface during ultrafiltration could be quantitatively expressed in terms of degree of fouling, which can be defined as follows:

$$F_n = 1 - PWP_n/PWP_0$$

where subscripts 0 and n refer to water permeation rates of fresh and fouled membrane. A higher value of F_n indicates higher extent of fouling. In order to evaluate the effect of fouling of UF membranes, the degree of fouling was evaluated as follows. Pure water permeation rates of fresh UF membranes

Table 6. Separation of Polyethyleneimine as a Function of Ionic Strength

	Polysulfone (PS-1)		Polyethersulfone (PES-2)	
Ionic Strength (mols L^{-1})	Flux (L m^{-2} h^{-1})	SR (%)	Flux (L m^{-2} h^{-1})	SR (%)
0.01	94.2	92.0	73.5	88.0
0.033	97.0	85.2	77.1	84.7
0.05	108.1	80.0	84.6	83.8
0.1	108.6	80.0	93.7	80.0

Conc. of feed = 100 ppm, pressure = 340 kPa.

were measured and were equilibrated in 100 ppm polyethyleneimine solutions for a definite amount of time. The equilibrated membranes were washed repeatedly with running water, and pure water permeability was measured. The changes observed in the PWP values were ascribed to irreversible absorption of polyethyleneimine onto the membrane surface. The pure water permeation rates, as well as the degree of fouling values of PS-1 and PES-2 membranes for varying solution pH and ionic strength, are given in Table 7. It can be seen that with decreasing solution pH the absorptive fouling increases as can be seen from the increasing degree of fouling values obtained for both the membrane systems. The degree of fouling values are found to be higher for PS-1 membranes as compared to PES-2 membranes, except in the case of pH-2 where the degree of fouling of both the membranes are nearly same. Polyethyleneimine gets protonated in acidic medium and becomes positively charged; the increased degree of fouling with decreasing pH indicates higher irreversible absorptive fouling of these membranes with positively charged macromolecular ligands. It also indicates better permeate fluxes are attainable if these membranes are used in conjunction with macromolecular ligands in higher solution pH. As compared to polyethersulfone, polysulfone-based UF membranes are relatively more prone to absorptive fouling. Polyethersulfone UF membranes appear to have a slightly better fouling resistance in comparison to polysulfone. With increasing ionic strength of the equilibrating solution, the degree of fouling values decreases for both the membrane systems. This indicates that the concentration and the charge of the ionic species present in the feed provide a shielding effect to the polyethyleneimine, resulting in reduced irreversible absorption. The polyethersulfone membrane shows a lower degree of fouling as compared to polysulfone.

Table 7. Effect of pH and Ionic Strength on Absorptive Fouling

		PS-1			PES-2		
pH	Ionic Strength (mols/L)	PWP_0 ($L\ m^{-2}\ h^{-1}$)	PWP_n ($L\ m^{-2}\ h^{-1}$)	F_n	PWP_0 ($L\ m^{-2}\ h^{-1}$)	PWP_n ($L\ m^{-2}\ h^{-1}$)	F_n
2.0	—	242	112	0.54	207	105	0.49
4.0	—	242	123	0.49	207	109	0.47
6.0	—	242	163	0.33	207	148	0.28
9.8	—	242	204	0.16	207	171	0.17
6.8	0.01	242	137	0.43	207	127	0.39
6.8	0.033	242	142	0.41	207	134	0.35
6.8	0.05	242	165	0.32	207	159	0.23
6.8	0.1	242	176	0.27	207	179	0.14

Time of equilibration = 24 hours, pressure = 340 kPa.

Separation of Ca^{2+} and Mg^{2+}

The individual separation behavior of calcium and magnesium chloride in the presence of PEI by PS-1 and PES-2 membrane samples are studied at two different solution pH, namely, 5.5 and 3.5. The concentration of the polyethyleneimine was maintained at 1000 ppm throughout the course of these experiments. The pH of the feed solution was adjusted by adding hydrochloric acid. The ionic strength of the solutions were adjusted to 0.05 mol/L in order to reduce the degree of fouling on the UF membrane samples. The separation data were collected for varying ratios of polyethyleneimine/metal ion at 340 kPa pressure. The % metal ion separation values are presented in Figs. 2 and 3. It should be noted that the separation of polyethyleneimine is around 80% and some low molecular weight polymeric ligand permeates through the membrane. The separation of metal ion obtained from the concentration of metal ion retained to the concentration of metal ion present in the feed does not reflect the amount of metal ion complexed to the polymeric ligand.

It can be seen from the figures that the separation of metal ion increases when the feed solution is less acidic. It is expected that the ethyleneimine units could combine with a proton via protonation reaction or could combine with a metal ion by complexation reaction. It appears that there is a competition between protons and metal ions for each ethyleneimine unit. When the pH increases, there are less hydrogen ions in the solution, and thus the amount of available imine units for metal ion complexation increases.

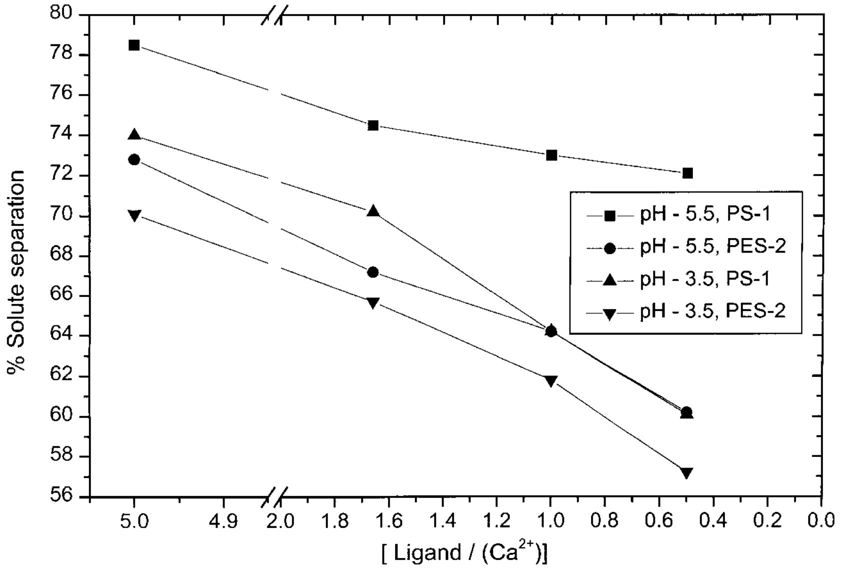

Figure 2. Separation behavior of Ca^{2+} in the presence of polyethyleneimine (PS-1) membrane.

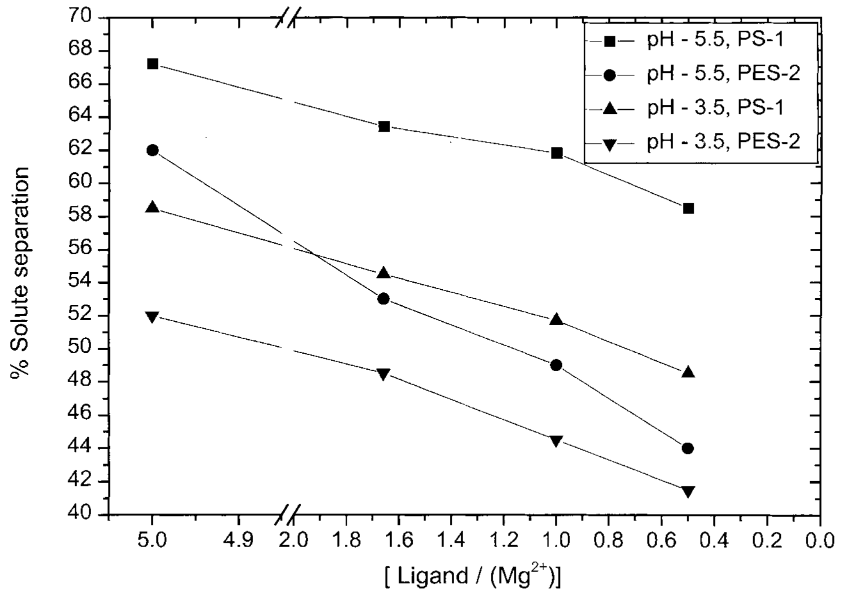

Figure 3. Separation behavior of Ca^{2+} in the presence of polyethyleneimine (PS-2) membrane.

It can also be seen that the metal ion separation is lower than the separation of polyethyleneimine, indicating the possibility that free uncomplexed metal ions permeating through the membranes. The separation of metal ions decreases for both the membranes at both solution pHs, when the concentration of metal ions are increased from 200 ppm to 2000 ppm. Also, it can be seen that there is more separation of both calcium and magnesium with the polyethersulfone membrane as compared to polysulfone membranes, which reflects the separation pattern seen for uncomplexed polyethyleneimine. The separation of magnesium ions is less as compared to separation of calcium ions. This could indicate the higher stability constant for calcium complexation as compared to magnesium complexation.

The effect of pressure on the separation behavior and permeate flux values for polysulfone and polyethersulfone membranes for calcium chloride in the presence of polyethyleneimine was studied and the results are presented in Fig. 4. The concentration of polyethyleneimine was maintained at 1000 ppm, and the concentration of calcium chloride was maintained at 2000 ppm during these experiments. It can be seen that with an increase in pressure from 170 kPa to 680 kPa, the permeate flux increases, although not linearly. At higher pressures, the permeate flux values appear to reach an asymptotic value indicating formation of a gel layer at the membrane surface. The permeate flux values are marginally higher for polyethersulfone membranes. The calcium ion separation also marginally increases with a

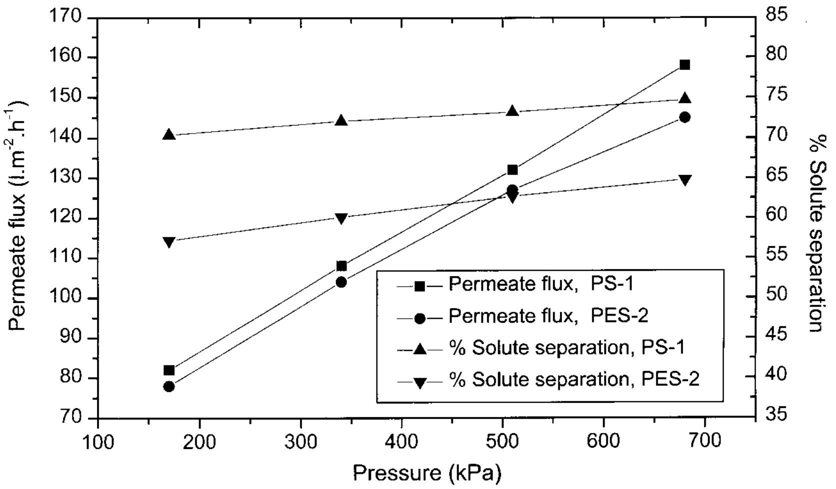

Figure 4. Separation behavior of Mg^{2+} in the presence of polyethyleneimine (PS-1) membrane.

corresponding increase in permeate flux, which could be due to the resistance offered by the additional gel layer formed at the membrane interface.

Microscopic Observations

Scanning electron micrographs of the skin surface and the porous surface of PS-1 and PES-2 membranes are given in Figs. 5–8. The skin surface of the PS-1 membrane sample is characterized by the presence of circular voids of varying dimensions, not exceeding 0.4 μ along with

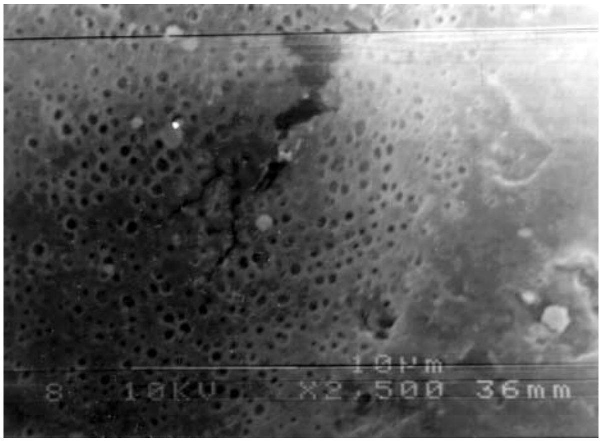

Figure 5. Separation behavior of Mg^{2+} in the presence of polyethyleneimine (PES-2) membrane.

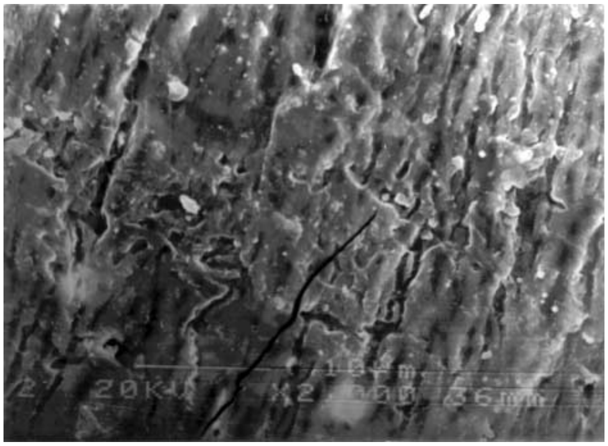

Figure 6. Separation behavior of Ca^{2+} in the presence of polyethyleneimine as a function of pressure (PS-1 membrane, pH of feed: 5.5).

random defects of a larger size. The skin surface of PES-2 membrane is characterized by a nonuniform layer devoid of circular voids noticed in PS-1 membranes. The presence of valleys and large size defects are noticeable. From the pure water flux data, it can be inferred that the large size voids are nonpenetrating. The porous side SEM photographs of both the membrane samples establish the asymmetric nature of these membranes. The porous side of PS membrane is characterized by the presence of deep ridges and valleys, whereas the porous side surface of PES-2 membrane contains

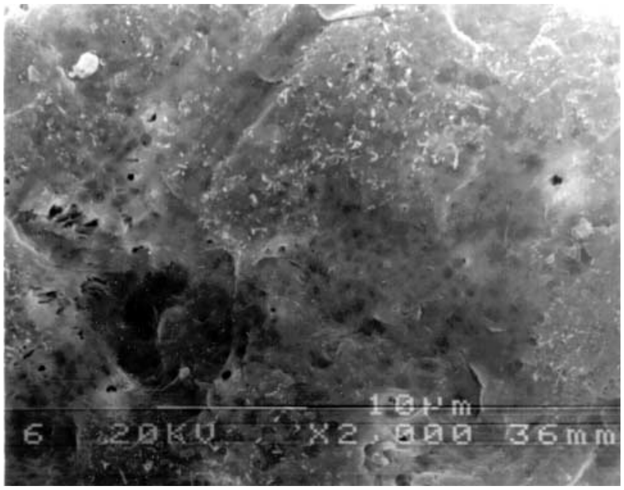

Figure 7. Separation behavior of Ca^{2+} in the presence of polyethyleneimine as a function of pressure (PES-2 membrane, pH of feed: 5.5).

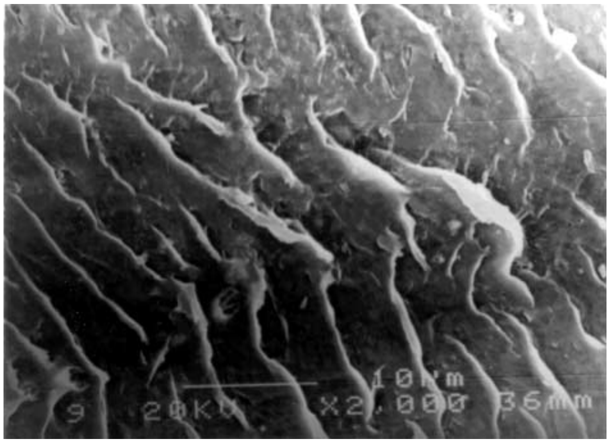

Figure 8. SEM photograph of the porous surface of PES-2 membrane.

random deep valleys. UF membrane samples used in metal ion separation studies were washed in running water, and the irreversibly fouled skin surface was viewed under scanning electron microscopy. Figures 9 and 10 indicate the SEM photographs of fouled skin surface of PS-1 and PES-2 membranes. It can be seen that the surface of PS-1 membrane is more uniformly covered by the precipitated polyethyleneimine as compared to PES-2 membranes, which supports a higher degree of fouling observed in these membranes.

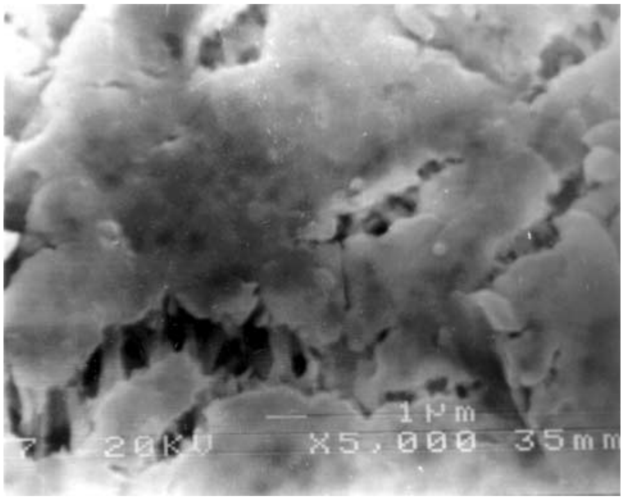

Figure 9. SEM photograph of the fouled skin surface of PS-1 membrane.

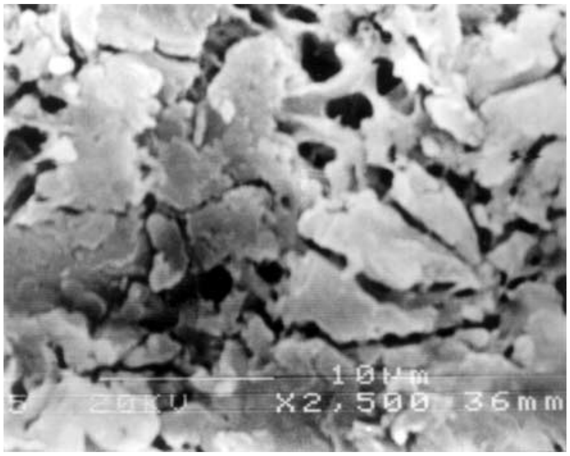

Figure 10. SEM photograph of the fouled skin surface of PES-2 membrane.

CONCLUSION

High permeate flux with low molecular weight cutoff UF membranes were prepared from polysulfone and polyethersulfone polymers. Polysulfone-based UF membranes give lower pure water permeability, compared to polyethersulfone-based UF membranes under identical casting conditions. However, with an increasing concentration of additives in the casting solution, the extent of increase in pure water permeability was found to be higher in the case of polyethersulfone-based UF membranes. Pressure-induced morphological changes are more significant in polyethersulfone-based UF membranes. UF membrane samples prepared under the casting condition presented in this paper give less than 20% separation for PEG 20,000 solute. However, the separation of polyethyleneimine is as high as 80% or higher. Higher ionic strength and pH of feed solution affect the polyethyleneimine separation as well as membrane fouling. Higher pH and lower ionic strength contribute to severe membrane fouling. Polysulfone-based UF membranes appear to be more susceptible to membrane fouling. Separation of calcium and magnesium are lower at lower pH and separation of magnesium is lower than the separation of calcium for both the membrane systems under identical conditions. With increasing ratio of polymeric ligand/metal ion, the metal ion separation increases.

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