

Separation of Humic Acid with Nanofiltration Polyamide Composite Membranes

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ABSTRACT: Humic acid, a natural organic matter, was separated with a polyamide (PA) composite membrane with a molecular weight cutoff (MWCO) of 500 g/mol. The PA composite membrane was prepared by the interfacial polymerization of piperazine and trimesoyl chloride on a polysulfone support with an MWCO of about 30,000 g/mol. The separation conditions through the membrane were varied, and factors affecting the permeation performance of the membranes, such as the concentration, pH, and storage time of the humic acid solutions, were studied. The surface chem-

istry of the membrane changed dynamically as a function of the operating time during the permeation tests, and the size and ζ potential of the colloid of humic acid solutions under different conditions were characterized with a ζ potentiometer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2847–2853, 2002

Key words: nanofiltration; polyamide; humic acid; membrane

INTRODUCTION

Natural organic matter (NOM) dissolved in natural water is attracting considerable attention from membrane researchers. Especially for the production of drinking water from surface water, NOM separation is very important. NOM dissolved in water can form trihalomethane (THM) with the chlorine added to the water for the reduction of microbiological health risks.¹ THM is a well-known carcinogen. NOM has usually been known as mixtures consisting of hydrophobic (humic and fulvic acids) and hydrophilic (amino acid and protein) materials with a broad range of molecular weights.^{2,3} Of the materials constituting NOM, humic acid (HA) has been known to form THM by the reaction with chlorine more easily than others. Because of this property, HA has to be removed from water before the addition of chlorine during the drinking water production process.

The conventional water-treatment processes, including coagulation and sand filtration, cannot remove enough NOM. There is a limitation because none of the chemical coagulants being used now is good enough to remove HA completely.⁴ Therefore, there is an urgent need for a new technology that can remove NOM from water almost completely. Membrane separation technology is now considered to be a strong alternative for removing NOM from water. In

particular, the nanofiltration (NF) process is regarded as a good candidate. The NF process with membranes is very good for removing organic compounds with low molecular weights from water mixtures effectively. The NF membranes have permeation properties between those of reverse osmosis and ultrafiltration (UF) membranes, high flux at a moderate operating pressure, and high rejection of low molecular weight organics, including multivalent ions.^{5–7}

On this basis, NF polyamide (PA) composite membranes were prepared by the conventional interfacial polymerization method and used for the separation of HA from water mixtures in this study. The details of the membrane preparation and the separation of HA are elaborated herein.

EXPERIMENTAL

Materials

UOP polysulfone (PSf) UF membranes with a molecular weight cutoff (MWCO) of about 30,000 g/mol, purchased from Fluid System (San Diego, CA), were used as supports for the formation of PA composite membranes. Piperazine (PIP) and trimesoyl chloride (TMC) as monomers and triethyl amine (TEA) as a catalyst, from Tokyo Kasei Co. (Tokyo, Japan), were used for the interfacial polymerization of PA active layers. Poly(ethylene glycol) (PEG) with a molecular weight of 600 g/mol (PEG 600), bought from Junsei Co. (Tokyo, Japan), and HA, from Aldrich Co. (Milwaukee, WI), were used as solutes of feed solutions. Other chemicals were also used as purchased without further purification.

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Preparation of the NF PA composite membranes

NF PA composite membranes were prepared by the conventional interfacial polymerization of PA active layers on the surfaces of microporous PSf supports.^{5,6} A PSf support, whose surface was cleansed with a dilute sulfuric acid solution in water (0.01M), was dipped into a 1.0 wt % PIP solution in water, in which 1.0 wt % TEA was also dissolved, for about 1 min, with some shaking. The surface of the support was then rolled with a rubber roller to remove the excess amount of the PIP solution that remained and was immersed in a 0.05 wt % TMC solution in hexane for 10 s for the interfacial polymerization of PA active layers on the PSf support. After this, it was dried in air at room temperature for 2 h, and the PA composite membrane so prepared was kept in distilled water before use.

Preparation of the HA solutions

HA solutions in water with a certain desired concentration were prepared by the dilution of a stock solution with a certain concentration. The details of the process are as follows: 2.0 g of HA was dissolved in 1.0 L of a 5N NaOH solution in water at an elevated temperature with constant stirring for some time because HA could be dissolved in water under basic conditions.⁸ After complete dissolution of the HA, the pH of the solution was adjusted to 7 by the slow addition of HCl with steady swirling. During the addition of HCl, some HA that dissolved in the solution was precipitated out. The precipitant was then removed from the solution by filtration with filter paper, and the concentration of the HA that remained dissolved in the solution was determined by the total organic carbon (TOC; TOC 5000A, Shimadzu, Tokyo, Japan). The stock solution so prepared was then diluted into solutions with such concentrations as 1, 2, 3, 4, 5, and 10 mg/L for use as feed solutions of the membrane separation.

Permeation testing

The separation of HA from the solution was carried out with an NF PA composite membrane prepared in this study. A typical NF test setup was used for this test, and the operating pressure was controlled from 100 to 400 psi with back-pressure regulators. The flux and rejection of the HA solution was determined by the conventional method. The flux was determined from the weight of the permeate gathered for some time, and the rejection was calculated with the following equation:

$$\text{Rejection (\%)} = 100 \times (C_f - C_p) / C_f$$

where C_f and C_p are the concentrations of the feed solution and permeate, respectively. The concentrations of HA and NaCl in a permeate or a feed solution was determined with an ultraviolet-visible spectrophotometer at 254 nm (UV₂₅₄; UV S-2100, Scinco, Seoul, Korea) and high-performance liquid chromatography (HPLC) equipment (501, Waters, Milford, MA) attached to an R401 differential refractometer as a detector, respectively.

With field emission scanning electron microscopy (FESEM; XL 30, Philips, Eindhoven, Netherlands), the FESEM photographs of a PA composite membrane after permeation tests were observed for the measurements of the cake thickness on the membrane and the morphologies for the determination of the membrane fouling process.

Characterization

The ζ potentials of the membrane surfaces under various conditions and colloid particles of the HA solution were measured with a ζ potentiometer (electrophoretic light scattering model ELS-8000, Otsuka, Tokyo, Japan). The particle size of the colloid of HA was also measured with the same ζ potentiometer. With an Ubbelohde viscometer, the viscosity of the HA solutions was measured to determine the behavior of the permeation of the HA solution through the PA composite membranes according to the time that the HA solution was kept at room temperature.

RESULTS AND DISCUSSION

Membrane formation

It has been widely believed that a membrane with ionic charges on its surface is good for the separation of water-soluble materials, with less fouling problems. On this basis, for the separation of HA from water, PA composite membranes based on PIP and TMC were prepared by conventional interfacial polymerization with UOP UF membranes with an MWCO of 30,000 g/mol as a support. As explained in the Experimental section, the concentrations of PIP and TMC for the interfacial polymerization of PA active layers were determined to be 1.0 and 0.05 wt %, respectively. The interfacial reaction time was 10 s at room temperature.

The fundamental properties of the PA composite membranes prepared are shown in Figures 1 and 2. From Figure 1, we find that the PA membrane showed a typical NF property: for a 1000 ppm PEG 600 solution in water, the flux and rejection at 200 psi through the PA membrane were about 2.5 m³/m² day and greater than 95%, respectively.

The ζ potential of the surface of the PA membrane shown in Figure 2 indicates that the surface of the membrane had anionic charges. The ζ potential of the

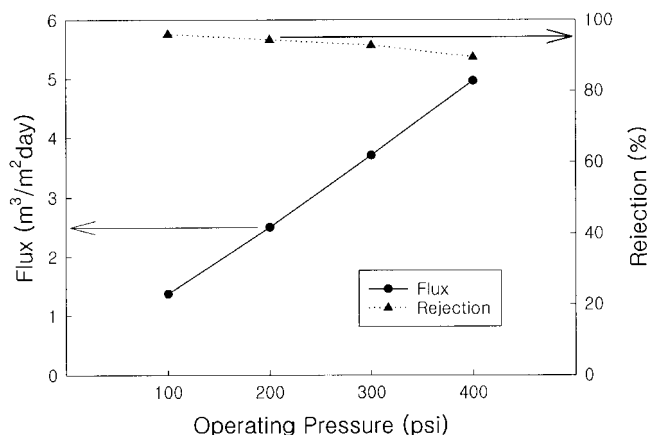


Figure 1 Flux and rejection as a function of the operating pressure through the PA composite membrane when a 1000 mg/L PEG 600 solution in water was used as a feed solution.

membrane surface measured with a 0.1 mM NaCl solution appeared to be about -45 mV, the minus value indicating anionic charges.

Separation of the HA solution

To determine the effect of the concentration of HA on the permeation of HA solutions through the PA composite membrane, various solutions with different concentrations of HA ranging from 1000 to 1.0 mg/L were prepared. Generally, the concentration of HA in surface water is less than 5 mg/L, depending on the conditions, but to determine the distinctive effect of the membrane on the separation of HA, rather high concentrations (e.g., 1000 ppm) were used in this study. Solutions with different HA concentrations were prepared by the dilution of a 1000 mg/L HA stock solution, as explained in the Experimental section. It should be noted that there was a certain

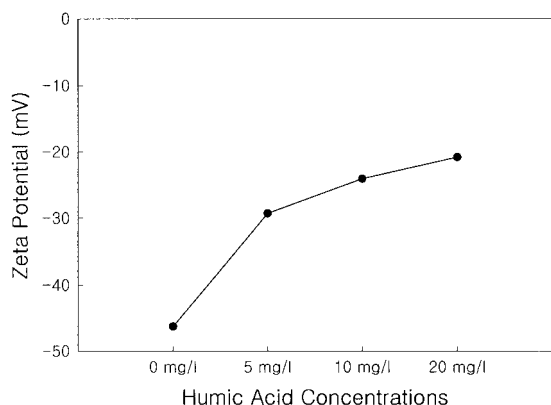


Figure 2 ζ potentials of the surfaces of the PA composite membranes after 20 h of permeation testing with HA solutions in water as a function of the concentration of HA. For the measurement of the ζ potentials of the surfaces of the membranes, a 0.1 mM NaCl solution was used.

TABLE I
Characteristics of the HA Solutions in Water Used

Solution	1	2	3	4	5	6
Concentration of HA (mg/l)	1.0	2.0	3.0	4.0	5.0	10.0
Concentration of NaCl (mg/l)	167	309	466	597	725	1,615
π^a (psi)	1.0	1.9	2.9	3.8	4.5	11.6

^a π = osmotic pressure.

amount of NaCl in the HA solution that depended on the HA concentration. In the preparation of the HA stock solution, the pH of the solution was adjusted to 7 by the addition of HCl to the solution. In this way, an excess amount of NaOH remained unreacted with HA in the solution reacted with HCl, resulting in the formation of NaCl. The concentration of NaCl in the solution was determined by both the calculation and measurement with HPLC equipment to which a refractometer detector was attached. The concentration of NaCl in each HA solution is shown in Table I, increasing with increasing HA concentration.

Figure 3 represents the flux of the HA solutions as a function of the operating pressure. It appeared to be very much dependent on the HA concentration, decreasing with increasing HA concentration. Even though the HA concentration changed slightly, the difference in the flux was relatively large. The large difference in flux between the HA solutions should be explained by the difference in the NaCl concentrations for the HA solutions. As shown in Table I, as the HA concentration varied from 1 to 10 mg/L, the NaCl concentration changed from 167 to 1615 mg/L. The large difference in the NaCl concentrations induced a large difference in the osmotic pressure, which acted against the operating pressure, decreasing the driving force working on the membrane. The osmotic pres-

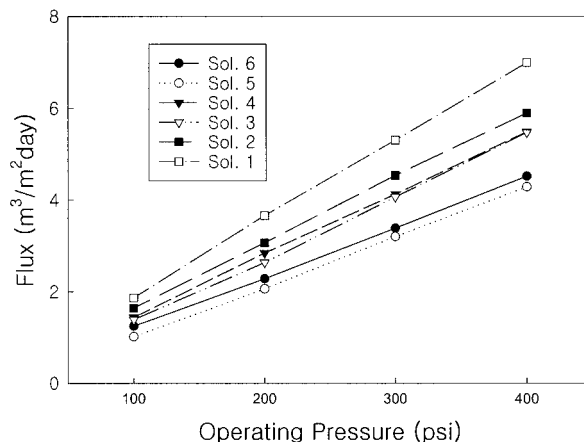


Figure 3 Fluxes as a function of pressure through the PA composite membrane when HA solutions with different concentrations of HA and NaCl, as shown in Table I, were used as feed solutions.

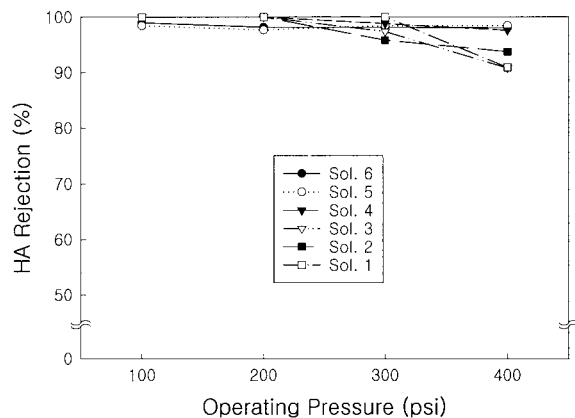


Figure 4 HA rejections as a function of pressure through the PA composite membrane when the HA solutions with different concentrations of HA and NaCl as shown in Table I were used as feed solutions.

sures developed by NaCl in the HA solutions are shown in Table I. By a combination of increasing NaCl and HA in the solutions, the flux decreased on a large scale with increasing HA concentration.

The behavior of the rejections of HA and NaCl shown in Figures 4 and 5 is, however, complicated. The rejection of HA up to a 300 psi operating pressure seemed not to be affected by the different HA concentrations and was close to 100%. However, the rejection of NaCl appeared to be very dependent on the concentration of feed solutions, decreasing with an increasing concentration. The behavior of the NaCl rejection is well understood by the solution diffusion model, in which the flux of the solute is proportional to the concentration of the solute:

$$J_A = -D_{Am} K_A \Delta c_A / \delta \quad (1)$$

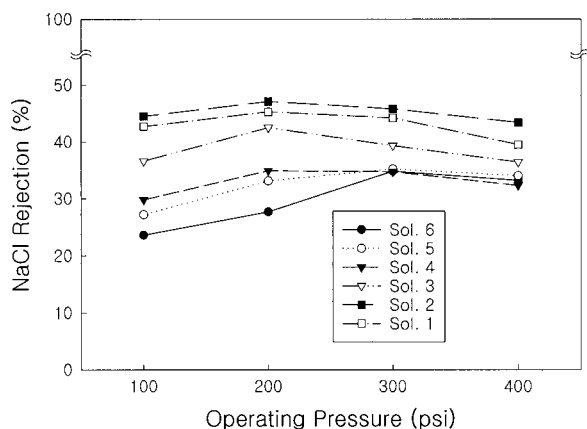


Figure 5 NaCl rejections as a function of pressure through the PA membrane when HA solutions with different concentrations of HA and NaCl, as shown in Table I, were used as feed solutions.

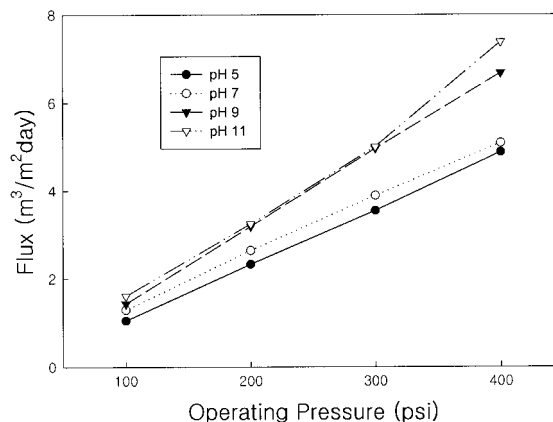


Figure 6 Fluxes as a function of pressure through the PA composite membrane when 5 mg/L HA solutions with different pHs were used as feed solutions.

where J_A is the solute flux, D_{Am} is the diffusion coefficient of the solute in the membrane, K_A is the distribution constant, Δc_A is the solute difference between both sides of the membrane, and δ is the membrane thickness.

For NaCl, therefore, the solute concentration of the permeate was increased by the combination of the increased solute flux with the decreased water flux as the concentration of HA increased, and this resulted in the lower rejections.

Effect of pH

HA is a material consisting of aromatic ring structures and different types of hydrophilic functional groups such as —OH and —COOH, which can be transformed into ionic states under different pH conditions. Different ionic characters of HA in different pH solutions, such as the content of the hydrophilic functional groups of HA in ionic states, will be expected to affect the permeation behaviors of HA solutions through the PA composite membranes. By the Donnan exclusion mechanism, the molecules with higher ionic content will be expected to be rejected better through the electrostatic repulsion acting between the same ions presented on the membrane surface and the molecules being rejected.

Figures 6–8 exhibit the flux and rejection of the 5 mg/L HA solutions with different pHs through the NF PA composite membranes, showing the influence of the solution pH on the permeation properties. With increasing pH from 5 to 11, the flux and NaCl rejection increased, indicating better repulsion between the membrane surface and solutes in the HA solution. However, the HA rejection remained unaffected by the different pHs. The increase in flux can be explained by less fouling of the membrane by HA. In other words, as the pH of the HA solution increased, the ionic part of HA could be increased in its content,

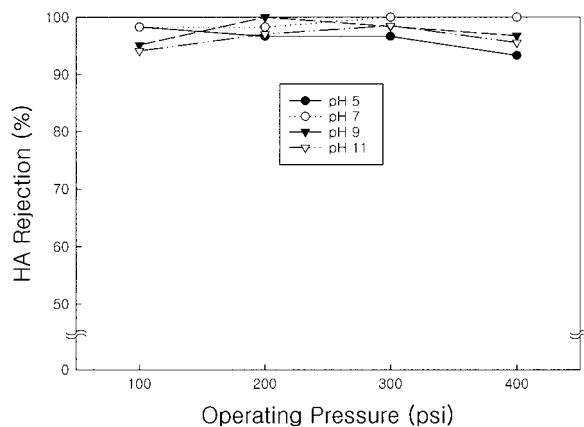


Figure 7 HA rejection as a function of pressure through the PA composite membrane when 5 mg/L HA solutions with different pHs were used as feed solutions.

especially at pHs greater than 7, by the reaction of HA with NaOH added into the solution to adjust the pH. The increased content of the anionic parts can then be effectively repulsed through the Donnan exclusion mechanism by the anions presenting on the membrane surface. The better repulsion between the HA and the membrane surface could prevent the HA from adhering onto the membrane surface, producing less fouling of the membrane and improving the flux. The increase in NaCl rejection also could be understood in the same way.

Effect of the storage time of HA

HA is an NOM that can be decomposed by microorganisms, its properties changing with time. In this study, HA solutions of different concentrations (1000, 5, and 2 mg/L) were kept for a certain period of time (4 days) under atmospheric conditions. They were used as feed solutions for membrane separation to determine how the permeation performance of the

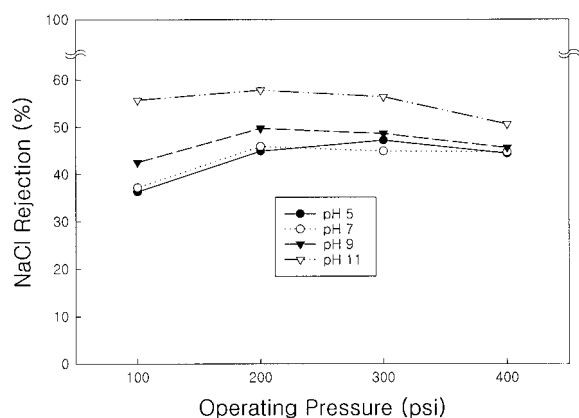


Figure 8 NaCl rejection as a function of pressure through the PA composite membrane when 5 mg/L HA solutions with different pHs were used as feed solutions.

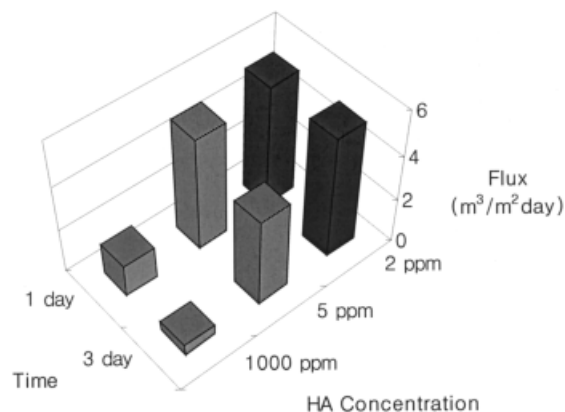


Figure 9 Fluxes as a function of the storage time and HA concentration at 200 psi through the PA composite membranes.

membrane was affected by the storage time of the HA solution.

Figure 9 presents the effect of the storage time on the permeation behavior of the HA solutions. As the storage time increased, the flux decreased. To determine the reason for this phenomenon, we characterized the HA solutions with an electrophoretic light scattering apparatus, trying to understand how HA was changed with time. Table II shows the properties of the 1000 mg/L HA solution as a function of storage time. The HA particles in solution decreased in size, but the viscosity of the HA solution increased with time. From this result, it can be suggested that with increasing storage time, the HA molecules remained as particles were dissolved further into the solution. Therefore, the radius of gyration of the HA molecules in solution was increased by the intramolecular repulsion between the ionic sites located in the molecules, combined with more hydration, increasing the solution viscosity and decreasing the diameter of the HA particles.

According to the solution diffusion model, the increase in the solution viscosity could reduce the flux of the solvent:

$$J_B = -C_{Bm}D_{Bm}v_B(\Delta p - \Delta \pi)/RT\delta \quad (2)$$

TABLE II
Characteristics of the 1000 mg/L HA Solution in Water as a Function of Storage Time

Characteristic	Unit	Storage time (days)		
		1	2	3
Diameter	nm	6540.8	6303.3	5361.3
Polydispersity	—	1.028	1.068	0.919
Viscosity	CP	0.964	1.010	1.080

pH = 7, temperature = 25°C.

where J_B is solvent flux, C_{Bm} is the concentration of the solvent in the membrane, D_{Bm} is the diffusion coefficient of the solvent in the membrane, ν_B is the viscosity of the solvent, R is the gas constant, T is the temperature, δ is the membrane thickness, Δp is the pressure difference between both sides of the membrane, and $\Delta\pi$ is the osmotic pressure difference between both sides of the membrane.

However, as the concentration of the HA feed solutions decreased from 1000 to 5 or 2 mg/L, the extent of the decrease in flux became smaller, as shown in Figure 9. This phenomenon is understandable if we consider the smaller changes in viscosity from the lower HA concentrations.

Long-time testing

Figure 10 presents the permeation behaviors of a 5 mg/L HA solution through the PA composite membrane as a function of the operating time. As expected, even at quite low concentrations of HA (5 mg/L) and NaCl (725 mg/L), the flux decreased gradually with the operating time at room temperature. After 20 h of operation at 200 psi, the flux decreased by about 24% to 2.2 m³/m² day by the membrane fouling induced from the concentration polarization in the vicinity of the membrane surface. Interestingly, the NaCl rejection also decreased with the operating time by the same extent as the flux, about 24%, whereas the rejection of HA remained greater than 98%. From this experiment, it was found that the NaCl rejection followed the solution diffusion rule, decreasing with a decrease in flux, but the rejection of HA did not.

From the FESEM photograph of the surface of the PA membrane shown in Figure 11, it was found that a fouling layer was formed on the surface of the membrane. The fouling layer was stable enough not to be washed away by simple shaking in distilled water for cleaning, indicating that the layer was a kind of dense

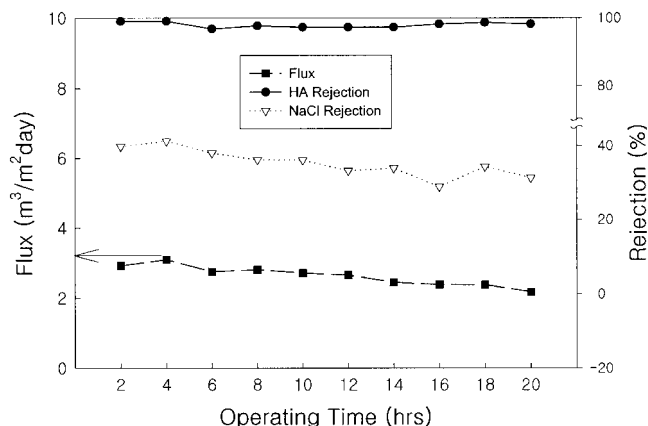


Figure 10 Permeation properties as a function of the operating time at 200 psi through the PA composite membranes when a 5 mg/L HA solution was used as a feed solution.

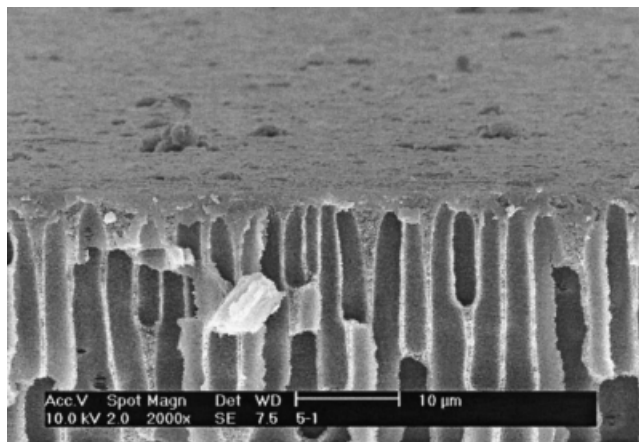


Figure 11 FESEM photograph of the surface and cross section of the PA composite membrane after 20 h of permeation testing with a 5 mg/L HA solution.

cake layer. The formation of the cake layer during the separation process could be suggested by the behavior of the HA rejection. The HA rejection, decreasing from 100 to 98% during the early operating stage up to 12 h, increased again with time. As the operation time reached 20 h, the rejection became almost the same as in the beginning stage, indicating that the fouling layer that accumulated on the membrane surface by the concentration polarization became a dense cake layer.

The behavior of the ζ potentials obtained from the membrane surface after 20 h of separation of the HA solutions with different concentrations, shown in Figure 2, also shows the surface chemistry of the membrane being changed by HA in the feed solution through membrane fouling. As the concentration of the HA solution increased, the absolute value of the ζ potential became smaller, indicating that the membrane surface was becoming hydrophobic. The increase in hydrophobicity would be unfavorable for the membrane, inducing more fouling.

CONCLUSIONS

PA composite membranes prepared by the interfacial polymerization of 1.0 wt % PIP in water and 0.05 wt % TMC in hexane showed a typical NF performance with an MWCO of about 500 g/mol and greater than 2.5 m³/m² day flux at a 200 psi operating pressure at room temperature. HA, an NOM, was effectively removed from water via NF with a PA composite membrane. The membrane performance for the separation of HA was very dependent on the separation conditions: the flux decreased with increasing concentrations and decreasing pHs of HA solutions. The rejection of NaCl contained in the HA solution followed the solution diffusion rule, increasing with increasing flux, whereas the rejection of HA remained close to

100% and was not affected by such separation conditions. Membrane fouling was encountered even in the separation of an HA solution with a concentration of 5 mg/L. The membrane surface became more hydrophobic by the fouling with HA solutions.

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