

Preparation and Characterization of Nanofiltration Membranes Fabricated from Poly(amidesulfonamide), and Their Application in Water–Oil Separation

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Received 26 September 2001; accepted 6 May 2002

ABSTRACT: Nanofiltration membranes prepared from selected types of poly(amidesulfonamide) (PASA) targeted to retain either sucrose, raffinose, or β -cyclodextrin were fabricated in conditions deduced from a chemometric method. Membrane performance was characterized by the permeation of solutions containing 1000 ppm carbohydrates and metal ions. To demonstrate the dependence of the membrane properties on the polymer structure, the separation characteristics of a series of four PASA homopolymers and four PASA copolymers were established. The results allowed us to screen out several promising PASA materials for the NF separation process. In addition, the superiority of the PASA materials, characterized by excellent retention and

high flux rate, was evident from the results of a study comparing it with polysulfonamide, poly(ether amide), and commercially available regenerated cellulose. As a means of pollution control, the PASA NF membranes have been proven to be effective in removing oil from oily wastewater. Under an operating pressure of 2–3 psi, a constant flux of 5 L m⁻² h⁻¹ and 99.6% retention of a solution of 5000 ppm olive oil could be achieved with the PASA membranes over a period of 430 h. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1803–1810, 2003

Key words: poly(amidesulfonamide); nanofiltration; membrane materials; oil–water separation

INTRODUCTION

Membrane separation technology represents one of the most effective and energy-saving applications to a wide range of separation processes, including ultrafiltration (UF) and reverse osmosis (RO).^{1,2} During the last decade nanofiltration (NF), the most recently developed process for membrane separation, has emerged as a valuable pressure-driven membrane process for separating monovalent from multivalent metal ions as well as retaining small neutral organic solutes with molecular weights between 300 and 1000 Da.^{3,4} In contrast to the more established reverse osmosis technique, the NF process requires a lower operating pressure, in the range of 50–100 psi, and has greatly enhanced permeation flux, from 10 to 100 L m⁻² h⁻¹ at a pressure of 100 psi. The practical applications for NF membranes have ranged from their use in the food industry for recovering small organic molecules such as sugars and peptides^{5,6} to their wide use in the treatment of industrial effluents contaminated with organics.^{7,8} To cope with the demand from a variety of industries, today most membrane manufac-

turers worldwide produce NF membranes. Commercial membranes are made mostly from polymers such as aromatic polyamide, polysulfone, and poly(ether sulfone).⁹

In response to the challenge of developing new membrane materials, for the past 10 years we have designed and synthesized a series of new types of poly(amidesulfonamide) (PASA).¹⁰ Subsequently, their suitability as new membrane materials for RO and UF applications have been explored and demonstrated.^{11,12} Experimental findings have revealed that this class of new membrane possesses several desirable membrane characteristics, including high intrinsic viscosity amenable to fabricating tough membranes, high chemical stability resistant to many corrosive chemicals, and hydrophilic properties favoring the permeation of water.¹³ In this article we describe our effort to prepare and characterize selective NF membranes from PASAs. The performance of porous membranes not only relies very much on the nature of the materials but also highly depends on the composition of the casting solution and the technical conditions adopted in the fabrication process. Guided by a suitable chemometric method, NF membranes targeted to retain sucrose, raffinose and β -cyclodextrin in the molecular weight range of 342–1135 can be prepared. To sort out the best material for NF applications, a comparative study on the performance of membranes derived from different homopolymers and copolymers of PASAs was undertaken. The potential appli-

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Contact grant sponsor: Research Grant Council of HKSAR; contract grant number: HKBU 2016/99P.

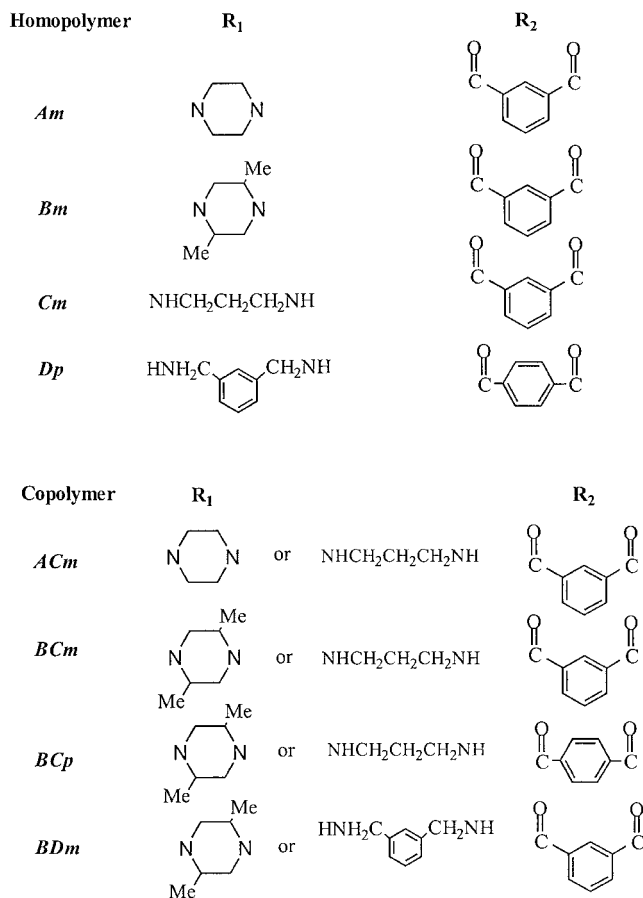
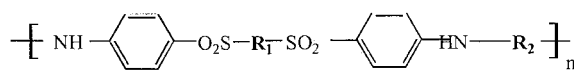


Figure 1 Structure of PASA homopolymers and copolymers.

cation of NF membranes fabricated from PASAs in the treatment of oily wastewater will be demonstrated.

EXPERIMENTAL

Materials

The PASA homopolymers PASA_{Am}, PASA_{Bm}, PASA_{Cm}, and PASA_{Dp} and the PASA copolymers PASA_{ACm}, PASA_{BCm}, PASA_{BCp}, and PASA_{BDm} were synthesized by low-temperature solution polycondensation as described elsewhere.^{10,14} Polysulfonamide (PSA) and poly(ether amide) (PEA) were prepared according to procedures described in the literature.¹⁵ Regenerated cellulose membranes with a MWCO of 1000 were purchased from Millipore (Bedford, MA). The structures of PASAs are shown in Figure 1. Dimethylacetamide (DMAc) (Redel-de Haen, Seelze, Germany) was dried by molecular sieve 4A (Merck, Darmstadt, Germany). Polyvinylpyrrolidone (PVP) and LiNO₃ (purchased from Aldrich, Milwaukee, WI) were used as pore forming agents. Analytical-grade

carbohydrate markers including glucose, sucrose, raffinose, and β-cyclodextrin (Aldrich) were used to characterize the NF membranes.

Apparatus

A water bath (Cole-Parmer, Model E1250-05) was employed to control the temperature of the gelation bath ($\pm 0.15^\circ\text{C}$ to the assigned temperature). A NF testing unit fabricated in-house was used. It consisted of a 10-L capacity feed reservoir connected to a high-pressure pump (Rannie, Dow) with a maximum discharged pressure of 1160 psi, a flow capacity of 8 L/min, and a plate-type NF filtration cell. A circular membrane with a diameter of 56 mm was placed in the test cell with the skin layer facing the incoming feed. The membrane was supported on nylon fabric, and rubber o-rings were used to seal the membranes and ensure a leak-free operation. Optical rotations of carbohydrate feed and permeated solutions were recorded at ambient temperature on a JASCO DIP-1000 polarimeter. The concentration of metal ions in the feed and permeated solutions was determined by a Perkin-Elmer Optima 3000 inductively coupled plasma (ICP) spectrometer. A homemade plastic cross-flow testing cell equipped with a rotary pump (Cole-Parmer), a regulating valve (Whitey), and a glass reservoir was used to conduct the durability test for PASA_{Am} NF membranes. The setup of the durability testing system is shown in Figure 2.

Asymmetric NF membrane casting

All NF membranes were fabricated from a casting solution with a well-defined composition of 12 wt % polymer, 2–5 wt % pore-forming agent and 83–86 wt % DMAc. Two copper wires (diameter = 0.235 mm) were tightly held on the two ends of a cleaned glass tube to control the thickness of the membrane formed. A suitable amount of the casting solution was spread on a clean and smooth glass surface that was pre-

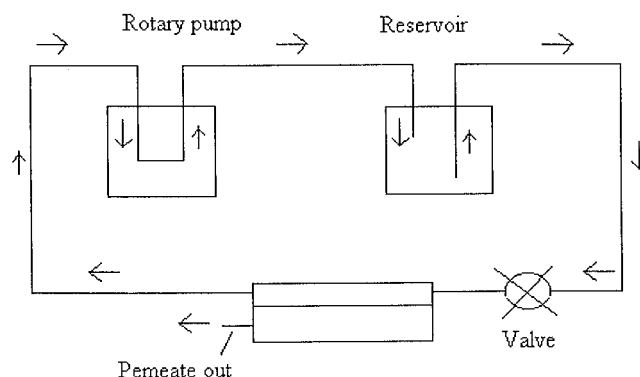


Figure 2 Schematic diagram of the durability testing system.

heated at the fixed evaporation temperature. The spread sheet of the polymeric material was kept at the defined temperature undisturbed for a selected period of evaporation time. Then the membrane was immersed in a gelation bath containing pure water at a controlled temperature for 30 min. The asymmetric membrane was formed in the gelation bath. To ensure the reproducibility of the membrane, two membranes were prepared for each of the selected fabrication conditions.

Evaluation of polymeric membranes

Each prepared NF membrane was placed in the filtration cell of the NF testing system and was prepressed under a pressure of 100 psi for 3 h. The solute concentration of the feed was 1000 ppm. The permeation flux (J) and the retention ability ($R\%$) of the membrane toward the permeation of carbohydrate solutions (i.e., glucose, sucrose, raffinose, β -cyclodextrin) and metal ion solutions (i.e., Cu^{2+} , Mg^{2+} , Ni^{2+} , Ca^{2+} , Na^+) were determined under an operating pressure ranging from 50 to 400 psi. Permeation flux can be calculated by the following equation:

$$J = Q/A\Delta t$$

where J is the permeation flux ($\text{l m}^{-2} \text{h}^{-1}$); Q is the permeation volume (L) of the testing solution; A is the effective area of the tested membrane (m^2), and Δt is the sampling time (h). The retention ability ($R\%$) of the carbohydrate markers and the rejection ($R\%$) of metal ions is defined as

$$R\% = \left(1 - \frac{C_f}{C_0}\right) \times 100\%$$

where C_0 is the initial concentration of the solute in the feed and C_1 is the concentration of the solute in the permeate. The concentrations of metal ions and carbohydrates were determined by ICP and the optical rotation measurements, respectively.

Use of NF membranes for oil–water separation

The viability of using the NF membranes in treating oily water was tested under the homemade dead-end NF testing cell (Fig. 2). The 5000 ppm olive oil aqueous solution was used as the feed. Under vigorous stirring, the feed solution was allowed to pass through the PASA_{Am} membrane in an operating pressure that ranged from 20 to 100 psi. The concentration of the oil in the permeate was determined by the ASTM standard gravimetric method.¹⁶

RESULTS AND DISCUSSION

Fabrication of NF membranes with tunable separation characteristics

The performance characteristics of porous membranes in separation processes including NF were highly dependent on the composition of the casting solution and the technical conditions adopted in the fabrication process. A number of experimental variables should be considered if viable membranes are to be developed. In this connection, the performance of the NF membranes can be tuned by varying a variety of experimental variables in the fabrication process. To confine the number of variables to a manageable number, based on our previous experience in developing selective UF membranes,¹² only dominant variables were chosen for this investigation. They were: the type and amount of pore-forming agents in the casting solutions, the evaporating time and temperature in the fabrication process, and the gelation temperature in the membrane-forming process. Traditionally, to map out the optimized conditions for making NF membranes with separation characteristics desirable for a particular permeant, a large number of experiments have to be conducted by varying one variable at a time while keeping other variables unchanged. In this way, the effect of each variable on the performance of the membranes can be unraveled. To obtain an optimized balance of retention and flux rate for a particular permeant, based on this systematic study, a unique set of fabrication conditions can be proposed. Obviously, to define the optimized conditions requires a long experimentation time and the use of a large amount of materials. However, the whole process of optimization can be expedited by the use of chemometric methods. To explore the viability of this approach, PASA_{Am} was selected as the polymeric material in making NF membranes. Thus, the optimized membranes M_s , M_r , and M_c , targeted to retain sucrose, raffinose, and β -cyclodextrin, respectively, were fabricated under the conditions suggested by the uniform design method (Table I). The details of the investigation will be reported elsewhere.

Effect of operating pressure on performance of the membranes

The separation of the optimized membranes was characterized by the permeation of four carbohydrate markers—glucose, sucrose, raffinose, and β -cyclodextrin—covering a molecular mass range from 180 to 1135. As shown in Figure 3, the retention abilities of all tested membranes were found to increase initially and then reach a constant value as the pressure was increased further. As the pressure was gradually increased from a relatively low value, more water was forced through the membrane, and the permeate was diluted. At a higher pressure both water and solute

TABLE I
Optimized Fabrication Conditions for NF Membrane Preparation Derived from the Uniform Design Method

Type of membrane	Permeant	Molecular weight	Type of additive	Gelation temperature (°C)	Amount of additive (wt %)	Evaporation temperature (°C)	Evaporation time (min)
M _s	Sucrose	342	LiNO ₃	30	5	65	9
M _r	Raffinose	504	PVP	10	5	70	5.5
M _c	β-Cyclodextrin	1135	LiNO ₃	20	3	70	3

molecules were forced to penetrate the membrane to a similar extent; thus, the membrane exhibited constant retention abilities. Furthermore, the retention selectivity of various optimized membranes toward different carbohydrate molecules was only moderate. The power of discrimination of the fabricated membranes appeared to be unable to clearly separate β-cyclodextrin from raffinose as well as raffinose from sucrose because of the extremely similar molecular size and properties of these pairs.

On the other hand, as shown in Figure 4, the flux rate of all membranes increased linearly with the increase of the operating pressure, which is a characteristic of pressure-driven processes. It is noteworthy that the flux rate of the membranes was in the descending order of M_c, M_r, M_s, each differing from the next by a factor of fivefold. This observation is consistent with the relative molecular size of the carbohydrate molecule intended to be separated. Membranes targeted to retain a small molecular marker such as sucrose should possess smaller pores, which exhibit the lowest flux rate. Under the same operating pressure, the permeation flux of the tested membrane appeared to be constant regardless of the nature of the permeants. Conceivably, because all carbohydrates are highly hydrophilic, surface adsorption of the penetrating molecules is unimportant. In fact, the flux rate of carbohydrate solutions was very close to that of pure water.

Separation of metal ions by optimized PASA membranes

To assess the viability of using the PASA membranes M_c, M_r, and M_s for water softening and wastewater treatment, the separation characteristics of the membranes toward common metal ions should be established. Thus, a mixture of Mg²⁺, Ca²⁺, Cu²⁺, Ni²⁺, and Na⁺, each, at the concentration of 1000 ppm, was allowed to pass through the membranes at different operating pressures. Figure 5 shows the rejection of three optimized membranes against metal ions under different pressures. In general, all membranes exhibited a relative low ability to retain metal ions, especially monovalent Na⁺. It should be noted that fabrication of M_c, M_r, and M_s, guided by the UD method, was specifically done for conditions targeted to retain

β-cyclodextrin, raffinose, and sucrose, respectively. The size of metal ions is much smaller than that of carbohydrate molecules. Understandably, for the permeation of metal ion solutions, the M_s with the smallest pores showed the highest rejection, whereas the M_c with the largest pores exhibited the lowest rejection of all metal ions. Apparently, the pore size of all membranes was just too big to retain small metal ions. On the other hand, the flux of the membranes toward metal ion solutions, as shown in Figure 6, was comparable to that of the permeation of carbohydrate solutions.

Comparison of performance of different PASA membranes

Based on the synthetic protocol developed in our laboratory, we were able to synthesize different types of PASA homopolymers and copolymers. It is well known that membrane separation properties are highly dependent on the nature of the constituted material and the membrane morphology. To a certain extent, membrane morphology can be controlled by fabrication conditions. We believed a comparative study on the separation characteristics of NF membranes derived from different PASAs would enable us to screen out the best material for the NF process. To this end, four PASA homopolymers and four PASA copolymers with the structures shown in Figure 1 were synthesized and used for the preparation of NF membranes. To set a common ground for comparison, membranes derived from all eight types of materials were prepared under a unique set of fabrication conditions deduced from the UD method for making the M_c membrane (Table I, last row). The membrane performance of the PASA materials is shown in Figures 7 and 8. As can be seen from a cursory examination of Figures 7 and 8, the membranes from different PASAs exhibited fairly diverse separation properties. With 1000 ppm β-cyclodextrin as the feed solution, a more than sixfold difference in the flux rate was found for PASA_{BCm} and PASA_{Cm}, whereas a fivefold difference in the retention ability was observed for PASA_{Am} and PASA_{Dp}. Such a wide range of differences in separation characteristics of PASAs is difficult to rationalize in simple terms. These differences could be the result of a combination effect of the fabrication condition

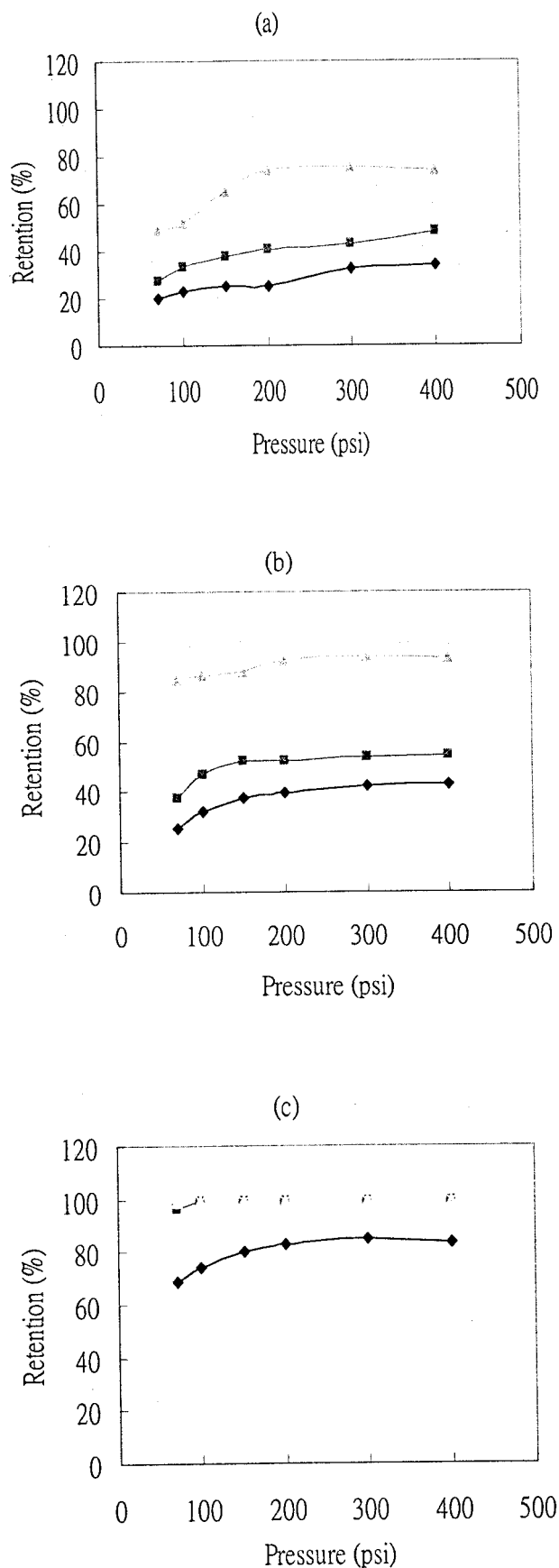


Figure 3 Plot of the retention of the optimized membranes (a) M_c , (b) M_r , and (c) M_s against applied pressure (◆: glucose; ■: sucrose; △: raffinose, χ β -cyclodextrin).

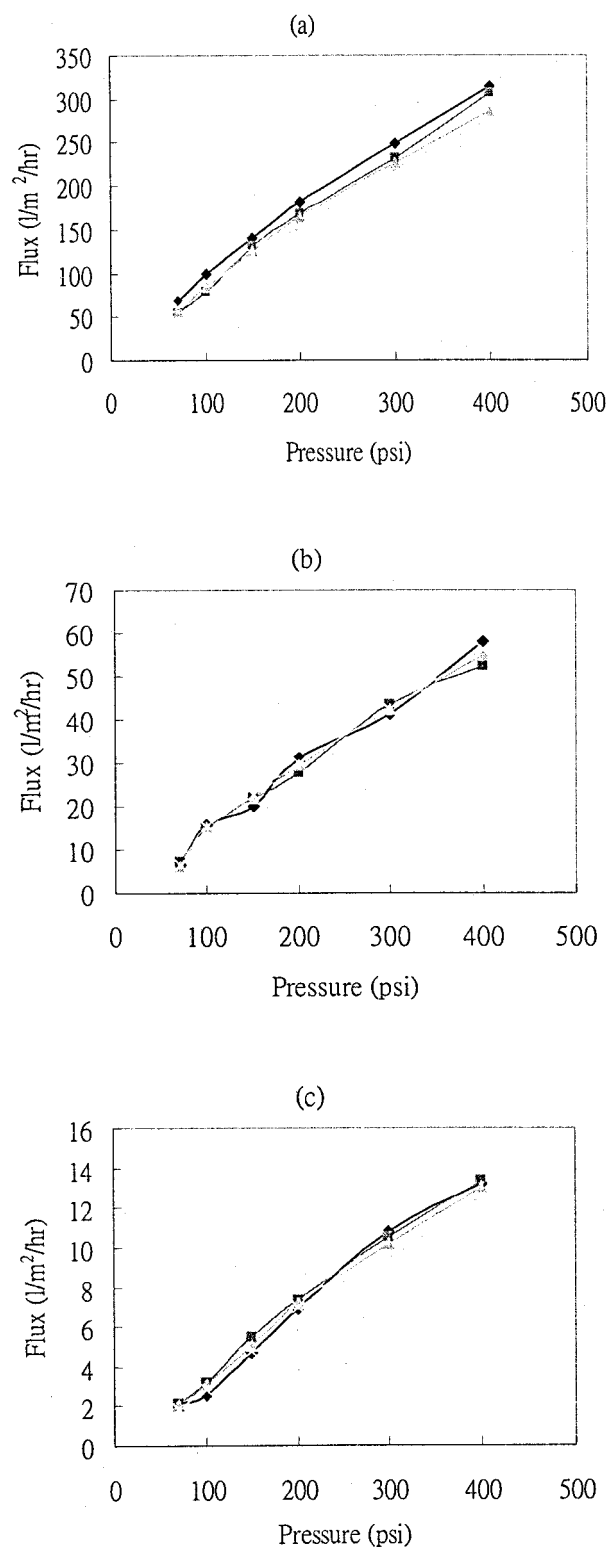


Figure 4 Plot of the flux of the optimized membranes (a) M_c , (b) M_r , and (c) M_s against applied pressure (◆: glucose; ■: sucrose; △: raffinose, χ β -cyclodextrin).

and the nature of the materials. Based on the good compromise of the retention ability and flux as a criterion to screen better materials for NF applications, in addition to $PASA_{Am}$, $PASA_{Ac}$, $PASA_{BCP}$, and $PAS-$

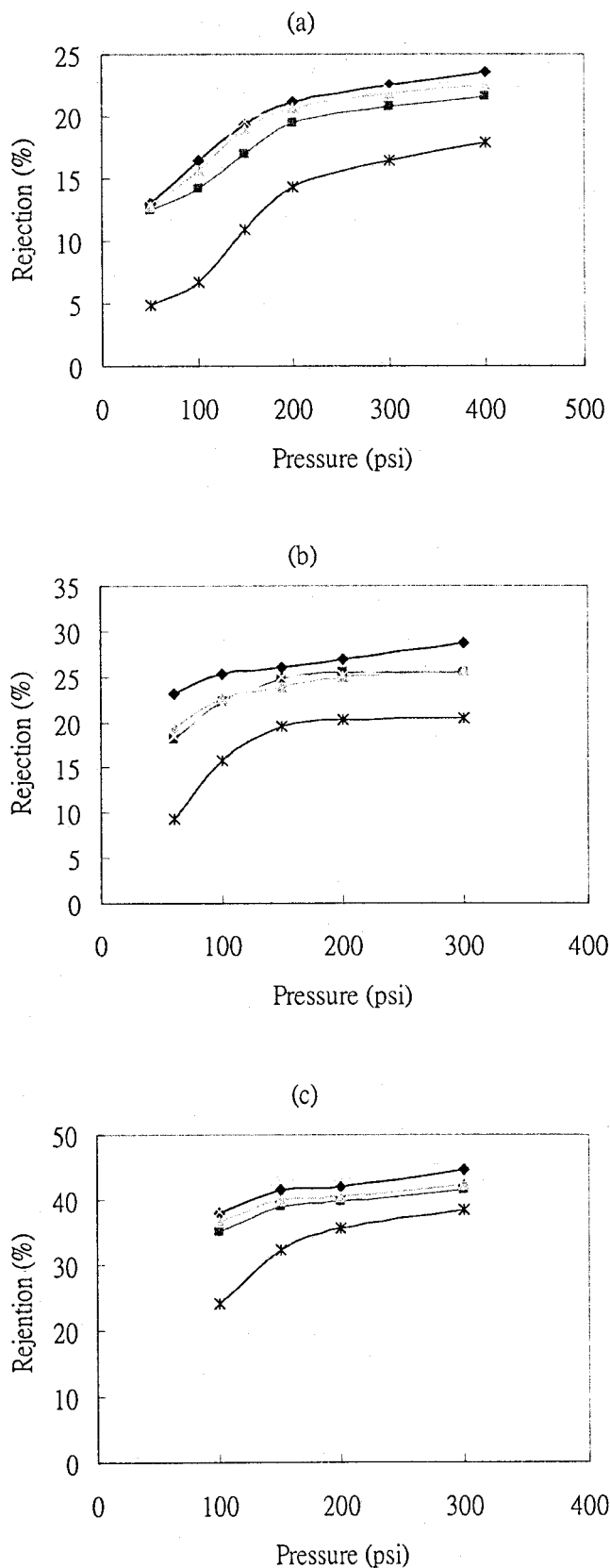


Figure 5 Plot of the retention of optimized membranes (a) M_c , (b) M_r , and (c) M_s against applied pressure (◆: Cu^{2+} ; ■: Mg^{2+} ; △: Ni^{2+} ; ×: Ca^{2+} ; ⋇: Na^+).

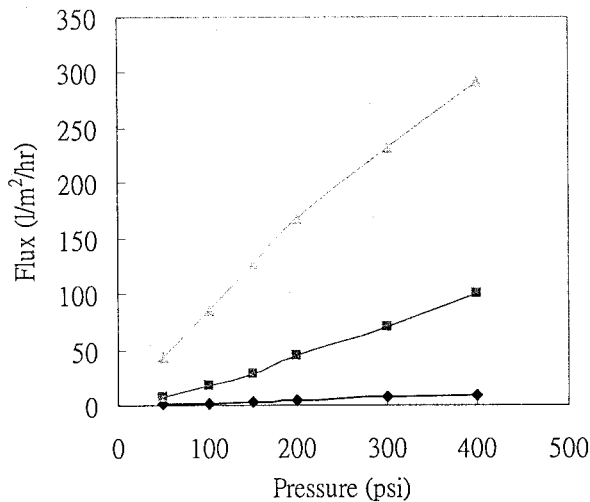


Figure 6 Plot of the flux of the optimized membranes (a) M_c (◆), (b) M_r (■), and (c) M_s (△) toward the permeation of metal solutions against applied pressure.

A_{Bm} emerged as the materials that are worthy of further exploration. It is noteworthy that in a previous study the RO characteristics of the same set of materials were found to be more uniform than those in the present study of the NF process.¹¹

Comparison of membrane performance of PASA with that of other polymeric materials

To determine whether PASA is a good material for making membranes in the NF process requires a study comparing the performance of membranes fabricated from other membrane materials with that of PASAs. For this purpose, PSA and PEA were synthesized for a comparative study. Their structures are shown in Figure 9. Subsequently, PSA, PEA, and $PASA_{Am}$ membranes fabricated in a unique set of fabrication conditions were prepared and evaluated by the permeation

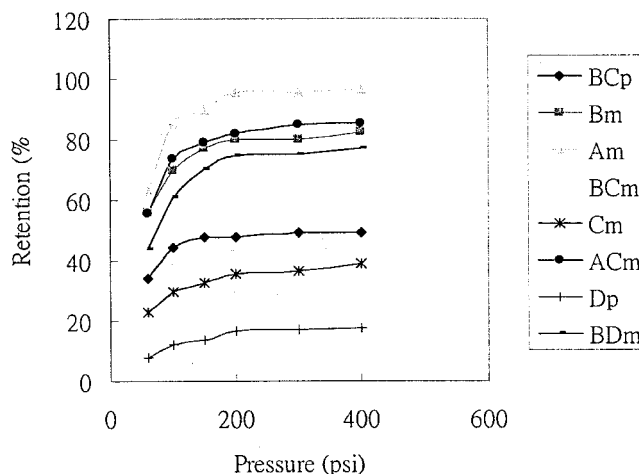


Figure 7 Plot of the retention of the optimized $PASA_{Am}$ membrane (M_c) with other types of PASA membranes against applied pressure.

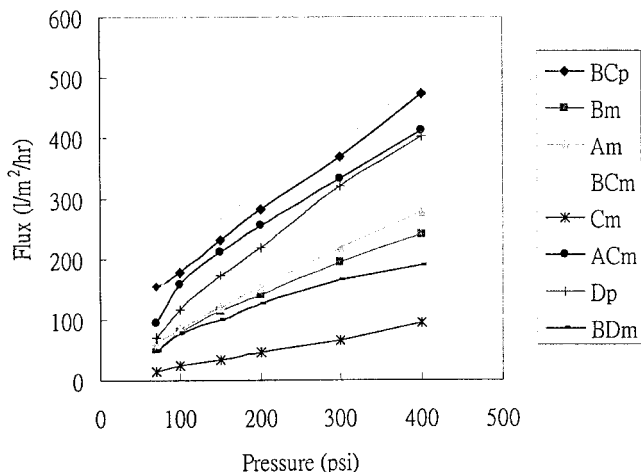


Figure 8 Plot of the flux of optimized PASA_{Am} membranes (M_c) with other types of PASA membranes against applied pressure.

of a 1000 ppm β -cyclodextrin solution. In addition, commercially regenerated cellulose (RC) membranes with an MWCO of 1000 were included for the comparative study. The retention and flux of the four types of membranes as a function of applied pressure were determined, and the results are shown in Figure 10. As indicated in Figure 10(a), membranes from RC, PASA_{Am}, and PEA exhibited an excellent retention to the permeant over a wide range of applied pressures. It is gratifying to note that the flux rate of PASA_{Am} membranes displayed a threefold enhancement compared with the flux rate of the commercial RC membranes. Undoubtedly, considering the need for a good compromise of retention with flux, PASA_{Am} stands out convincingly as the best material for the NF process.

Application of NF membranes in oil-water separation

To evaluate the viability of using PASA NF membranes in treating the effluents from local restaurants, the retention and flux of PASA_{Am} NF membranes targeted to retain β -cyclodextrin (i.e., M_c) were determined toward the permeation of a 5000 ppm olive oil aqueous solution. As shown in Figure 11, the membranes exhibited not only an outstanding ability to retain oil but also a large flux rate. Even at the lowest

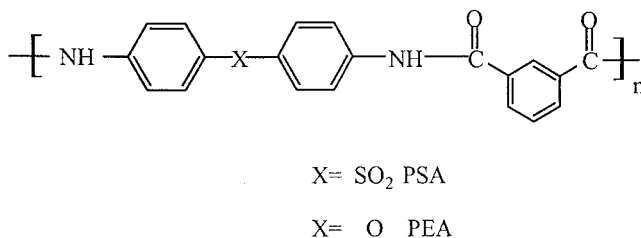


Figure 9 Structures of PSA and PEA.

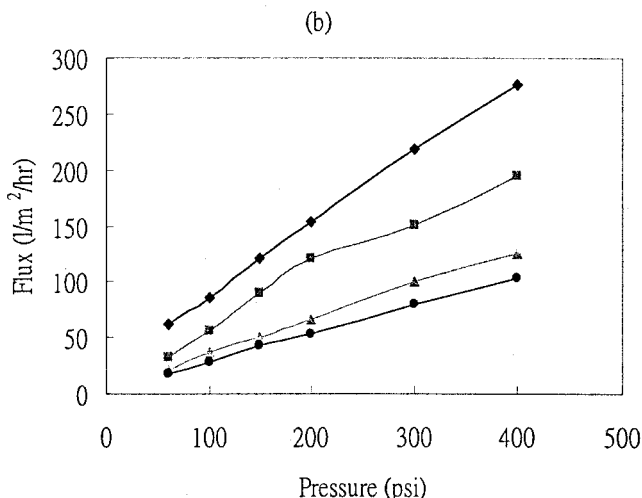
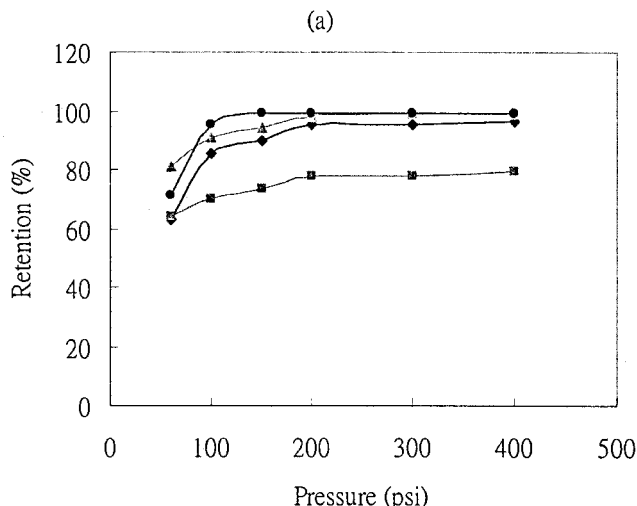


Figure 10 (a) Plot of the retention of optimized PASA_{Am} membranes (M_c) with different types of polymer membranes against applied pressure; (b) plot of the flux of optimized PASA_{Am} (M_c) with different types of polymer membranes against applied pressure (◆: PASA_{Am}; ■: PSA; △: PEA; ●: RC).

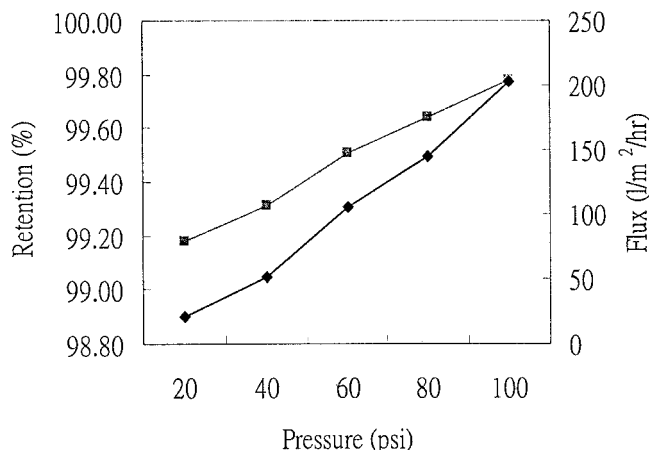


Figure 11 (a) Plot of oil retention of optimized PASA_{Am} membrane against applied pressure (■: retention; ◆: flux).

pressure, 20 psi, a one-stage separation of the 5000 ppm oil solution through the membrane generated permeated solution that could comply with the local EPD discharge limit (i.e., < 50 mg/L of effluent). Better separation could be achieved when a higher applied pressure was used. Consistent with this comparative study, PASA_{Am} outperformed PSA and PEA in and thus was a better membrane material for oil-water separation, as shown in Figure 12. In contrast to the PSA and PEA membranes, PASA_{Am} membranes not only possessed an excellent retention ability but also exhibited a much faster flux rate. A clear flux retardation took place for both PSA and PEA membranes as the concentration of oil in the feed was increased, which is indicative of the occurrence of membrane fouling. The more hydrophilic PASA_{Am} membrane appears to be less vulnerable to the fouling

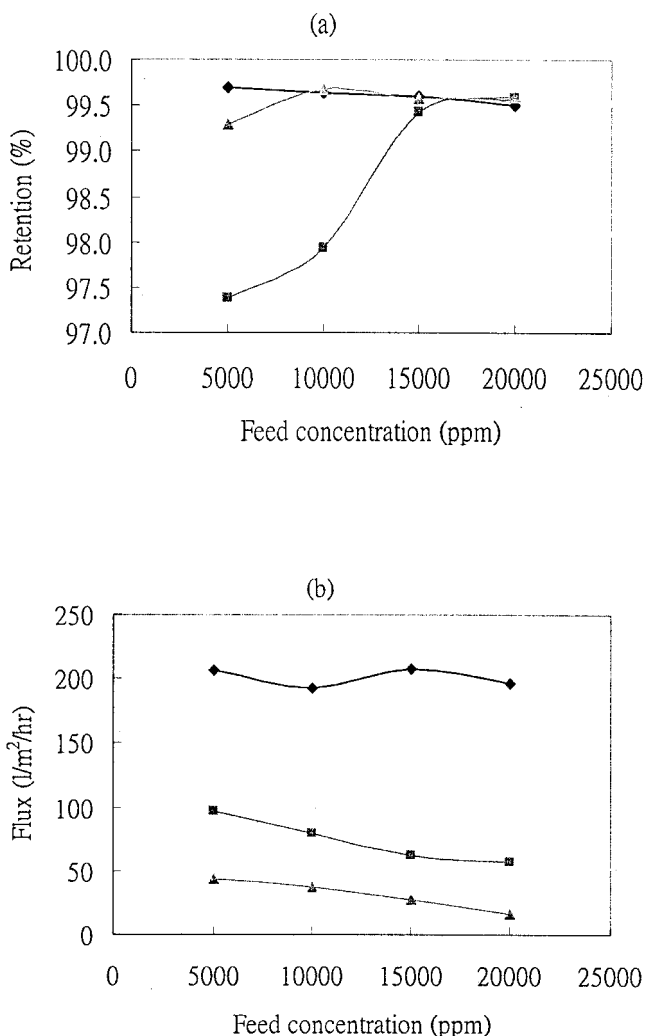


Figure 12 (a) Retention ability and (b) flux of PASA_{Am}, PSA, and PEA membranes against feed concentration of oily samples at 100 psi (◆: PASA_{Am}; ■: PSA; △: PEA).

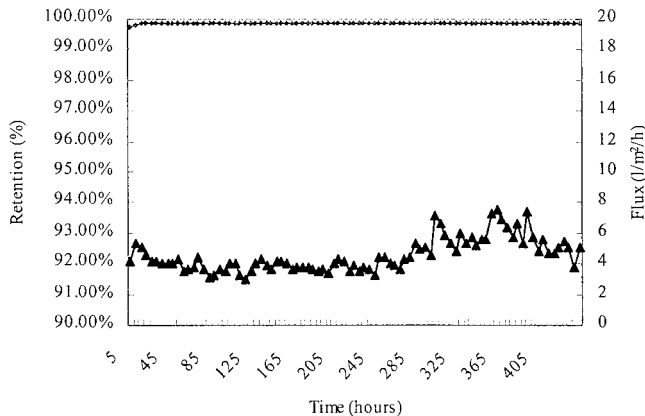


Figure 13 Plot of the performance of PASA_{Am} membranes against operating time for the permeation of 5000 ppm olive oil solution under a pressure of 2–3 psi (■: retention; ◆: flux rate).

problem. An additional durability test confirmed the suitability of using PASA for oil separation. When the membrane was subjected to a continuous run of a 5000 ppm oil feed solution, a very steady and constant flux at around 5 L m⁻² h⁻¹ and a high retention of greater than 99.8% were observed over a period of 430 h (Fig. 13). It is envisaged that PASA_{Am} is a suitable material that can be used in the NF_{Proc} process for the removal of oil from restaurant wastewater.

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