ORIGINAL ARTICLE

Preparation and characterization of interfacial polymerised membrane from 3,5-diaminobenzoic acid

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Abstract

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Preparation and characterization of interfacial polymerised membrane from 3,5-diaminobenzoic acid
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Thin Film Composite (TFC) polyamide membranes were prepared by interfacially polymerizing secondary amide (piperazine) and highly hydrophilic aromatic primary amide (3,5-diaminobenzoic acid) with trimesoyl chloride onto the polysulfone support. The salt rejection and flux of these composite membranes were measured at various feed pressures. Incorporation of the 3,5-diaminobenzoic acid cause an increase in hydraulic permeance and flux but loss in the rejection of NaCl and Na_2SO_4. Higher concentration of 3,5-diaminobenzoic acid produced a loose and defected skin layer but small quantity of 3,5-diaminobenzoic acid can improved the flux and rejection of Na_2SO_4. The reaction between the 3,5-diaminobenzoic acid, piperazine and trimesoyl chloride was further confirmed using Fourier Transform Infrared (FTIR).

Key words : 3,5-Diaminobenzoic acid, piperazine, interfacial polymerization

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Interfacial polymerization (IP) method is one of the widely used method to manufacture the thin film composite (TFC) membrane. Through this method, the skin layer and the polysulfone support layer can be optimised separately in terms of water flux and solute rejection. In the preparation of TFC membranes, attention has always been focused on how to produce a skin layer that is ultra-thin and dense. However, the polymeric material involved in the skin layer formation should be treated as equally important in membrane synthesis.

The materials used to produce the ultrathin skin layer include the aliphatic or aromatic diamine (Cadotte, 1981, Sundet 1985, Fibiger, 1988, Tomaschke, 1989), polysulfonamide (Trushinski *et al.*, 1997), aromatic diester and a combination of ester and amide group in polyesteramide (Jayarani, Kulkarni, 2000). Piperazine, m-phenylenediamine, for example, are the most popular primary and secondary diamine used in the preparation of the high rejection ultrathin reverse osmosis and nanofiltration membrane. However, the membrane produced is less hydrophilic than the conventional cellulose acetate membrane. Since a higher ratio of hydrophilicity to hydrophobicity in the polymer could result in an increase in water flux of the membranes, polymeric material with hydrophilic group would be useful for developing membranes. Introduction of amine group having a pendant carboxylic group like 3,5-diaminobenzoic acid into the polypiperazinamide backbone is expected to result in an improvement of permeability.

The research for the introduction of 3,5-diaminobenzoic acid in preparing the interfacial polymerized nanofiltration membrane is not well established. Although some RO/NF membranes have been fabricated using 3,5-diaminobenzoic acid, most of the membranes were limited to the asymmetric form and did not include thin film composite membrane. For example, Gupta prepared the asymmetric polyamide membrane from 3,5-diaminobenzoic acid with 4,4-diphenyl-dicarboxylic acid chloride, isophthaloy and terephthaloyl. The moisture regain data of the polyamides clearly indicated that polymer possesses a sufficient degree of hydrophilicity necessary for making the membranes for RO technique. The moisture regain was found to be within the range of 8.4%-8.9% (Gupta, 1997). The pendant carboxylic group of the prepared polyamides, due to its hydrophilic nature, was helpful in improving the product rate. Another researcher produced a composite reverse osmosis membrane having an active layer of copolymer from aromatic polyester (4,4'-dihydroxydiphenyl ether) with aromatic diamine of diaminobenzoic acid (Kim, 1997). The resulting composite membrane was found to have a salt rejection rate of 94% and water permeability of 2,526 l/m^2.day.

3,5-diaminobenzoyl piperazine was prepared as an dimer which was then interfacially reacted with trimesoyl chloride and/or terephthaloyl chloride to form composite reverse osmosis membrane. Compared to the wholly aromatic m-phenylene diamine membranes, the novel benzoyl piperazine membrane produced both higher water and salt transport. These membranes have performances ranging from reverse osmosis to nanofiltration and thus have utility in low pressure desalination and/or organic solute separation (Tomaschke, 1999). However, the process to synthesize these dimers is lengthy.

Co-polyamide membrane made from the mixture of m-phenylene diamine with 3,5-diaminobenzoic acid was carried at a low temperature process in dimethylacetamide to produce a highly reduced co-polymer which exhibited good reverse osmosis properties (Konagaya, 2000).

From the above findings, it can be concluded that 3,5-diaminobenzoic acid is a potential material in membrane development. The purpose of this paper therefore is to study the possibility to use the interfacially polymerization method to prepare a membrane that is improved in its flux and rejection compared to the conventional polypiperazinamide membrane.

Experimental

Material

The polysulfone (Udel P-1700) was purchased from Union Carbide. N-methylpyrrolidone and trimesoyl chloride were purchased from Fluka. Sodium sulphate, piperazine and 3,5-diaminobenzoic acid were supplied by Merck company. Triethylamine was obtained from from RDH. Sodium chloride was purchased from Mallinkrodt. Polyvinylpyrrolidone, PVP-10 (MW= 10,000) was a product of Sigma.

Preparation of thin film composite (TFC) copolyamide membranes

TFC membranes were prepared by interfacial polycondensation the reactants in both the aqueous and organic phase and form an ultraithin layer on a polysulfone microporous support. The polysulfone support was prepared by casting a 200 μm layer of polysulfone solution onto a nonwoven polyester sheet. The polysulfone solution prepared by dissolving 18 wt% of polysulfone (Udel P-1700) in N-methylpyrrolidone (NMP) with 15wt% polyvinylpyrrolidone (PVP) as a pore former. After casting, the membrane was immersed in deionised water to form the porous structure. The membrane then was kept in distilled water overnight to rinse off the excess NMP and PVP.

The aqueous solutions contain 4wt% of triethylamine and 4wt% diamines mixture [3,5-diaminobenzoic acid (BA) and piperazine (PIP)]. The mixtures of diamines are a) 4% PIP, b) 3.5% PIP+0.5%BA, c) 3%PIP+1%BA, d) 2%PIP+ 2%BA, e) 1PIP+3%BA and f) 0%PIP+4%BA.

The polysulfone membrane was taped on a glass plate, then dipped into the above aqueous diamine solution for 5 minutes at ambient temperature. The impregnated membrane was drained for 1 minute and then dipped into an n-hexane solution of 0.2%(w/v) Trimesoyl chloride (TMC) for 2 minutes. The membranes were allowed to dry under ambient condition overnight.

Membrane testing

Membrane testing was carried out in the Amicon 8200 stirred cell at three different pressures: 250kPa, 350kPa and 450kPa. Feed solutions were pure water, 0.01M NaCl solution and 0.01M Na_2SO_4 solution. The permeate concentration were measured using conductivity meter (Hanna HI8633). Each membrane underwent pressure treatment at 450kPa for 1 hour before testing and it was equilibrated for each pressure for the passage of the first 20ml. Samples was obtained for the next 10ml.

Skin sample preparation for FTIR studies

The composite membrane which consist of the non-woven polyester, polysulfone support layer and skin layer of co-polyamide was immersed into N,N-Dimethylformamide for about 5 minutes. The polysulfone and polyamide skin layer was separated from the non-woven poly-ester sheet. The layer was removed and rinsed in N,N-Dimethylformamide several times until polysulfone was totally separated from the skin layer. The remaining skin layer was filtered and washed several times with deionised water. The skin was drieded in an oven at 70°C. FTIR studies for the prepared skin layer were conducted using KBr pellet technique.

Results and Discussion

Effect of pressure on flux and rejection

Co-polyamide membranes based on the different ratios of PIP and BA were tested for the effect of pressure on both the flux and rejection. The data of flux and rejection for pure water, 0.01 M NaCl solution and 0.01 M Na_2SO_4 under the effect of different pressures for different diamine mixtures are shown in Tables 1 to 5. Figure 1 showed the plots of water flux versus operating pressure for all the membranes. The solid lines are the best fit of the data to the equation:

$$Jv = Lp(\Delta P-\Delta\pi)$$

where Lp is the hydraulic permeance ($m.s^{-1}.kPa^{-1}$), Jv is volume flux (m/s), ΔP is the trans-

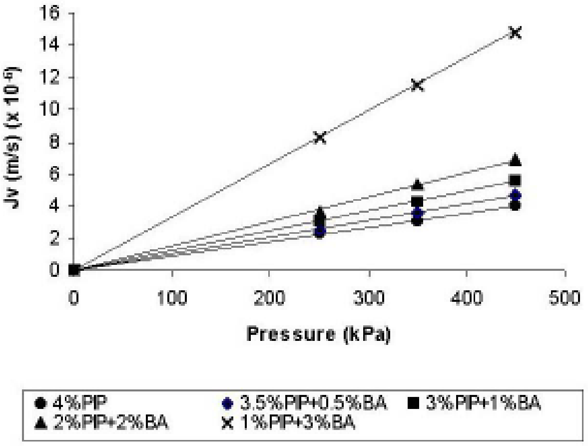

Figure 1. Effect of pressure on pure water flux for different diamine ratio membrane

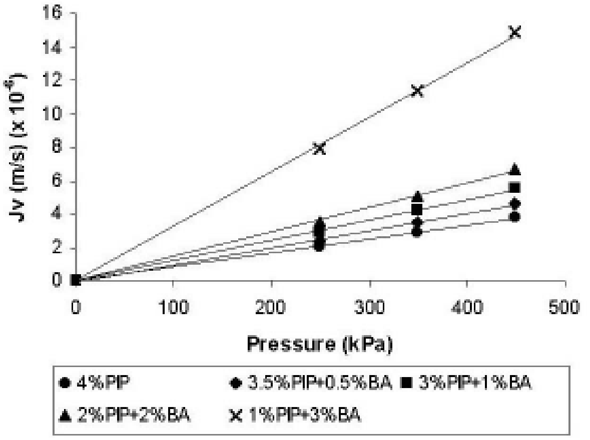

Figure 2. Effect of pressure on 0.01M NaCl flux for different diamine ratio membrane

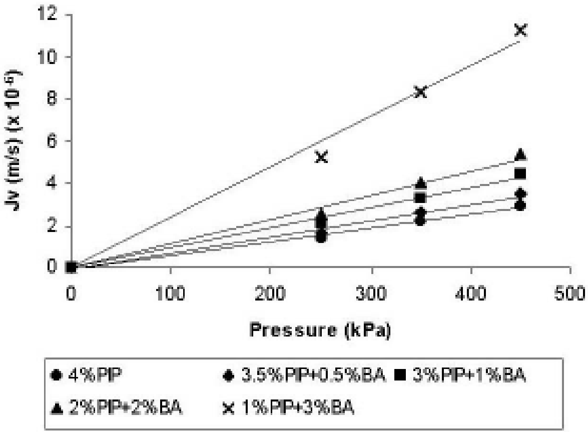

Figure 3. Effect of pressure on 0.01M Na_2SO_4 flux for different diamine ratio membrane

membrane hydraulic pressure difference (kPa).

Figure 2 and 3 also show a linear relationship between pressure and flux thus confirm the linear equation of Kimura-Sourirajan.

The effect of pressure on the solute rejection exhibits different characteristics. For NaCl, the rejection is higher as the pressure increases while for Na_2SO_4 there is not much difference in rejection in the range of pressure studied.

Effect of concentration of 3,5-diaminobenzoic acid on rejection and flux

A comparison of the rejection and flux profiles of NaCl and Na_2SO_4 for different membranes is shown in Figures 4 to 5. It was noted that, by increasing the concentration of 3,5-diaminobenzoic acid, the rejection of NaCl become poorer but the product rate was improved espec-

Table 1. Effect of pressure on flux and rejection for membranes from 4% piperazine

	Volumetric flux ($J_v \times 10^{-6}$ m/s)			Rejection (R)	
Pressure (kPa)	Pure water	0.01M NaCl	0.01M Na_2SO_4	0.01M NaCl	0.01M Na_2SO_4
0	0	0	0	0	0
250	2.29	2.03	1.39	0.3289	0.9655
350	3.07	2.87	2.17	0.3757	0.9715
450	4.06	3.76	2.92	0.4184	0.9702

Table 2. Effect of pressure on flux and rejection for membranes from 3.5% piperazine and 0.5% 3,5-diaminobenzoic acid

	Volumetric flux ($J_v \times 10^{-6}$ m/s)			Rejection (R)	
Pressure (kPa)	Pure water	0.01M NaCl	0.01M Na_2SO_4	0.01M NaCl	0.01M Na_2SO_4
0	0	0	0	0	0
250	2.45	2.40	1.63	0.2829	0.9560
350	3.62	3.47	2.57	0.3192	0.9780
450	4.73	4.64	3.49	0.3539	0.9728

Table 3. Effect of Pressure on Flux and Rejection for Membranes from 3%Piperazine and 1% 3,5-diaminobenzoic acid

	Volumetric flux ($J_v \times 10^{-6}$ m/s)			Rejection (R)	
Pressure (kPa)	Pure water	0.01M NaCl	0.01M Na_2SO_4	0.01M NaCl	0.01M Na_2SO_4
0	0	0	0	0	0
250	3.05	2.91	2.09	0.2676	0.8603
350	4.26	4.21	3.24	0.2902	0.8628
450	5.59	5.55	4.44	0.3144	0.8490

Table 4. Effect of Pressure on Flux and Rejection for Membranes from 2%Piperazine and 2% 3,5-diaminobenzoic acid

	Volumetric flux ($J_v \times 10^{-6}$ m/s)			Rejection (R)	
Pressure (kPa)	Pure water	0.01M NaCl	0.01M Na_2SO_4	0.01M NaCl	0.01M Na_2SO_4
0	0	0	0	0	0
250	3.64	3.50	2.52	0.1788	0.9142
350	5.38	5.03	3.96	0.2063	0.9025
450	6.87	6.69	5.41	0.2167	0.8952

ially at 3% 3,5-diaminobenzoic acid where a tremendous increase in flux observed. The hydraulic permeance Lp increased by the increased of BA contents. Lp was determined from the slope of pure water flux versus transmembrane pressure. The data are shown in Table 6.

This phenomenon might due to the less dense membrane produced from 3,5-diaminobenzoic acid resulting from the bigger average pore size. Another interesting feature observed here is that although the product rate increased, Na_2SO_4 permeation test showed that the loss of rejection ability is not significant as compared to the NaCl. This can be explained if both the steric effect and charge effect on charged solutes transport across negatively charged membrane were

Table 5. Effect of Pressure on Flux and Rejection for Membranes from 1%Piperazine and 3% 3,5-diaminobenzoic acid

	Volumetric flux ($J_v \times 10^{-6}$ m/s)			Rejection (R)	
Pressure (kPa)	**Pure water**	**0.01M NaCl**	**0.01M Na_2SO_4**	**0.01M NaCl**	**0.01M Na_2SO_4**
0	0	0	0	0	0
250	8.30	7.88	5.25	0.0845	0.8684
350	11.59	11.36	8.31	0.0957	0.8766
450	14.85	14.91	11.23	0.1224	0.8676

Table 6. Effect of %BA on the Hydraulic Permeance

%BA	%PIP	Lp ($m.s^{-1}.kPa^{-1}$) × 10^{-2}
0	4	0.8965
0.5	3.5	1.0353
1	3	1.2304
2	2	1.5184
3	1	3.3072
4	0	*a*

***a* : Membrane produced not stable to be tested**

considered. The diffusion coefficient for NaCl is 1.61×10^{-9} m^2s^{-1} while for Na_2SO_4 the diffusion coefficient is 1.23×10^{-9} m^2s^{-1} and the effective size for NaCl and Na_2SO_4 are 0.15nm and 0.20nm respectively (Schaep, 2001). From the diffusion coefficient and effective size data, it is not difficult to understand that the rejection of NaCl is poorer than that of Na_2SO_4.

On the basis of Donnan-exclusion, a higher co-ion valence will cause a higher salt retention. For charged components an electrostatic interaction takes place between the component and the membrane, as most nanofiltration membranes are charged (mostly negative). As a result, the co-ions SO_4^{2-} with valency –2 are highly retented compare to Cl^- which only have valency –1. By increasing the pore size, the steric hindrance effect was reduced. However, in this case there is no drastic drop or maintained rejection of Na_2SO_4 ; this might be due to the steric hindrance loss being counter-balanced by the increasing electrostatic hindrance because of the increasing charge density produced by the of 3,5-diaminobenzoic acid. The rejection profile of Na_2SO_4 is clearly shown in Figure 5.

Addition of small amount of 3,5-diaminobenzoic acid can improved the flux as well as the rejection of co-ions. This is shown in the Figure 6 that a mere 0.5% 3,5-diaminobenzoic acid improved both the rejection of Na_2SO_4 and product rate, but at higher loading concentration the increase in flux was followed by a drop in rejection. However, this phenomenon is not shown in Figure 7 for 1-1 monovalence NaCl salt. For this 1-1 valency NaCl solution, as the BA concentration increased, the flux also increased but the rejection ability dropped. A higher concentration of 3,5-diaminobenzoic acid is not practical because a membrane with surface defect will occur due to the less stable and highly gelled nature of the polyamide from this material.

FTIR bonding confirmation

The polycondensation of piperazine, 3,5-diaminobenzoic acid and trimesoyl chloride which produced the polyamide structure was confirmed using the Fourier Transform Infrared (FTIR) method. Figure 8 shows the FTIR spectrum of polyamide membrane skin layer formed by 4% Piperazine and 2%Piperazine + 2% 3,5-diaminobenzoic acid. The representative amides functional groups like C=O ($1609cm^{-1}$ – $1618cm^{-1}$) and C-N ($1403cm^{-1}$-$1494cm^{-1}$) are found. Since the

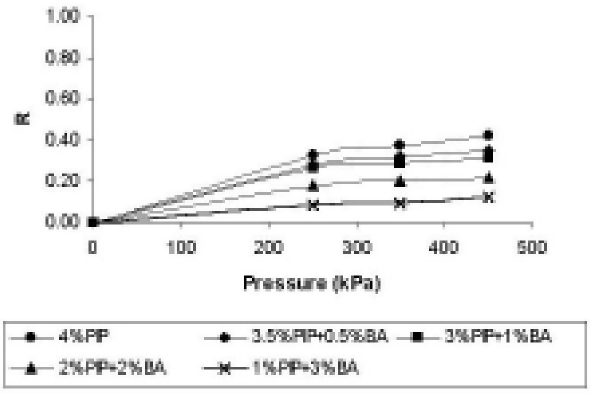

Figure 4. **Effect of pressure on rejection of 0.01M NaCl for different diamine ratio membrane**

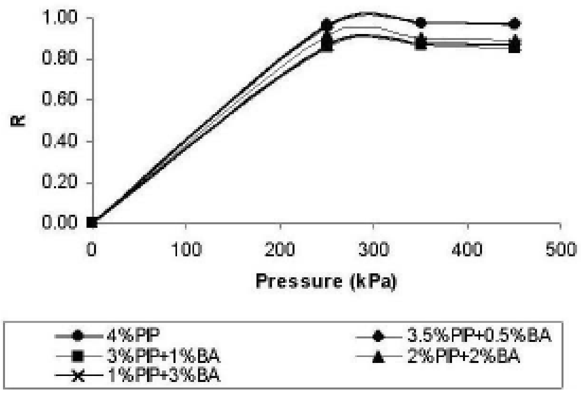

Figure 5. **Effect of pressure on rejection of 0.01M Na_2SO_4 for different diamine ratio membrane**

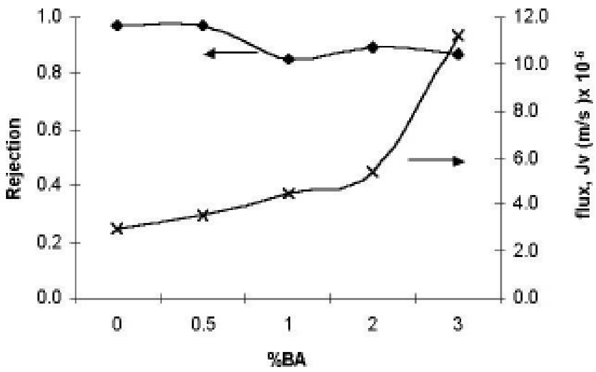

Figure 6. **Effect of concentration of 3,5-diaminobenzoic acid on rejection and flux for 0.01M Na_2SO_4 solution**

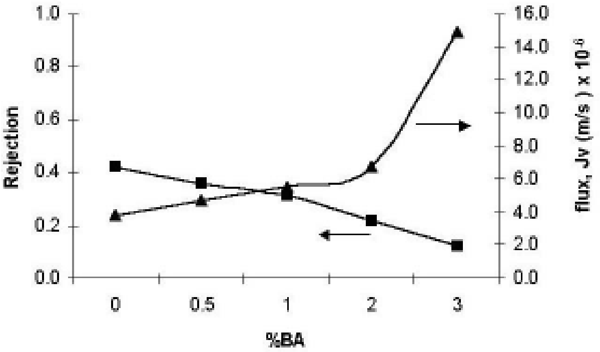

Figure 7. **Effect of concentration of 3,5-diaminobenzoic acid on rejection and flux for 0.01M NaCl solution**

unreacted carbonyl chloride will be hydrolised to form carboxylic group also, carboxylic group is not a suitable indicator to prove the incorporation of 3,5-diaminobenzoic acid into the polypiperazinamide backbone. However, the crosslinking product between piperazine and trimesoyl chloride will produce only secondary amide –CONR- (without –NH group) while the crosslinking product between trimesoyl chloride, piperazine and 3,5-diaminobenzoic acid will produce both the primary (-CONHR-) and secondary amides group. The –NH group can only be found around the wavenumber 3736cm^{-1}, 3018cm^{-1} and 1550cm^{-1} in membranes with 3,5-diaminobenzoic acid. The –OH (3436cm^{-1}) and C=O (1609cm^{-1} – 1618cm^{-1}) which is found in both membranes proved the existence of carboxylic acid in both formulations. These spectra confirmed that polyamide layer was formed and the reaction between 3,5-diaminobenzoic acid and trimesoyl chloride really took part although 3,5-diaminobenzoic acid alone formed a very gelled/unstable skin structure.

Conclusion

By incorporating 3,5-diaminobenzoic acid in the diamine mixture, product rate was in-

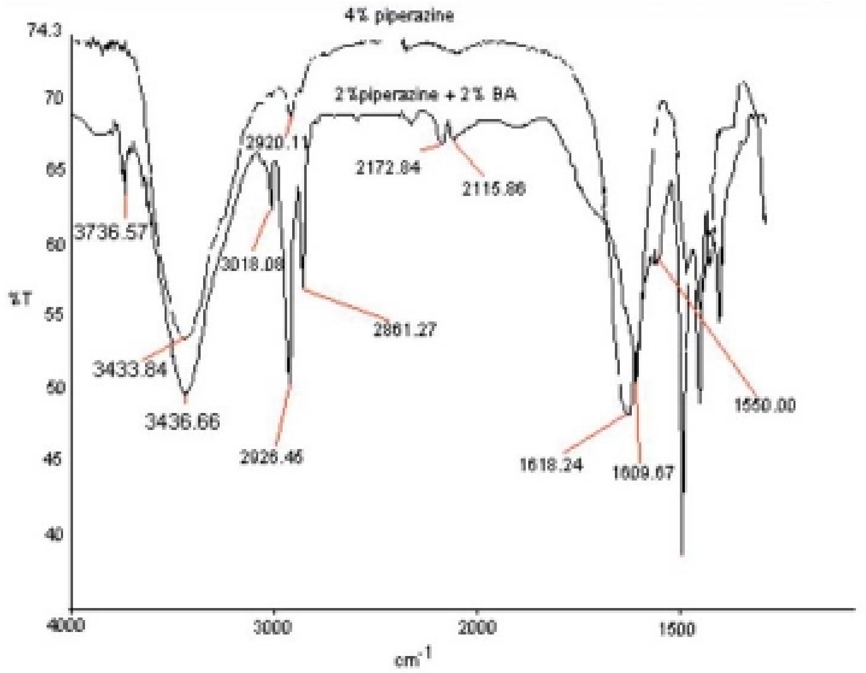

Figure 8. FTIR spectrum of thin film polyamide with 4% PIP and 2% PIP + 2% BA

creased. However, the retention ability for NaCl was reduced indicating that a loose structure of skin layer was obtained. The effect of BA on retention of Na_2SO_4 is less significant than that of NaCl which implies that anionic surface charge density increased and counter-balanced the loss of rejection due to the poor steric hindrance of thin film layer. Higher content of 3,5-diaminobenzoic acid produced a defective skin layer but a small amount of 3,5-diaminobenzoic acid can improve both the flux and rejection of Na_2SO_4. The defective skin layer gave a very poor performance membrane especially in NaCl separation.

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