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Preparation and Performance Optimization of a Composite Charged Mosaic Membrane *via* Interfacial Polymerization

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A composite charge-mosaic membrane was prepared *via* interfacial polymerization by coating a thin selective layer onto the surface of a micro-porous polyethersulfone hollow fiber membrane. 2,5-Diaminobenzene sulphonic acid, polyethylemine and trimesoyl chloride were selected as the monomers and 4-(chloromethyl) benzoyl chloride and trimethyl amine as the chemical modification agents. The process was optimized by means of uniform design and the model was in good agreement with the experimental data. For the binary mixtures, the rejection for the inorganic salts was less than 30 % and the rejection for sucrose was approximately 90 %. The separation performance in the ternary mixtures was also studied and the separation factor decreased with the increasing of salt concentration and the interaction between salt and organics had some effect upon separation factor. Finally, the results of SEM and atomic force microscope showed that a dense selective layer on the support membrane was formed after interfacial polymerization.

Key Words: Composite charged mosaic membrane, Interfacial polymerization, Optimization, Uniform design.

INTRODUCTION

For the separation of salts and organics, conventional nanofiltration (NF) technologies have been used. The monovalent salts, such as NaCl or NaOH, could pass through the nanofiltration membrane, while organics are retained[1]. For the object to be dealt with bivalent salts and organics, nanofiltration membranes could not achieve very low rejection for bivalent salts and high rejection for organics with molecular weights of 200-1000 dalton[2]. On the contrary, a charged mosaic membrane is likely more applicable.

The concept of a charged mosaic membrane was first proposed by Sollner[3]. A charged-mosaic membrane consists of a set of anion and cation exchange elements regularly arranged and separated by the neutral matrix, each element providing a continuous pathway from one bathing solution to the other. When pressure and concentration gradient are established across the membrane, the anions and the cations of electrolytes can flow in parallel through their respective pathways without a violation of macroscopic electro neutrality, resulting in a circulation of current between the individual ion-exchange elements. As a result, the charge-mosaic membrane shows greater permeability of salts than that of the non-electrolytes[4]. At the early study stage of mosaic membrane, Weinstein and Caplan[5] prepared a model membrane by embedding cation-exchange beads and anion-exchange beads in a silicone rubber matrix. Since then, many attempts have been reported to prepare charged mosaic membranes by chemical modifications of a two-phase polymer system, such as, multiblock copolymers[6,7], laser-induced graft polymerization[8-10] and polymer blends[11-15]. In recent years, a novel hybrid charged mosaic membranes have been prepared through a coupling reaction and zwitterionic process[16,17]. Higa *et al*.[18] reported the preparation of charged mosaic membranes from laminated structures of charged poly (vinyl alcohol) (PVA) membranes, which had potential applications to desalination of salt water at low salt concentrations.

These studies can greatly promote the progress of charged mosaic membrane, but most of them are quite complicated, time consuming and the flux of membranes were lower because the membranes were thicker in general. In early studies, the charged mosaic membrane with a thin selective layer on a support membrane was fabricated by interfacial polymerization[4,19-23].

Based on early studies, the aim of this paper is to optimize the preparation conditions of the composite charge-mosaic membrane. The uniform design method will be applied and the experimental data will be processed by SPSS software so as to obtain the model that can be used to calculate the effect of various factors on the separation performance of the composite charge-mosaic membrane. In addition, the morphology of the charged mosaic membrane is observed by SEM and atomic force microscope.

EXPERIMENTAL

Chemicals used for membrane preparation were commercially purchased, including polyethersulfone (PES) (Uitrason E6020p, Amoco Research Center), trimesoyl chloride (TMC), 4-(chloromethyl) benzoyl chloride, polyethylemine (PEI) (Acros organics) and 2,5-diaminobenzene sulfonic acid (DIA) (Fluka). Moreover, *N*-dodecane, trimethylamine, sodium dodecyl sulfate (SDS) and other chemicals were purchased from Shanghai Chemical Reagents Co., National Pharmaceutical Group of China. Polyethersulfone hollow fiber support membrane was prepared using a spinning machine in our lab. The inner diameter of membrane was 0.63 mm. The fiber thickness was 0.35 mm. Water flux of the support membrane was measured as 300-350 L m^{-2} h^{-1} under 0.1 MPa.

Fabrication of composite charged mosaic membrane: Firstly, amine solution including 2,5-diaminobenzene sulfonic acid and polyethylemine was introduced into the lumen side of polyethersulfone hollow fibers and the excess amount of solution on the surface of the substrate was released after maintaining 0.5 h. And then, *N*-dodecane solution including trimesoyl chloride and 4-(chloromethyl) benzoyl chloride was brought in contact with the impregnated hollow fibers and the interfacial polymerization was carried out. A selective layer on the support membrane was formed after interfacial polymerization. Next, polyethersulfone hollow fibers with a selective layer were immersed in a 5 % trimethylamine solution for 24 h to convert the chloromethylated groups into cationic quaternary ammonium groups and the composite charged mosaic membranes were prepared successfully. In order to promote interfacial polymerization reaction, sodium dodecyl sulfate (SDS) was used as a surfactant, sodium hydroxide and sodium carbonate as an acid receptor. Principle of interfacial polymerization reaction was shown in Fig. 1 and the interfacial polymerization device for hollow fiber membranes was shown in Fig. 2.

Membrane characterization

Characterization of membrane separation performance: The device of membrane separation performance was shown in Fig. 3, which was used to measure the flux and rejections for different solutes. Several kinds of salts were used, including NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. The initial concentrations of all the salts were 0.01 mol L^{-1}. The concentration of the salts was measured by microprocessor conductivity meter (Model LF 537, Wissenshaftlish-Technische Werkstatten and Germany). Moreover, four kinds of low molecular weight organics were used in our experiment, including xylenol orange (M = 760.6 g/mol, negatively charged), nitroso-R-salt (M=377.2 g/mol, negatively charged), sucrose (M = 342 g/mol) and glucose (M = 180 g/mol). The initial concentrations of all the organics were 500 mg L^{-1}. The concentrations of all the organics were measured by a UV/VIS scanning spectrophotometer (PU 8720, Philips). In general, the pressure of feed inlet and outlet was 0.4 and 0.36 MPa, respectively. About 4 L of feed was pumped in the test loop with the constant temperature bath to keep feed at 25 ± 1 ºC. Inlet and outlet pressures in the membrane module were adjusted by pump variable speed motor and outlet valve.

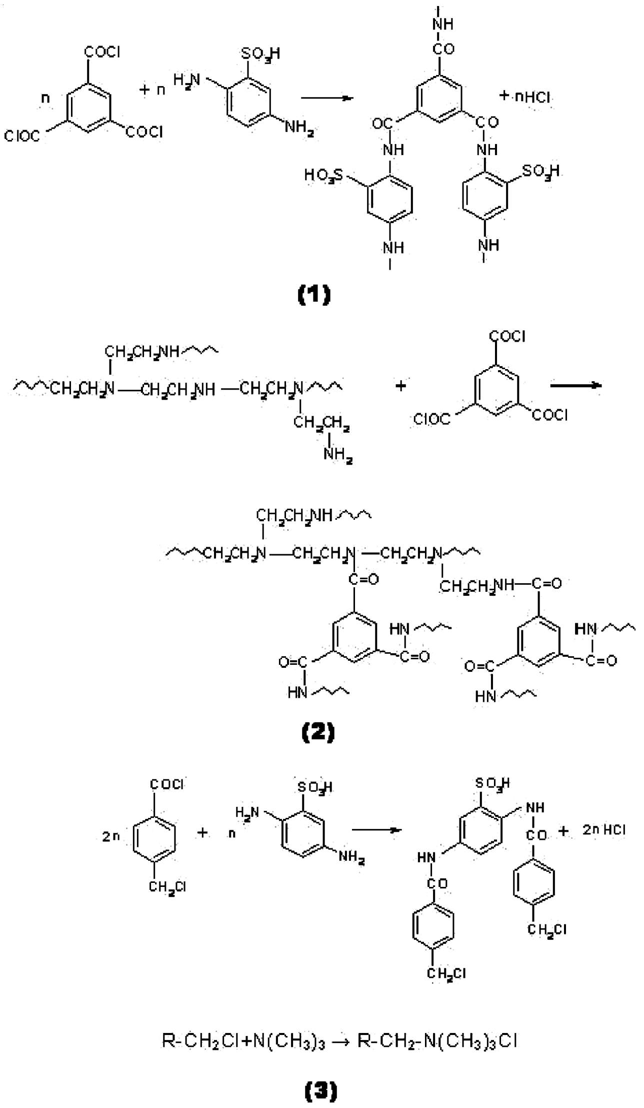

Fig. 1. Schematic illustration of interfacial polymerization for the charged mosaic membrane

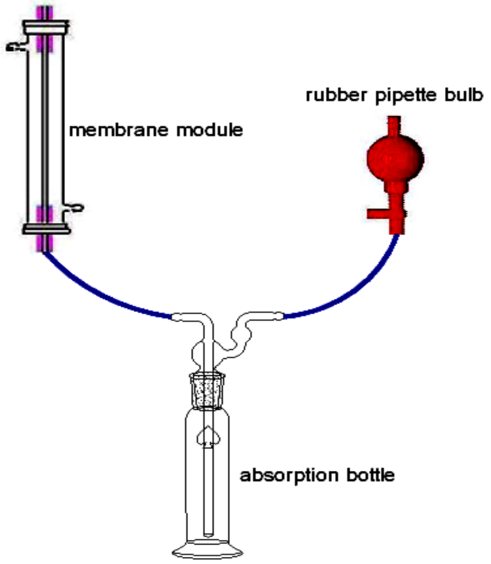

Fig. 2. Schematic diagram of experimental setup for the interfacial polymerization of hollow fiber membrane

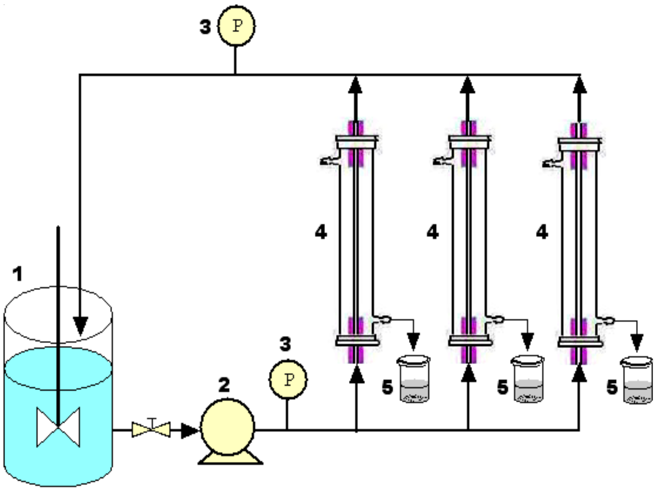

Fig. 3. Schematic diagram of device for the flux and rejection (1 feed tank; 2 pump; 3 pressure gauge; 4 membrane module; 5 permeate collector)

Permeation fluxes of membranes were obtained as follows:

$$J_V = V/(A \times t) \quad (1)$$

where, J_v is the permeation flux of membrane (L m^{-2} h^{-1}); V is the volumetric flow rate of permeate (m^3); A is the active area of membrane (m^2); t is the time (h).

Rejection of the membranes was defined as:

$$R = (1-C_p/C_f) \times 100 \% \quad (2)$$

where, R is the rejection; C_f and C_p represent the concentration of feed and permeate, respectively.

In addition, for the salt/organic/water mixture system, the membrane selectivity for the salt and organic is usually expressed as the separation factor (α) (eqn. 3).

$$\alpha = \frac{1-R_A}{1-R_B} \quad (3)$$

In the eqn. 3, R_A is the rejection of salt; R_B is the rejection of organics.

Characterization of membrane structure and morphology: FT-IR spectra of step products were obtained by using a Bruker Vector-22 Fourier transform infrared spectrometer in the region of 4000-400 cm^{-1}. The morphology of the membranes was examined by a field emission scanning electron microscopy (FESEM) using a JEOL FE-SEM JSM 6400-F scanning microscope. The atomic force microscope (AFM, Nanoscropy IIIa, America) was performed in the air using an X imaging system with cantilevers operating in the intermittent-contact mode (AAC mode), slightly below their resonance frequency of approximately 290 kHz in the air.

Experiment design: All the experiments were optimized by means of uniform design principles[24] and the results and experimental data were processed and analyzed by SPSS software to obtain qualitative and quantitative results. Under optimized conditions, the charged mosaic membrane was prepared.

RESULTS AND DISCUSSION

Optimization of preparation conditions: In the preparation process of charged mosaic membrane *via* interfacial polymerization, the monomer composition, the types and amount of additives, interfacial polymerization time have an important influence on the membrane performance. In our previous study[21], the appropriate concentrations of trimesoyl chloride and 2,5-diaminobenzene sulfonic acid have been obtained, selecting the concentration of trimesoyl chloride and 2,5-diaminobenzene sulfonic acid as 2.0 % and 1.0 %, respectively. In this study, the effect of interfacial polymerization time (x_1), surfactant concentration (x_2), concentration of acid receptor (x_3), 4-(chloromethyl) benzoyl chloride concentration (x_4) and polyethylemine concentration (x_5) on the membrane separation performance was mainly studied. In the experiment, five factors were investigated and each factor selected five levels based on preliminary experimental results. Therefore, $U^*_{10}(10^8)$ was used as the table of uniform design and the five factors were organized in the columns 1, 3, 4, 5 and 7 according to the principle.

The separation of Na_2SO_4 (0.01 mol L^{-1}) and glucose (500 mg L^{-1}) in the Na_2SO_4/glucose/water system was selected as the research object and the effect of various factors on separation performance of the composite charged mosaic membrane was studied in detail using uniform design method. The uniform design scheme and experiment results were listed in Table -1. And then, the experimental data was carried out regression analysis by means of SPSS software.

TABLE 1
SCHEMES OF UNIFORM DESIGN AND THE RESULTS

Run	x_1 (min)	x_2 (w %)	x_3 (w %)	x_4 (w %)	x_5 (w %)	α
1	2	0.10	0.40	1.5	1.7	1.70
2	2	0.15	0.50	2.5	1.4	2.340
3	5	0.25	0.35	1.0	1.1	3.330
4	5	0.05	0.45	2.5	0.8	2.800
5	8	0.10	0.55	1.0	0.5	2.500
6	8	0.2	0.35	2.0	1.7	3.340
7	11	0.25	0.45	0.5	1.4	3.260
8	11	0.05	0.55	2.0	1.1	2.240
9	14	0.15	0.40	0.5	0.8	1.400
10	14	0.20	0.50	1.5	0.5	1.300

x_1: Interfacial polymerization time; x_2: Surfactant concentration; x_3: Concentration of acid receptor; x_4: 4-(Chloromethyl) benzoyl chloride concentration; x_5: polyethylemine concentration

Regression equation of separation factor was selected as follows:

$$\alpha = b_0 + \sum_{i=1}^{m} b_i x_i + \sum_{i=1}^{m}\sum_{j=1}^{m} b_{ij} x_i x_j \quad (4)$$

Regression analysis was carried out using backward method and the results were listed in Tables 2-4. The correlation coefficient in Table-2 and F-value in Table-3 showed that the model regression was very significant. In Table-4, the results of t test showed that significance level of each coefficient was higher. The model equation (eqn. 5) was obtained by nonstandard regression coefficient.

$$a = 2.363 + 0.168\ x_1 - 0.0241\ x_1^2 + 15.85 x_2^2 + 0.0543 x_4^2 - 0.993\ x_5 + 0.149\ x_5 x_1 \quad (5)$$

The comparison of model calculation and experimental values was shown in Table-5. The results showed that the model values were in good agreement with the experimental results.

Selection the optimal conditions: From eqn. 5, surfactant concentration (x_2) and 4-(chloromethyl) benzoyl chloride concentration (x_4) should take the maximum. Herein, surfactant was mainly used to improve the contact conditions of two phases and 4-(chloromethyl) benzoyl chloride were used to introduce the anion-exchange groups. However, as 4-(chloromethyl) benzoyl chloride belongs to be a compound of single functional degree which led to terminating effect on interfacial polymerization reaction, so 4-(chloromethyl) benzoyl chloride should be limited to some extent.

TABLE 2
MODEL SUMMARY IN SPSS FOR THE SEPARATION FACTOR

R	R^2	Corrected R	SD
0.997	0.994	0.981	0.108

TABLE-3
ANOVA IN SPSS FOR THE SEPARATION FACTOR

Source	SS	df	MS	*F*-value	Significance level
Regression sum of square	4.844	6	0.807	343.8	0.000
Residual sum of square	0.007	3	0.002		
Sum	4.851	9			

TABLE 4
COEFFICIENTS IN SPSS FOR THE SEPARATION FACTOR

	Nonstandard regression coefficient	Standard regression coefficient	t	Significance level
Constant	2.363		12.90	0.001
x_1	0.168	1.024	5.24	0.014
x_5	-0.993	-0.605	-9.45	0.003
x_1x_1	-0.0241	-2.403	-18.46	0.000
x_2x_2	15.85	0.493	18.19	0.000
x_4x_4	0.0543	0.169	5.94	0.010
x_1x_5	0.149	1.025	12.62	0.001

x_1: Interfacial polymerization time; x_2: Surfactant concentration; x_3: Concentration of acid receptor; x_4: 4-(Chloromethyl) benzoyl chloride concentration; x_5: polyethylemine concentration

In addition, by eqn. 5, there is an obvious interaction between polyethylemine concentration and the interfacial polymerization time. The partial derivative of eqn. 5 for x_1 and x_5 is shown as follows:

$$0.168-2 \times 0.02407\ x_1 + 0.149x_5 = 0 \tag{6}$$

$$-0.993 + 0.149\ x_1 = 0 \tag{7}$$

Combining partial derivative equations (eqns. 6 and 7), x_1 ($x_1 = 6.664$) and x_5 ($x_5 = 1.026$) could be obtained.

The effect of interfacial polymerization time on the separation factor was shown in Fig. 4 by analyzing eqn. 5. With the interfacial polymerization reaction time increasing, the rejection for salts decreased. The possible reasons were as follows: the thickness of selective layer increased, the pore size of the membranes became smaller resulting in increasing the rejection, charged capacity of the membranes would also increase resulting in the decrease of the salt rejection. The effect of the interfacial polymerization time on the structure of the membranes was very complex, thereby affecting the separation factor, so there was a maximum. It should be noted that the selective layer thickness of the upward trend became slow in later stage reaction owing to the self-inhibition of the interfacial polymerization.

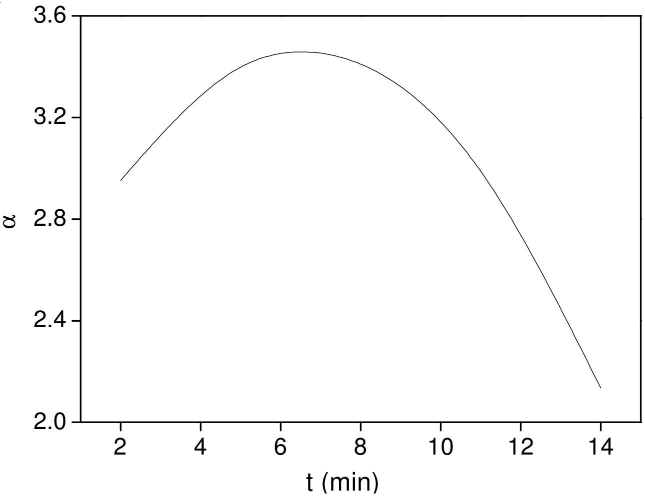

Fig. 4. Effect of interfacial polymerization time on the separation factor

As polyethylemine concentration increased, the amount of positive charge in the membrane increased. The optimal condition is that the amount of positive charge is equal to the amount of negative charge of 2,5-diaminobenzene sulfonic acid. Moreover, from eqn. 5, the concentration of acid receptor had little impact on the separation factor. From the reaction mechanism, the acid receptor was mainly used to neutralize generated HCl in the interfacial polymerization, which was very important to enhance the reaction rate and the degree of polymerization and it should be taken as 0.45 %. Under the optimal condition, the average separation factor was 3.12. The value was closer to the model prediction, which showed that the regression equation could be used for the calculating separation performance of the charge-mosaic membrane.

Separation performance of composite charged mosaic membrane: In the operating pressure of 0.4 MPa at 25 ºC, the separation performance of the composite charged mosaic membrane was tested in detail. The flux and rejections for salts and organics was listed in Table-6. The results showed that the rejections of the bivalent salts were greater than that of the monovalent salts, but the maximum did not exceed 30 %. The rejection of sucrose was close to 90 % and the rejection of xylenol orange was up to 96 %. Therefore, the composite charged mosaic membrane could be used for the separation of inorganic salts and low molecular weight organics. Compared with the charged mosaic membrane prepared by other approaches, the composite charged mosaic membrane *via* interfacial polymerization could achieve higher flux at a lower

TABLE-5
COMPARISON OF THE THEORETICAL VALUES WITH EXPERIMENTAL VALUES

	1	2	3	4	5	6	7	8	9	10
Experimental values	1.70	2.34	3.33	2.80	2.50	3.34	3.26	2.24	1.40	1.30
Theoretical values	1.702	2.340	3.373	2.782	2.479	3.356	3.207	2.266	1.242	1.300
Fractional error (%)	+ 0.12	0	+ 1.30	- 0.64	- 0.84	+ 0.48	- 1.6	+ 1.2	- 11.3	0

TABLE 6
FLUX AND REJECTIONS OF THE CHARGE-MOSAIC MEMBRANES

	H_2O	NaCl	Na_2SO_4	$MgCl_2$	$MgSO_4$	Nitroso-R-salt	Xylenol orange	Sucrose	Glucose
J_v (L m^{-2} h^{-1})	63.4	58.8	41.5	40.2	36.1	31.5	18.0	43.6	43.5
R (%)		15.2	26.2	24.6	25.0	80.66	96.3	90.4	76.4

operating pressure owing to the thin selective layer and small resistance.

It was noteworthy that although the molecular weight of nitroso-R-salt is greater than the molecular weight of sucrose, the rejection of nitroso-R-salt is less than that of sucrose, since the charged material could pass through charged mosaic membrane more easily than the neutral material. This phenomenon is consistent with transfer law of the charged mosaic membrane. Although the xylenol orange features a negative charge in aqueous solution, its rejection is still higher because of its large molecular weight. It is not difficult to see that the sieve effect and Donnan effect are two important factors for impacting the separation performance of the charged mosaic membrane.

The effect of operating pressure on the flux and rejection was also studied and the results were shown in Figs. 5 and 6. Fig. 5 showed that the permeation flux was basically proportional to the operating pressure. Fig. 6 showed that the rejections of salts increased with the increase of the operating pressure. For the organics, the operating pressure had little impact on the rejection. It could be expected that, for the separation of organics and inorganic salts, as the operating pressure increased, the permeation flux increased, but the selectivity decreased. Therefore, a good separation result of organics and inorganic salts could be obtained by selecting the appropriate operating conditions.

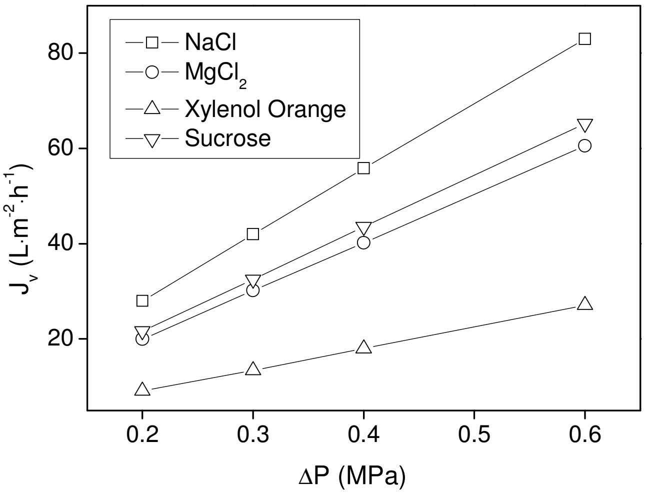

Fig. 5. Effect of operating pressure on the flux

The effect of NaCl concentrations on the separation factor for mixtures of dyes and NaCl was shown in Fig. 7. The results showed that the separation factor of xylenol orange and NaCl was higher than that of nitroso-R-salt and NaCl because of the molecular weight of xylenol orange (M = 760.6) was higher than the molecular weight of nitroso-R-salt (M = 377.2). The effect NaCl and Na_2SO_4 concentrations on the separation factor for mixtures of various sugars and NaCl was shown in Fig. 8 and Fig. 9, respectively. Similarly, the separation factor of sucrose and salts was higher than that of glucose and salts because of the large molecular weight of sucrose. However, with the increase in the concentration of inorganic salts, all the separation factors decreased and a great amount of salt might improve the ion exchange groups on the attraction of ions in the solution resulting in the double charged layer channel within the membrane pores larger.

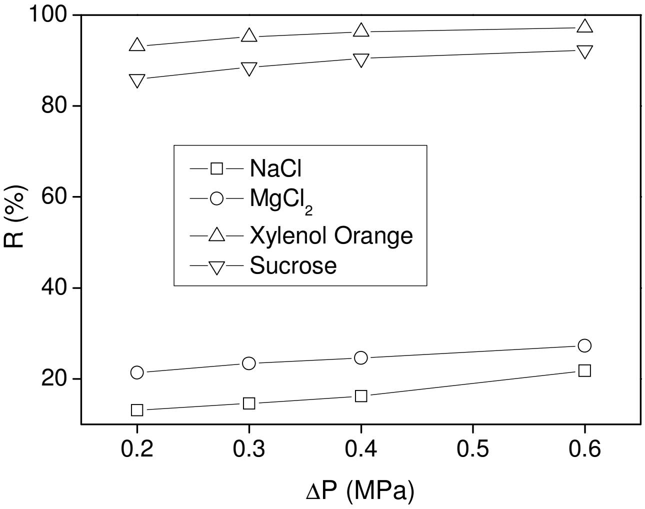

Fig. 6. Effect of operating pressure on the rejection

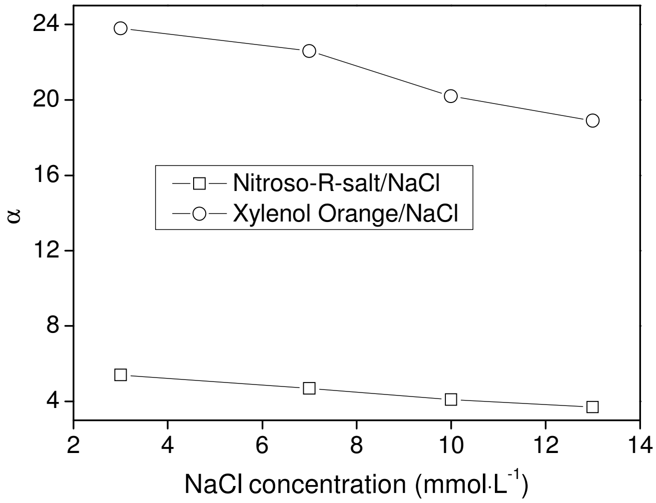

Fig. 7. Effect of NaCl concentrations on the separation factor for mixtures of various dyes and NaCl

Compared with other charged mosaic membrane prepared by other methods, the composite charged mosaic membranes prepared by interfacial polymerization in this study had the good selectivity and higher flux (Table-7).

Morphology and structure of composite charged mosaic membrane: Fig. 10 shows the FT-IR spectrum of the interfacial polymerization between trimesoyl chloride and

TABLE 7
COMPARISON OF SEPARATION PROPERTIES OF VARIOUS CHARGED MOSAIC MEMBRANES

Methods	Operating pressure (MPa)	Flux ($m^3 m^{-2} s^{-1}$)	Selectivity	Reference
Multiblock copolymer	3	2.8×10^{-8}	J_s(KCl)/J_s(sucrose) = 200	[7]
Irradiation grafting	10.5	1.7×10^{-6}	J_s(carbamide) ≈ 0	[25]
	-	7.8×10^{-8}	J_s(KCl)/J_s(sucrose) = 70	[26]
Blend	4	8.5×10^{-6}	R(Na_2SO_4) < 20; R(sucrose) > 90	[10]
Interfacial polymerization	0.4	1.72×10^{-5}	R(Na_2SO_4) < 26; R(sucrose) > 90	This study

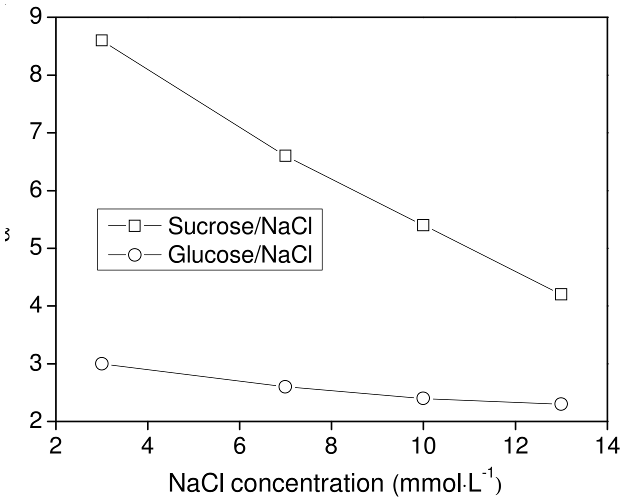

Fig. 8. Effect of NaCl concentrations on the separation factor for mixtures of various sugars and NaCl

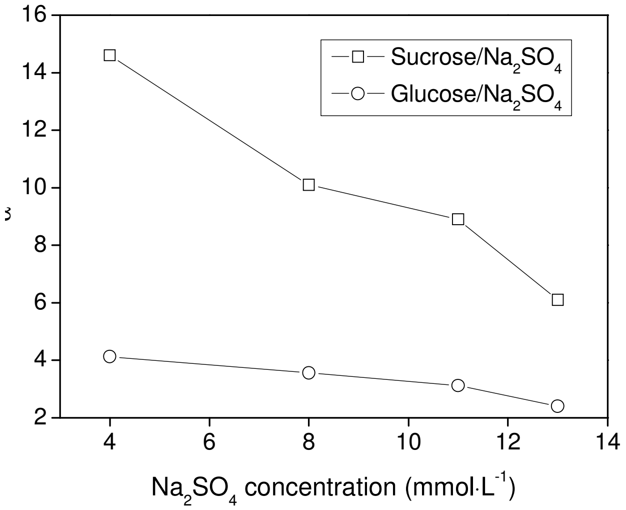

Fig. 9. Effect of Na_2SO_4 concentrations on the separation factor for mixtures of various sugars and Na_2SO_4

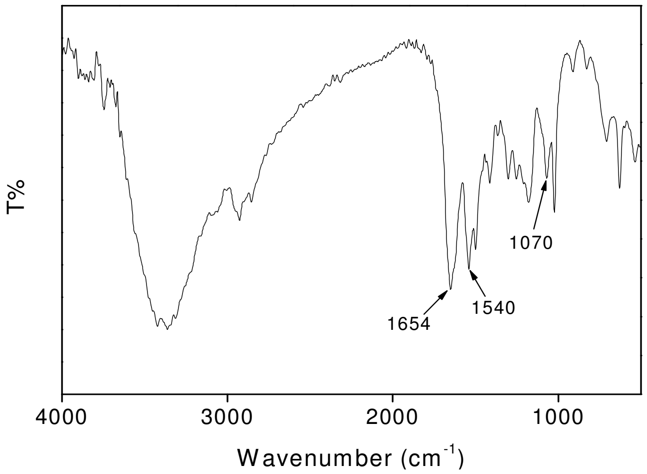

Fig. 10. FT-IR spectrum of the interfacial polymerization between trimesoyl chloride and 2,5-diaminobenzene sulfonic acid, polyethylemine

2,5-diaminobenzene sulfonic acid, polyethylemine, in which the characteristic absorption peaks of -CON-, $-NH_2$ and $-SO_3H$ appear at 1654, 1540 and 1070 cm^{-1}, respectively. This result showed that the interfacial polymerization successfully took place between trimesoyl chloride and 2,5-diaminobenzene sulfonic acid, polyethylemine. Fig. 11 shows the surface morphology of the support membrane and the composite charge mosaic membrane. Fig. 12 shows the atomic force microscope images of the support membrane and the composite charge mosaic membrane. The surface of the composite charge mosaic membrane became dense, smooth and uniform after interfacial polymerization. Obviously, a good selective layer on the support membrane was formed successfully.

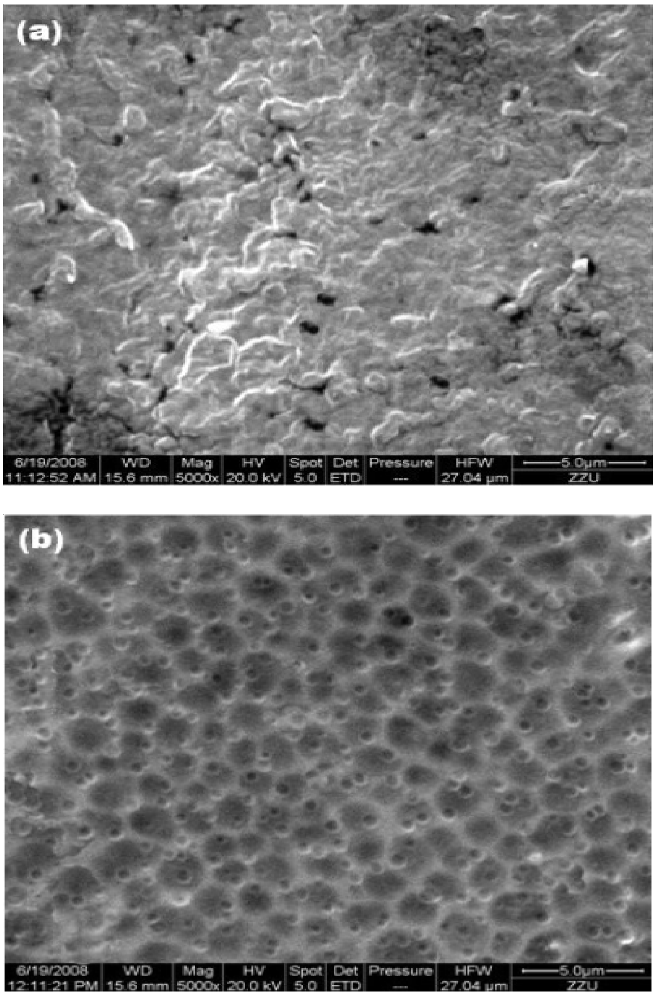

Fig. 11. Surface morphology of the support membrane (a) and the composite charge mosaic membrane (b)

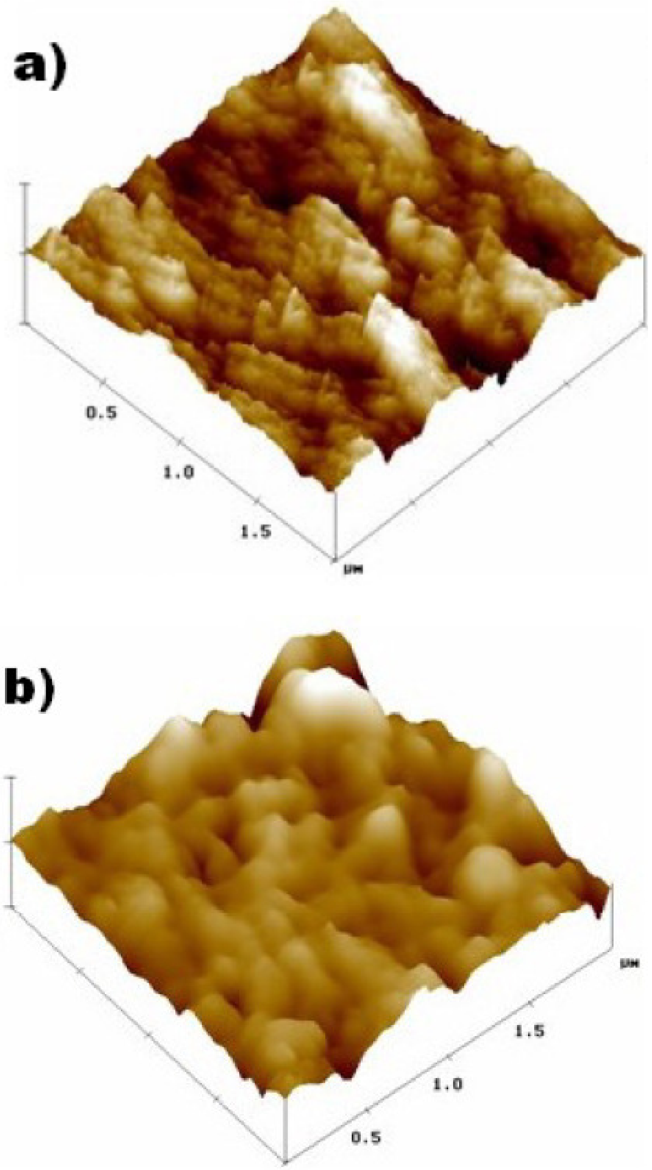

Fig. 12. Atomic force microscope images of the support membrane (a) and the composite charge mosaic membrane (b)

Conclusion

A composite charge-mosaic membrane was prepared *via* interfacial polymerization by coating a thin selective layer onto the surface of a micro-porous polyethersulfone hollow fiber membrane, which was able to effectively deliver electrolytes and hold back low molecular weight organics. The preparation conditions were optimized by means of uniform design and the regression equation was obtained using SPSS software. The model was in good agreement with the experimental data.

For the binary mixtures, inorganic salts/water and organics/water, the rejection for the inorganic salts was less than 30 % and the rejection for sucrose was approximately 90 %. In addition, for the ternary mixtures, as the salt concentration increased, the separation factor decreased owing to the interaction between salt and organics. SEM and atomic force microscope showed that a dense selective layer on the support membrane was formed and membrane surface became smooth and uniform after interfacial polymerization. Therefore, the composite charged mosaic membrane could be used for the separation of inorganic salts and low molecular weight organics.

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