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Preparation, structure characteristics and separation properties of thin-film composite polyamide-urethane seawater reverse osmosis membrane

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ABSTRACT

A novel thin-film composite (TFC) seawater reverse osmosis membrane was developed by the interfacial polymerization of 5-chloroformyloxyisophthaloyl chloride (CFIC) and metaphenylenediamine (MPD) on the polysulphone supporting membrane. The performance of the TFC membrane was optimized by studying the preparation parameters, which included the reaction time, pH of the aqueous-MPD solution, monomer CFIC concentration, additive isopropyl alcohol content in aqueous solution, curing temperature and time. The reverse osmosis performance of the resulting membrane was evaluated through permeation experiment with synthetic seawater, and the structure of the novel membrane was characterized by using SEM, AFM and XPS. Furthermore, the separation properties of the TFC membrane were tested by examining the reverse osmosis performances of various conditions, the boron rejection performance and the long-term stability. The results show that the desired TFC seawater reverse osmosis membrane has a typical salt rejection of 99.4% and a flux of about 35 L/m^2 h for a feed aqueous solution containing 3.5 wt.% NaCl at 5.5 MPa, and an attractive boron rejection of more than 92% at natural pH of 7–8; that the novel seawater reverse osmosis membrane appears to comprise a thicker, smoother and less cross-linking film structure. Additionally, the TFC membrane exhibits good long-term stability.

1. Introduction

Due to increasing demand for water, both potable and for irrigation, coupled with a decrease in suitable water sources, suppliers have to turn to alternatives. Seawater (SW) desalination or treatment of high saline, eventually contaminated surface waters have been considered [1]. The reverse osmosis (RO) process which uses polymeric membranes to achieve molecular separation excels all other methods of desalination and is the most efficient technique to desalt seawater. In order to maximize the solute separation ability and efficiency, one has to develop membranes from available polymers having suitable pore size combined with the appropriate chemical nature of the polymer. So far, two main types of polymeric reverse osmosis membranes have been developed for seawater desalination, namely asymmetric membrane and thin-film composite (TFC) membrane. The latter one, which is characterized by a thin and dense surface film supported by a reinforced porous matrix, has become commercial materials for reverse osmosis. Nowadays, the thin-film composite membranes are widely used in commercial single pass seawater desalination plants around the world, because they offer a combination of high flux and high selectivity unmatched by other types of reverse osmosis membranes [2–6].

Thin-film composite reverse osmosis membrane is usually obtained by forming an ultra-thin dense layer on a porous substrate through interfacial polymerization. Polymerization reaction takes place at the interface of the two liquids which are insoluble to each other. The keys to the interfacial polymerization method are to select the right partition coefficient of the reactions in the two-phase solution and to set appropriate diffusion speed of the reactants so as to achieve the ideal degree of densification of the ultra-thin layer [7,8]. The performance of the composite membranes is mainly determined by two important factors: (1) ultra-thin layer chemistry, which is an inherent property of the monomers employed in polymerization and (2) preparation conditions of the ultra-thin layer on the porous support.

Today, most commercial thin-film composite seawater desalination reverse osmosis membranes, such as SW30 series made by Filmtec Corporation, SWC series by Hydranautics, TM series by Toray Industries and so on [8–12], are based on a polyamide thin-film made by interfacial polymerization of an aromatic polyamine such as m-phenylenediamine (MPD), with one or more aromatic polyacyl halides (for example, trimesoyl chloride (TMC)). They all exhibit good performance in desalination of seawater

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and are already in mass production. However, significant interest still remains in discovering more energy-efficient, contaminant-selective, and fouling resistant TFC membranes for seawater desalination using high performance materials. Additionally, the thin-film composite RO membrane for seawater desalination still has not been commercialized in China and there will be a long way to go before it is commercialized.

Polyamide-urethane formed by the reaction of a haloformyloxy-substituted acyl chloride with an aromatic polyamine is a novel high performance material for the preparation of separating layer of TFC membranes. The reverse osmosis membrane prepared through the interfacial polymerization of 5-chloroformyloxyisophthaloyl chloride (CFIC) with MPD exhibits improved solute rejection and permeation properties during the desalination of brackish water (BW) [13,14]. However, almost no work has been done to study the preparation and performance of the thin-film composite polyamide-urethane seawater reverse osmosis membrane.

This study focuses on the development of seawater reverse osmosis membrane from CFIC and MPD by *in situ* interfacial polymerization process, and investigating the seawater desalination properties. The aim is to enhance the salt rejection and water flux of the thin-film composite polyamide-urethane reverse osmosis membrane for seawater desalination by optimizing interfacial polymerization conditions. Parametric studies were conducted by varying reaction time, pH of the aqueous-MPD solution, monomer CFIC concentration, additive IPA content in aqueous solution, curing temperature and time. The reverse osmosis performance of the resulting membrane was evaluated through permeation experiment with synthetic seawater, and the structure of the TFC membrane was characterized by using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Furthermore, the separation properties of the TFC membrane were tested by examining the reverse osmosis performances of various conditions (such as feed concentration, pH and operating pressure), the boron rejection performance and the long-term stability.

2. Experimental

2.1. Materials and regents

The microporous polysulphone supporting film with molecular weight cut-off above 100,000 g/mol and water permeability of approximately 76 L/m^2 h bar was supplied by the Development Center of Water Treatment Technology, SOA, Hangzhou, China. Monomer MPD (purity >99.5%) was purchased from Shanghai Amino-Chem. Co. Ltd. China, and key functional monomer CFIC (purity >99.0%) was synthesized in our laboratory according to the method reported by Zhou et al. [14]. Triethylamine (TEA) (liquid, 99.5%; Sigma–Aldrich) was used to prepare the aqueous phase amine solution and its pH value was adjusted using camphor sulfonic acid (CSA) (powder, 99.0%; Sigma–Aldrich), while the organic phase solution was prepared using the analytical grade IP1016 solvent (isoparaffin type hydrocarbon oil) from the IDEMITSU Chemical Co. Ltd. Powder H_3BO_3 (99.5%) was used to prepare model solutions for boron rejection tests. All the other regents were of analytical grade unless specified.

2.2. Membrane preparation

The thin-film composite polyamide-urethane RO membrane was prepared through interfacial polymerization technique in an assembly clean room. To begin with, the aqueous solution was prepared by MPD (2.0 wt.%, or 0.185 mol/L) in the mixing aqueous solution of TEA (approximately 3.0 wt.%, or 0.296 mol/L) and isopropyl alcohol (IPA) (0–12.0 wt.%) with pH adjusted by CSA, whereas the organic solution was composed of CFIC (0.1–0.3 wt.%, or 2.65–7.94 mmol/L) and IP1016 solvent. Then, the microporous polysulphone supporting membrane was clamped between two Teflon frames (thickness: 0.8 cm; inner length: 20 cm; and inner width: 15 cm), and the aqueous-MPD solution was poured onto the top surface of the supporting membrane and allowed to soak for at least 2 min. The surface was rolled with a soft rubber roller to eliminate any little bubbles formed in the process of soaking. Excess solution was drained off the surface by standing the holder on the top and bottom edge until no excess liquid exists. The holder was then held at an angle of 30° and the organic solution of CFIC was poured into the frame from top to bottom; the holder was then lowered quickly. After a certain period of residence time, the excess organic solution was removed off the surface, and the frame with membrane was held in a hot air dryer for certain time so that a skin layer was formed on the support membrane. Finally, the resulting membrane was successively washed in hot (40–50 °C) running water for 10 min, in hot running aqueous solution of methanol (40–50 °C) for 10 min, in pure water of room temperature for 10 min, and stored in $NaHSO_3$ solution (1.0 wt.%) until it was testing.

2.3. Membrane characterization

Membrane samples used for the chemical and morphological structure analysis are washed with deionized (DI) water and dried under vacuum before characterization.

Scanning electron microscopy of the composite membrane is performed with a JSM-5610LV instrument. Magnifications up to 20,000 are obtained.

Quantitative surface roughness analysis of the composite membranes is measured using AFM imaging and analysis (Park Instrument Auto Probe CT). Membrane samples are fixed on a specimen holder and 3 μm × 3 μm areas are scanned by tapping mode in air. The surface roughness is reported in terms of the average plane roughness (Ra), root mean square roughness (Rms) and 10-point mean plane roughness (Rz) [15].

Surface chemical characterization of the composite membranes is carried out by XPS (PerkinElmer PHI 5000C ESCA System, USA), with Mg/Al Dual Anode Hel/Hell ultra violet source (400 W, 15 kV, 1253.6 eV). The spectra are taken with the electron emission angle at 54° to give a sampling depth 10 nm, by a concentric hemispherical energy electron analyzer operating in the constant pass energy mode at 29.35 eV, using a 720-μm diameter analysis area. The obtained data is analyzed through PHI ACCESS ESCA-V6.0F software package.

2.4. Membrane performance evaluation

Reverse osmosis performance tests of the resulting membranes were performed using cross-flow membrane filtration equipment with five parallel permeation cells. Membrane coupons with a diameter of 40 mm (effective area: 12 cm^2) were soaked in deionized water for at least 2 h prior to loaded to the test kit, and then pressured at 5.5 MPa for 30 min with DI water before the permeation tests to ensure stable membrane. After that, the water flux and salt rejection performance tests were conducted with pure sodium chloride aqueous solution under certain operating conditions (temperature, pressure, solute concentration and pH); and the boron rejection tests were carried out with synthetic seawater containing 5 mg/L boron at 5.5 MPa and different feed pHs.

The water flux was determined by direct measurement of the permeate flow in terms of liter per square meter per hour (L/m^2 h). The salt and boron rejection rate was calculated using the following equation: rejection (%) = 100 × (1 − (C_p/C_f)), where C_p and C_f were solute concentrations in permeate and feed, respectively. The salt concentrations in permeate and feed solutions were determined by measuring the chloride ion (Cl^-) content using titration method, while the boron concentrations in feed and permeate were measured using spectrophotometric curcumine method [16].

All the results presented were an average data obtained from five membrane samples with standard deviation of measured values indicated by the error bars.

2.5. Testing long-term stability of the composite membrane

Long-term test was conducted at operating pressure of 5.5 MPa with 3.5 wt.% NaCl solution to investigate the performance stability of the composite membrane. Periodical measurements were carried out to check the permeability and salt rejection of the membrane.

3. Results and discussion

3.1. Performance optimization of the TFC polyamide-urethane seawater RO membrane

Thin-film composite membranes having an ultra-thin skin layer on the reinforced polysulphone support membrane were prepared by *in situ* interfacial polymerization of MPD in water with CFIC in organic solvent. In general, the performance of the composite membrane is determined by the chemistry and the preparation conditions of the ultra-thin selective layer. The former is an inherent property of the reactants taken to form the selective layer while the latter plays an important role in determining the structure of the interfacially polymerized film and subsequently the membrane performance [17].

In forming the thin-film, when the two monomer solutions are brought into contact, both monomers partition across the liquid–liquid interface and react to form a polymer; however, polymerization occurs predominantly in the organic phase due to the relatively low solubility of most acid chloride in water. Therefore, it is common to use a large excess of amine over acid chloride, which drives partitioning and diffusion of the amine into the organic phase [18,19].

In the study, the concentration of monomer MPD in aqueous phase solution is 2.0% (w/v), the other preparation conditions that are decisive in determining the properties of the composite membrane are reaction time, pH of the aqueous-MPD solution, monomer CFIC concentration, additive IPA content in aqueous solution, curing temperature and time, which are discussed below.

3.1.1. Reaction time

The reaction time of polymerization from 10 to 90 s was investigated firstly under the following membrane preparation condition: 2.0 wt.% MPD and 3.0 wt.% TEA in H_2O with pH adjusted to 8.3 by CSA; 0.15 wt.% CFIC in IP1106. The results of the water flux and rejection to 3.5 wt.% NaCl solution are presented in Fig. 1 (at 5.5 MPa operating pressure).

It can be seen that, with the reaction time increasing from 10 to 30 s, the NaCl rejection increases from about 98.0 to 99.1%, and then almost levels off. On the other hand, the water flux drops appreciably from about 38 to 26 L/m^2 h when the reaction time increases from 10 to 60 s, and then decreases slightly.

It is well known that the interfacial polymerization between a diamine and acid chloride occurs on the organic side of the aqueous–organic interface, and the reaction is diffusion-controlled and exists in a self-limiting phenomenon. The reaction time plays an important role in determining the extent of polymerization, and thereby the cross-linking and thickness of top skin layer as well as the resulting membrane performance [17,20]. The top skin layer thickness of the composite membrane increases with increasing polymerization time, and when the thickness of the thin layer is enough to prevent diamine diffusing from aqueous phase into the organic phase, the top layer thickness will stop growing. Thus, for a short reaction time, the extent of cross-linking is low and the top skin layer is thin; as a result, the permeability of both water and salt is high. As the reaction time extends, the increase of the extent of polymerization will lead to increase in both thickness as well as cross-linking of the skin layer, which results in reduced water flux and increased salt rejection. After a certain period of reaction, the water flux and salt rejection will almost stay constant because both of the thickness and compactness of selective skin layer are almost fixed [21].

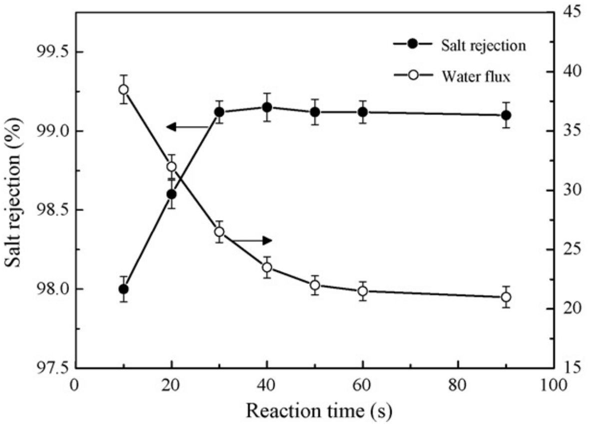


Fig. 1. Effect of interfacial reaction time on salt rejection (●) and water flux (○) of the resulting membrane testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0 (MPD = 2.0 wt.%; CFIC = 0.15 wt.%; curing temperature = 80 °C; curing time = 10 min; aqueous pH = 8.3).

In the study, 30 s is considered as an optimal reaction time, which shows relatively high salt rejection and proper water flux.

3.1.2. The pH of aqueous phase solution

To further increase the separation performance of the composite membrane, the pH of the aqueous phase solution which affected the formation of the top skin layer was investigated. In the study, the pH of aqueous phase solution was adjusted by addition of CSA. Fig. 2 is the experimental results of the water flux and salt rejection of the membranes which were prepared under different pH of aqueous phase at reaction time about 30 s and the other preparation parameters were the same as the former.

It is illustrated that the flux decreases dramatically when the pH of aqueous solution increases from 7.5 to 9.0, which corresponds to an increase in the salt rejection of the membrane. However, the membrane performance has a break if the pH of aqueous-MPD solution is increased to 10.0.

It is known that the hydrogen chloride is formed during the interfacial polymerization, and the removing of hydrogen chloride is beneficial to the processing of the positive reaction of the chemical equilibrium [8]. The TEA in the aqueous-MPD solution is an acid acceptor and accelerates the MPD–CFIC reaction by neutralizing hydrogen chloride producing during amide formation. Then the polymer with high molecular weight will form at high pH and result in a dense skin layer on the membrane surface; therefore, the membrane shows a high salt rejection and low water permeability at high pH of the aqueous phase solution.

However, the strength of the acid acceptor affects the degree of concurrent hydrolysis, and hence, membrane structure and perfor-

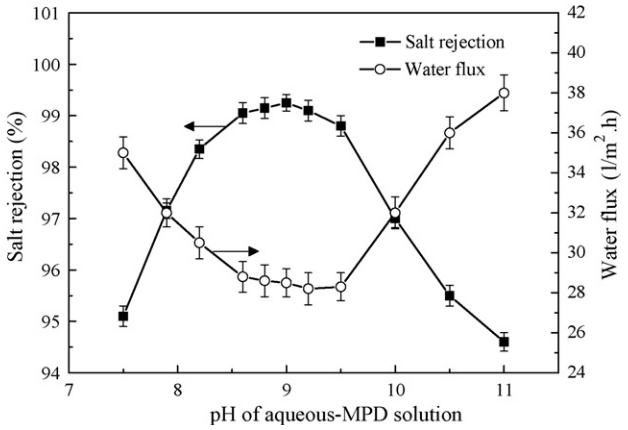


Fig. 2. Effect of pH of aqueous-MPD solution on salt rejection (■) and water flux (○) of the resulting membrane testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0 (MPD = 2.0 wt.%; CFIC = 0.15 wt.%; reaction time = 30 s; curing temperature = 80 °C; curing time = 10 min).

mance. When the pH of aqueous-MPD solution is increased to 10.5, the hydrolysis of CFIC will lead to form less cross-linking and looser MPD–CFIC film, and hence, membrane permeability increases and salt rejection decreases. Considering both good salt rejection and higher water permeability, pH of 9.0 was chosen as the optimum for aqueous phase solution.

3.1.3. *The concentration of monomer CFIC*

Since the concentration of the monomer CFIC in the organic phase plays an important role in the preparation of polyamide-urethane TFC membrane by interfacial polymerization, the influence of the changes of the concentration of CFIC was investigated to optimize the performance of the TFC membrane. Fig. 3 shows the performances of poly (MPD–CFIC) composite membranes prepared using different CFIC concentrations but keeping the other variables constant. It can be seen from the figure that the salt rejection of the membrane increases greatly from about 97.8 to 99.3%, whereas water flux decreases sharply from about 36 to 25 L/m^2 h when CFIC concentration increases from 0.10 to 0.2 wt.% at a fixed MPD concentration of 2.0 wt.%, and then both decrease slightly with further increase in CFIC concentration.

The observed salt rejection and water flux behavior of the membranes with CFIC concentration may be explained in terms of both the chemical and morphological changes that occur during the formation of polyamide skin layer. According to Morgan [22], the interfacial polymerization between a diamine and acid chloride occurs on the organic side of the aqueous–organic interface. The concentrations of monomers have a greater effect on the rate of polymerization and thereby the thickness and morphology of the polyamide skin layer. At lower concentration of monomer CFIC, the rate of polymerization is expected to be low because of the insufficient concentration of monomer CFIC at the interfacial reaction zone, and the formed selective skin layer is thin and loose; as a result, the membrane poorly rejects the salt but permeates more amount of water. For higher CFIC concentrations, the rate of polymerization is faster and selective skin layer is somewhat thicker and compacter; thus, higher rejection and lower water flux can be expected for the membrane. Further increase in the concentration, however, tends to have almost no effect on the rate and extent of polymerization and thereby has less effect on membrane properties.

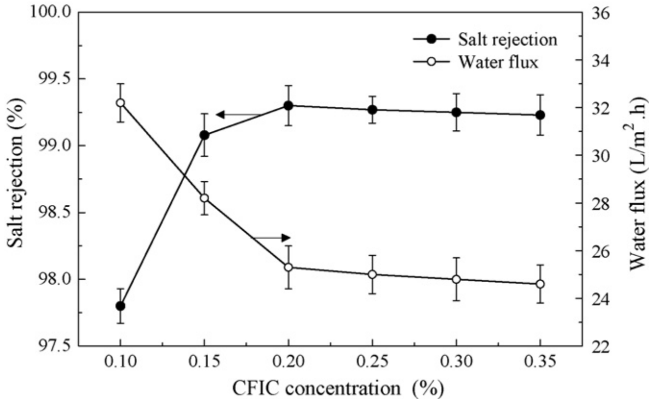


Fig. 3. Effect of CFIC concentration on salt rejection (●) and water flux (○) of the resulting membrane testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0 (MPD = 2.0 wt.%; reaction time = 30 s; aqueous pH = 8.8; curing temperature = 80 °C; curing time = 10 min).

3.1.4. *Curing temperature and time*

Heat curing is often required to facilitate the removal of residual organic solvent from nascent polyamide-urethane and to promote additional cross-linking by dehydration of unreacted amine and carboxyl groups. Curing temperature of the nascent polyamide composite membrane has a profound influence on the performance. Reverse osmosis performance of membranes cured at different conditions (temperatures and times) was evaluated. Salt rejection and water flux data to 3.5 wt.% NaCl solution are shown in Table 1.

As shown in Table 1A, both of the water flux and salt rejection increase with the curing temperature increasing from 45 to 90 °C, but drop off as the curing temperature is further increased. The increase in salt rejection and water flux at lower curing temperatures may be due to the increased densification or additional cross-linking of the selective skin layer and the loss of residual solvent in the film, respectively. The decrease in water flux at higher curing temperatures could be due to the pore shrinkage in the support membranes and the deeply densification of the skin layer, while the lower water permeability will lead to a higher concentration of salt in permeate and thus a relatively lower salt rejection. Similar results are also reported for polyamide membranes formed with different curing conditions on polysulfone supports [23].

With increasing curing time, complete evaporation of organic solvent from the membranes is achieved and the permeability is higher. Curing significantly longer than the minimum time needed

Table 1
Effect of curing conditions on TFC RO membrane performance.

Curing temperature (°C)	Salt rejection (%)	Water flux (L/m^2 h)
(A) Variation of curing temperature at 10 min curing time		
45	97.50 ± 0.18	23.4 ± 0.8
60	98.05 ± 0.1	24.2 ± 0.7
75	99.05 ± 0.12	25.8 ± 0.8
90	99.25 ± 0.09	26.4 ± 0.9
110	98.50 ± 0.16	25.2 ± 0.8
Curing time (min)	**Salt rejection (%)**	**Water flux (L/m^2 h)**
(B) Variation of curing time at 90 °C curing temperature		
3	98.35 ± 0.12	24.6 ± 0.8
5	98.65 ± 0.1	25.4 ± 0.7
10	99.35 ± 0.15	26.2 ± 0.7
15	99.07 ± 0.17	24.7 ± 0.8
20	98.55 ± 0.18	23.5 ± 0.6

[a]Test conditions: feed: 3.5% NaCl aqueous solution, pressure: 5.5 MPa, temperature: 25 °C and pH 7.0. [b]Preparation conditions: MPD = 2.0 wt.%; CFIC = 0.20 wt.%; reaction time = 30 s; aqueous pH = 8.7.

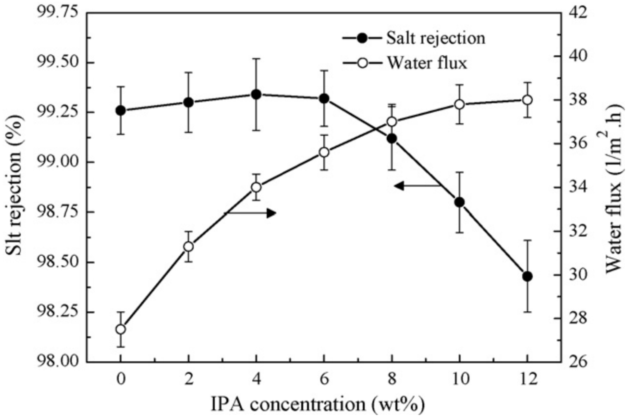


Fig. 4. Effect of IPA content in aqueous solution on salt rejection (●) and water flux (○) of the resulting membrane testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0 (MPD = 2.0 wt.%; CFIC = 0.20 wt.%; reaction time = 30 s; aqueous pH = 8.8; curing temperature = 90 °C; curing time = 10 min).

to remove the solvent also may result in shrinkage or annealing of support membrane pores, which decreases water permeability.

3.1.5. IPA content in aqueous-MPD solution

It is known from literature that the use of additives in monomer solutions can influence the rate and extent of interfacial polymerization as well as the extent of cross-linking [24], and addition of small amounts of hydrophilic water-soluble polymers or a polyhydric alcohol to the amine solution can produce high flux thin-film composite polyamide reverse osmosis membranes with good rejection [25].

Thus, further attempt was made to improve the product water flux of the TFC membrane by adding additive IPA to aqueous-MPD solution. Water flux and salt rejection of the resulting membranes formed with different concentration of IPA added to the aqueous-MPD solution are plotted in Fig. 4. It is shown in the figure that, in all the cases, the water flux ascends dramatically, while the salt rejection increases slightly at lower IPA concentrations (less than 6 wt.%) and descends considerably at higher IPA contents in aqueous-MPD solution. The possible reason for decrease in salt rejection at higher IPA content is the formation of relatively "loose" skin layer which poorly rejects the salt while permeating more amounts of water.

3.1.6. Optimal preparation conditions for the TFC polyamide-urethane seawater RO membrane

Based on the studies above, conditions necessary for obtaining good performance thin-film composite polyamide-urethane seawater reverse osmosis membranes were established. The optimal polymerization conditions are as follows: MPD = 2.0 wt.%; CFIC = 0.20 wt.%; reaction time = 30 s; aqueous-MPD solution pH = 9.0; curing temperature = 90 °C; curing time = 10 min; IPA content in aqueous solution = 5.0 wt.%. Accordingly, laboratory scale thin-film composite polyamide-urethane seawater reverse osmosis membranes were prepared using the above conditions and their performance data are given in Table 2, and compared with those of the thin-film composite polyamide RO membranes based on MPD and TMC. The polyamide RO membranes were prepared by interfacial polymerization technique using the same method as described in Section 2.2 on the same type of porous polysulphone support membrane.

As can be seen from Table 2, the polyamide-urethane membrane gives an average trial-to-trial performance of 99.35% salt rejection with a flux of 34.8 L/m^2 h for 3.5% NaCl solution at 5.5 MPa operating pressure. The salt rejection of the novel polyamide-urethane membrane is higher than that of the polyamide membrane prepared in this paper, and is generally suitable for single pass seawater desalination, but the flux of the membrane should be further improved for commercial application. Additionally, results of the lab scale trials also indicate the reproducibility of the preparation conditions established during the earlier parameter experiments.

Table 2
Salt rejection and water flux of the lab scale TFC membranes prepared under the optimal polymerization conditions.

Trial no.	Salt rejection (%)[a]	Water flux (L/m^2 h)[a]
(A) Thin-film composite RO membranes based on MPD and CFIC		
1	99.24	34.5
2	99.38	35.4
3	99.46	34.2
4	99.27	35.8
5	99.40	34.0
Average	99.35 ± 0.09	34.8 ± 0.8
(B) Thin-film composite RO membranes based on MPD and TMC[b]		
1	99.18	40.8
2	99.30	39.2
3	99.26	40.5
Average	99.25 ± 0.06	40.2 ± 0.9

[a] Test conditions: feed: 3.5% NaCl aqueous solution, pressure: 5.5 MPa, temperature: 25 °C and pH 7.0.

[b] Preparation conditions: MPD = 2.0 wt.%; TMC = 0.15 wt.%; reaction time = 20 s; aqueous-MPD solution pH = 8.7; curing temperature = 85 °C; curing time = 10 min; IPA content in aqueous solution = 5.0 wt.%.

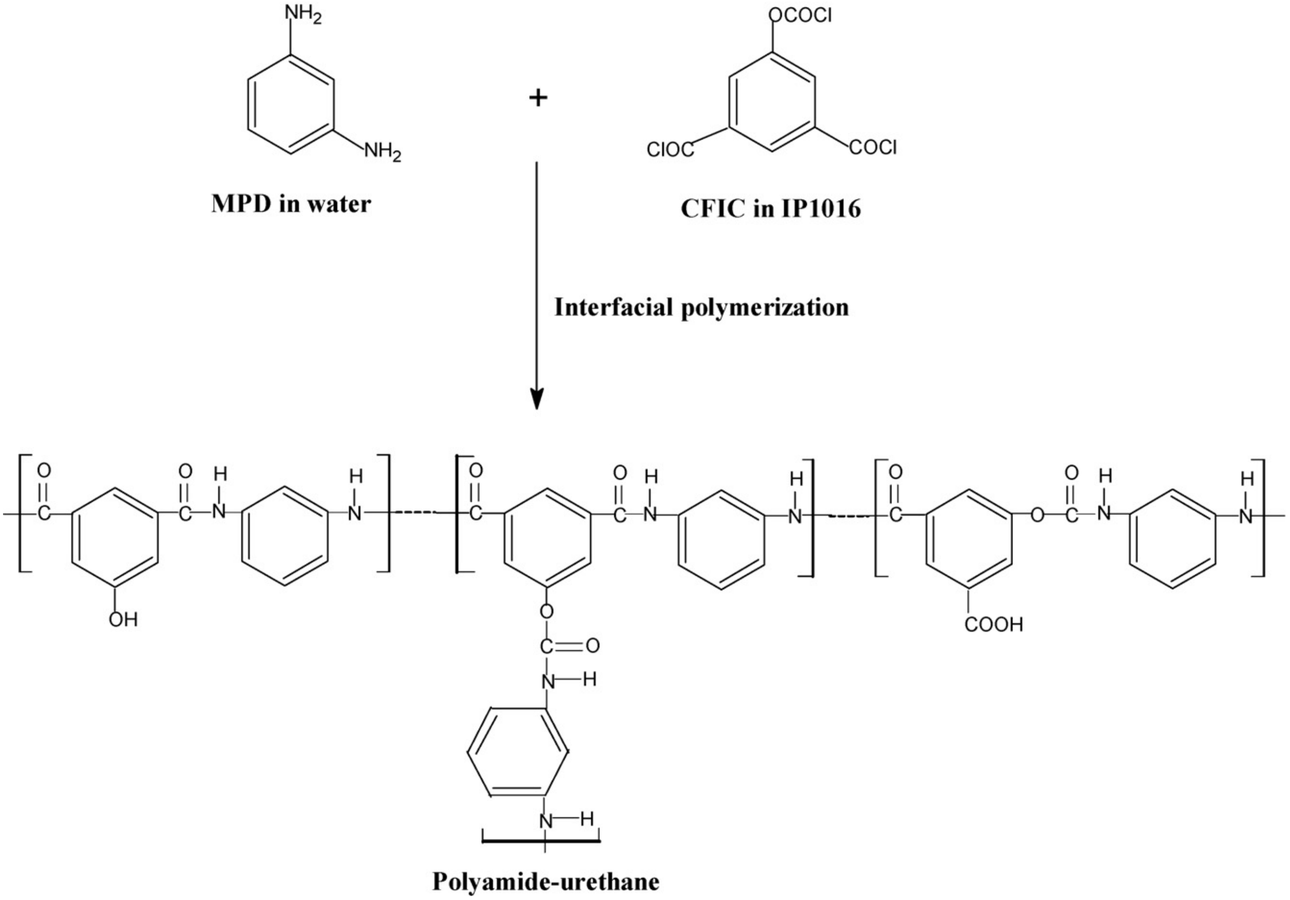
3.2. Structure characteristics of the TFC polyamide-urethane seawater RO membrane

The structure characteristics of the TFC polyamide-urethane SW RO membrane are studied through comparing the structural differences between SW and BW RO membranes prepared from MPD and CFIC. In this paper, thin-film composite BW RO membrane was also prepared through interfacial polymerization of MPD and CFIC on porous polysulphone support membrane, the preparation conditions for the thin-film composite BW RO membrane are as follows: MPD = 2.0 wt.%; CFIC = 0.08 wt.%; reaction time = 30 s; aqueous-MPD solution pH = 8.8; curing temperature = 90 °C; curing time = 6 min; IPA content in aqueous solution = 10.0 wt.%. The BW RO membrane prepared has a typical salt rejection of about 99.2% and a flux of about 56 L/m^2 h for a feed aqueous solution containing 0.2 wt.% NaCl at 1.55 MPa, and exhibits NaCl rejection of about 90.5% and permeate flux of about 43 L/m^2 h for a feed aqueous solution containing 3.5 wt.% NaCl at 5.5 MPa. The chemical and morphological structure of the resulting BW RO membrane and SW RO membrane prepared in Section 3.1.6 (trial no. 1) are studied and discussed as follows.

3.2.1. Skin layer chemical structure of the TFC polyamide-urethane seawater RO membrane

According to Zhou et al. [14], the chemical structures of the monomers used and the expected polyamide-urethane skin layer are shown in Scheme 1. The poly (MPD–CFIC) chain is expected to contain the cross-linked structure, non-cross-linked structure containing carboxylic acid group and linear structure containing hydroxyl group. The functional groups of carboxylic acid and hydroxyl arise due to the partial hydrolysis of the acyl chloride unit and chloroformyloxy unit of CFIC during the interfacial polymerization.

The surface atomic composition and their concentration ratios of the TFC polyamide-urethane BW and SW RO membranes are shown in Table 3. It is obviously from Table 3 that, there is a distinguished excess of oxygen with respect to the correspond-



Scheme 1. Structure of polyamide-urethane skin layer formed by interfacial polymerization of MPD with CFIC.

Table 3
Surface atomic composition of the skin layer and their concentration ratios.

Unit		C%	O%	N%	O/C	N/C	O/N
Data of XPS analysis	SW RO membrane	73.18	17.06	9.76	0.2331	0.1334	1.748
	BW RO membrane	73.25	16.20	10.55	0.2212	0.1440	1.535
Data of calculated	Linear polymer with pendant COOH	68.2	22.7	9.1	0.33	0.13	2.50
	Totally cross-linked polymer	72.0	16.0	12.0	0.22	0.17	1.33
	Linear polymer with pendant OH	73.7	15.8	10.5	0.21	0.14	1.50

ing theoretical ratio for totally cross-linked polyamide-urethane (O/N = 1.33), which indicates the existing of linear polymer chain structures in the skin layer of the TFC polyamide-urethane SW and BW RO membranes. Furthermore, the larger value of oxygen-to-nitrogen ratio indicates a high content of linear polymers, especially the linear polymer with pendant COOH in the surface of TFC polyamide-urethane SW RO membrane.

3.2.2. Morphological structure of the TFC polyamide-urethane seawater RO membrane

Morphological structure of the composite membranes is characterized by using SEM and AFM. Representative SEM images of the cross-section and surface of the TFC polyamide-urethane SW and BW membranes are provided in Fig. 5. It can be seen clearly that both of the thin-film composite SW and BW RO membranes take on a composite structure, namely a thin active functional layer existing on the porous polysulphone support membrane; that the skin layer of the thin-film composite SW RO membrane (Fig. 5a) is thicker than that of the BW RO membrane (Fig. 5b); that the thickness of the skin layer of the SWRO membrane (about 0.6 μm) is higher than those of the commercial RO membranes (usually between 0.2 and 0.5 μm [5]), this may be a possible reason for the relatively lower permeability (around 35 L/m^2 h) of the SW RO membrane prepared in this paper compared with those of the commercial SWRO membranes (around 51 L/m^2 h [5]) for a feed aqueous solution of 3.5% NaCl at 5.5 MPa; and that the surface feature of the thin-film composite SW RO membrane (Fig. 5c) appears more nodular compared to the ridge-and-valley morphology of the thin-film composite BW RO membrane (Fig. 5d). Furthermore, as shown in Fig. 6 and Table 4,

Table 4
Surface roughness values of thin-film composite RO membranes by AFM.

Membrane	Ra[a] (nm)	Rms[b] (nm)	Rz[c] (nm)
BW RO membrane	54.71	69.59	269.3
SW RO membrane	24.62	32.53	212.4

[a] Average plane roughness.
[b] Root mean square roughness.
[c] 10-point mean plane roughness.

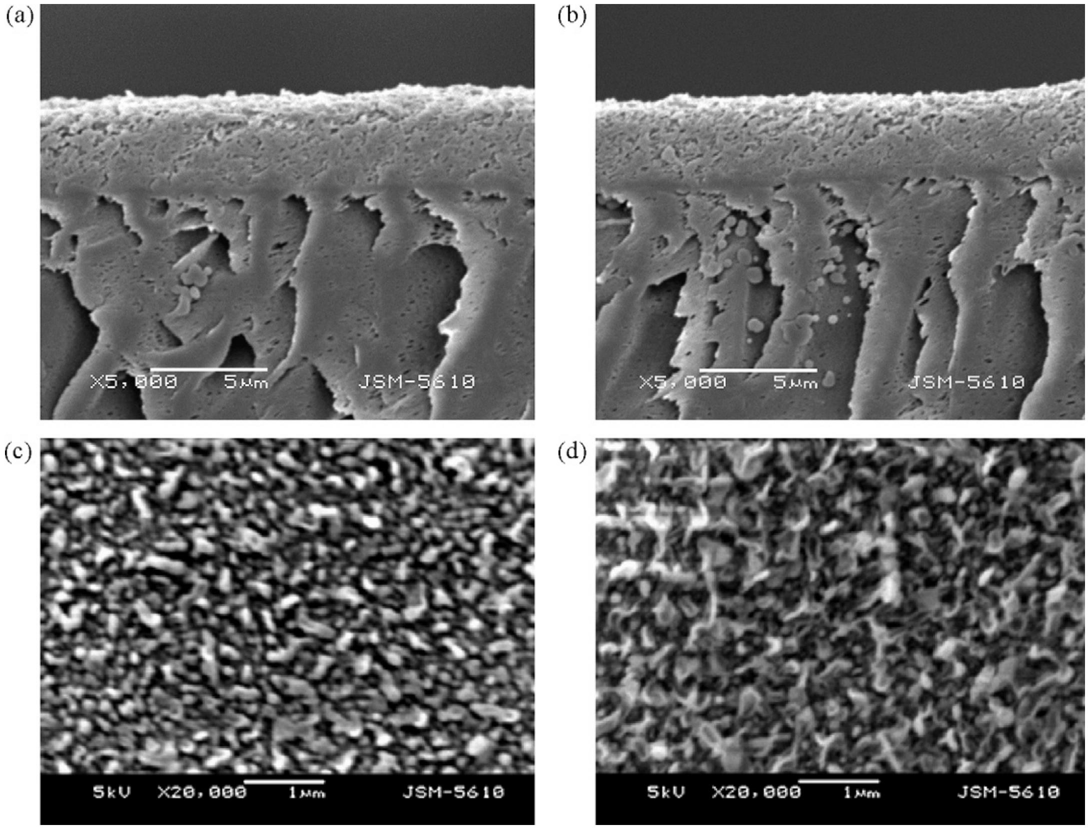


Fig. 5. SEM images of (a) cross-section of SW RO membrane, (b) cross-section BW RO membrane, (c) surface of SW RO membrane and (d) surface of BW RO membrane.

the nodular morphology of the TFC polyamide-urethane SW RO membrane is smoother than the ridge-and-valley morphology of the TFC polyamide-urethane BW RO membrane according to AFM surface roughness analysis.

3.3. Separation properties of the TFC polyamide-urethane seawater RO membrane

3.3.1. Effect of feed pH on membrane performance

The effect of feed pH on the salt rejection and flux to 3.5 wt.% NaCl solution was determined for the TFC polyamide-urethane SW RO membrane (trial no. 1) by adjusting the feed pH with HCl and NaOH. The experimental results shown in Fig. 7 indicate that the novel TFC membrane prepared in this paper is generally applicable through the pH range of 5–11 for seawater desalination, the salt rejection of the membrane is found to reach its summit at pH around 8.5, while the flux of the membrane mounts gradually as the feed pH increases. The acid transport through the membrane would account for the fall-off in salt rejection for the feed pHs below 5. The possible reason for increase in flux with pH is the increase of the number of negative charges, leading to more repulsion between the polymer segments and thus an increase of the free volume in the membrane matrix.

3.3.2. Effect of feed concentration on membrane performance

The feed concentration effect experiment was performed with the thin-film composite polyamide-urethane SW RO membrane (trial no. 2) by changing the NaCl concentration in the feed aqueous solution and the results of salt rejection and flux to NaCl aqueous solution of different concentrations is shown in Fig. 8. It is apparent from the figures that, as the feed NaCl concentration increases from 2.0 to 4.5 wt.%, the salt rejection of the membrane decreases slightly, while the flux of the membrane declines sharply because of the increase of osmotic pressure. It is also worth mentioning that the salt rejection of the membrane still remains more than 99.2% even the feed NaCl concentration is up to 4.5 wt.%.

3.3.3. Effect of operating pressure on membrane performance

The effect of the operating pressure on salt rejection and water flux to 3.5 wt.% NaCl aqueous solution was also determined for the TFC polyamide-urethane SW RO membrane (trial no. 3) by testing under different operating pressures and the results are shown in Fig. 9. What is apparent from the graph is that, as the operating pressure increases from 3.5 to 6.0 MPa, the salt rejection ascends and levels off at 4.5 MPa, while the flux of the membrane increases almost linearly. It can be explained by the fact that the permeate flux is directly proportional to the net operating pressure, whereas the solute diffusion across the membrane on the other hand is not affected by the applied pressure, so an increase in water flux with applied pressure will result in a low salt concentration in the permeate and thereby an increase in salt rejection. While the low water permeate flow rate across the membrane would account for the fall-off in salt rejection for pressures below 4.5 MPa.

3.3.4. Boron rejection performance of the TFC seawater RO membrane

Considering the application of the TFC polyamide-urethane SW RO membrane for the production of drinking water from seawater, the boron rejection performance of the TFC membrane was studied, and the experiment was performed with 3.5 wt.% NaCl aqueous solution containing 5 mg/L boron at 5.5 MPa and different pHs. The data presented in Fig. 10 are the average values of three measurements for each value of pH. As can be seen from Fig. 10, the novel TFC polyamide-urethane SW RO membrane (trial no. 4) exhibits a typical boron rejection of 92.0% at the natural pH of 7–8, and the boron rejection of the TFC membrane is largely dependant on pH

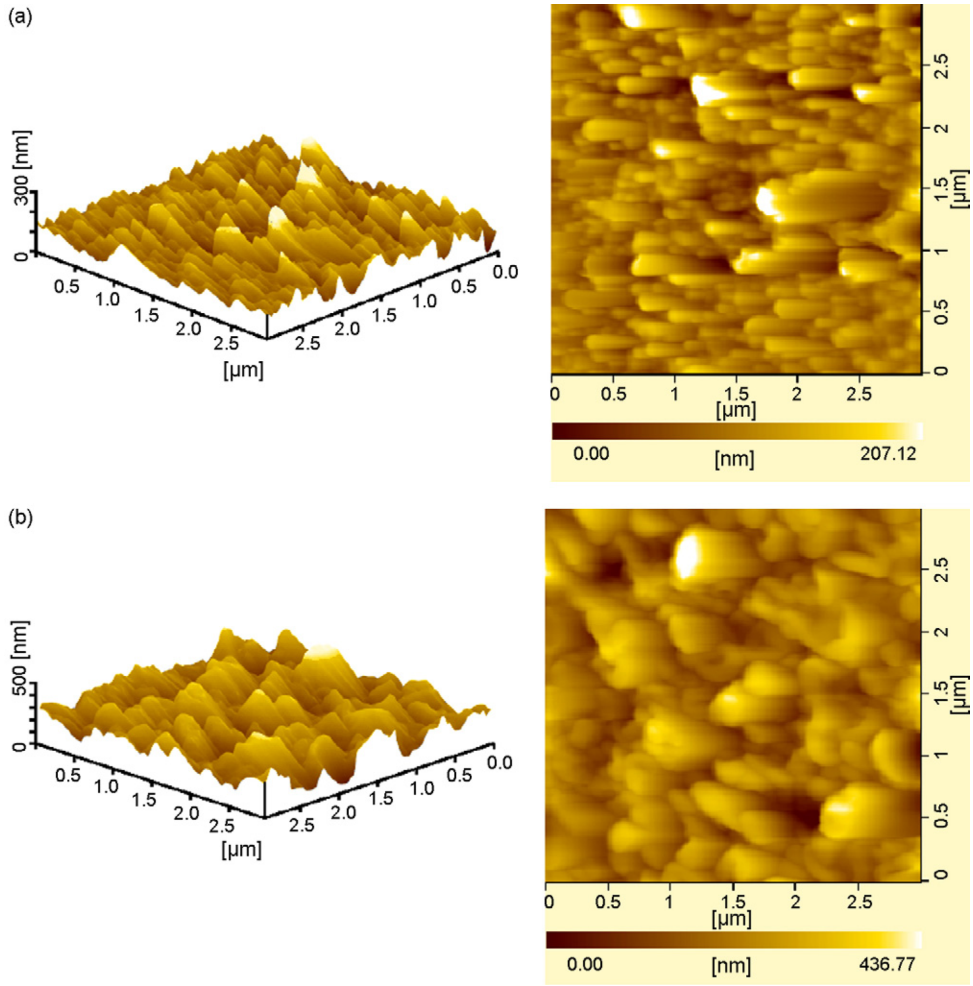


Fig. 6. AFM images of the surface of (a) SW RO membrane and (b) BW RO membrane.

and ascends as pH increases. The changing behavior of the boron rejection of the novel membrane with the feed pH is consistent with the previous studies on polyamide TFC membranes [26–28].

Redondo et al. [29] reported that boron is usually present in water as boric acid, a weak acid which dissociates according to:

$$H_3BO_3 \leftrightarrow H^+ + H_2BO_3{}^- \quad pK_a\ 9.14 \tag{1}$$

$$H_2BO_3{}^- \leftrightarrow H^+ + HBO_3{}^{2-} \quad pK_a\ 12.74 \tag{2}$$

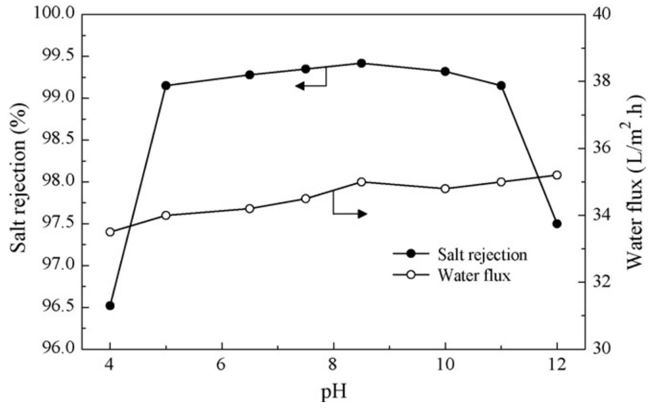


Fig. 7. Effect of feed pH on salt rejection (●) and water flux (○) of the TFC membrane (trial no. 1) testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa and 25 °C.

$$HBO_3{}^{2-} \leftrightarrow H^+ + BO_3{}^{3-} \quad pK_a\ 13.80 \tag{3}$$

At lower pH the major species is boric acid in molecular form. Due to the absence of ionic charges, the hydration of the molecule cannot enhance those charges and is less strong. This results in a smaller size and less rejection of the molecule by the membrane. The dissociated form on the other hand will be fully

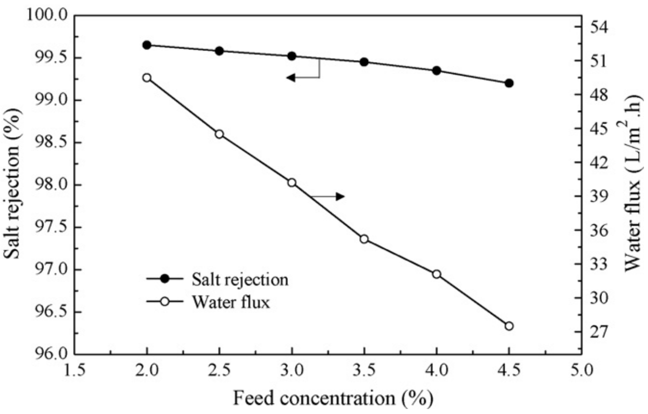


Fig. 8. Effect of feed concentration on salt rejection (●) and water flux (○) of the TFC membrane (trial no. 2) testing with NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0.

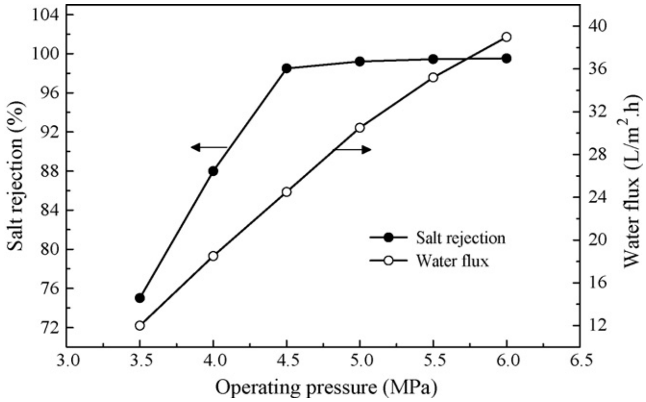


Fig. 9. Effect of operating pressure on salt rejection (●) and water flux (○) of the TFC membrane (trial no. 3) testing with 3.5 wt.% NaCl aqueous solution at 5.5 MPa, 25 °C and pH 7.0.

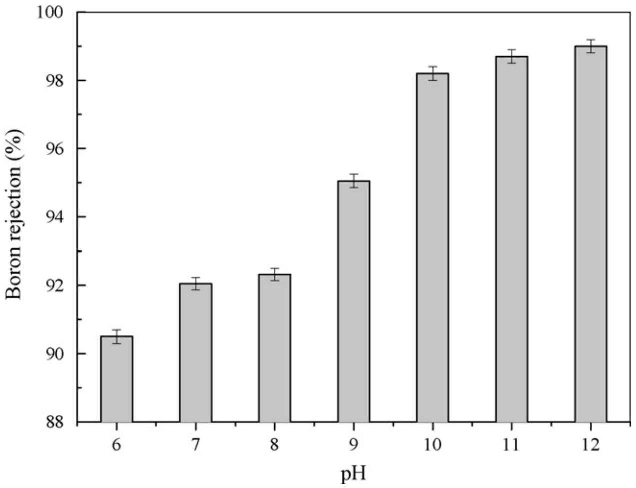


Fig. 10. Boron rejection of the TFC polyamide-urethane seawater RO membrane (trial no. 4) testing with 3.5 wt.% NaCl aqueous solution containing 5 mg/L boron at 5.5 MPa, 25 °C and different pHs.

hydrated, resulting in a large radius and an enhancement of the negative charge of the ion. This in turn results in higher rejection, both by exclusion and repulsion by the negatively charged membrane.

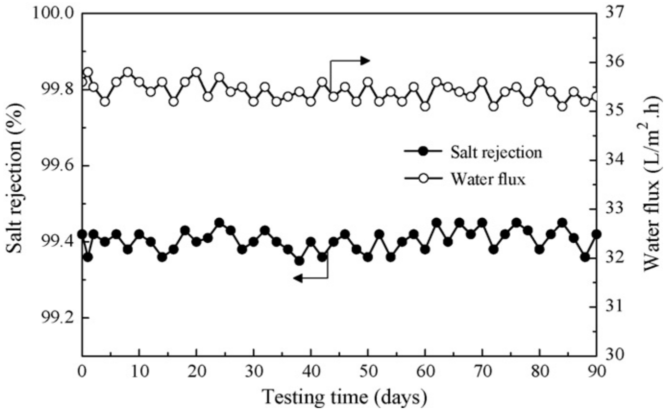


Fig. 11. Variation of s alt rejection (●) and water flux (○) of the TFC seawater RO membrane (trial no. 5) with testing time (feed: 3.5% NaCl, temperature: 25 °C, pressure: 5.5 MPa and pH 7.0).

3.3.5. Stability of the TFC seawater RO membrane in long-time running

The mechanical property and performance stability is very important for a seawater desalination reverse osmosis membrane. Thus, a long-term reverse osmosis test was carried out at 5.5 MPa with synthetic seawater of 3.5 wt.% NaCl aqueous solution. The water fluxes and salt rejections of the studied TFC membrane (trial no. 5) during 90 days of operation are shown in Fig. 9. It is obviously from the graph hat the novel TFC membrane exhibits good long-term performance stability. Furthermore, over the testing period, the salt rejection of the novel membrane fluctuates between 99.36 and 99.45%, while the flux of the novel membrane fluctuates between 35.1 and 35.8 L/m^2 h (Fig. 11).

4. Conclusions

High performance thin-film composite polyamide-urethane seawater reverse osmosis membrane can be prepared through the interfacial polymerization of MPD with CFIC on porous polysulphone support membrane. The optimal polymerization conditions for the TFC polyamide-urethane seawater RO membrane are as follows: MPD = 2.0 wt.%; CFIC = 0.20 wt.%; reaction time = 30 s; aqueous-MPD solution pH = 9.0; curing temperature = 90 °C; curing time = 10 min; IPA content in aqueous solution = 5.0 wt.%. The desired thin-film composite polyamide-urethane seawater reverse osmosis membrane fabricated under the optimized preparation conditions has a typical salt rejection of 99.4% and a water flux of about 35 L/m^2 h for a feed solution containing 3.5 wt.% NaCl at 800 psi (5.5 MPa), and an attractive boron rejection of more than 92% at natural pH of 7–8.

The structure characteristics studies reveal that the novel thin-film composite polyamide-urethane seawater reverse osmosis membrane prepared in this paper appears to comprise a thicker, smoother and less cross-linking film structure.

The systematic performance studies show that the novel thin-film composite membrane prepared in this paper is suitable for single pass seawater desalination, and can be generally applicable through the pH range of 5–11. Both of the salt rejection and flux of the composite membrane increase with the increasing of operating pressure and decrease with the increasing of feed NaCl concentration. The salt rejection of the novel composite membrane still remains more than 99.2% even the feed NaCl concentration is up to 4.5 wt.%. Long-term running tests indicate that the novel thin-film composite polyamide-urethane seawater reverse osmosis membrane possesses high performance stability.

Acknowledgments

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