Preparation and Characterization of High-Selectivity Hollow Fiber Composite Nanofiltration Membrane by Two-Way Coating Technique

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ABSTRACT: A novel coating technique, named as two-way coating (TWC), was explored to prepare hollow fiber composite (HFC) nanofiltration (NF) membrane through interfacial polymerization from piperazine (PIP) and trimesoyl chloride (TMC) on the lumen side of hollow fiber polysulfone ultrafiltration membrane with an effective membrane area of 0.4 m^2. The optimum preparation conditions were systematically investigated and obtained as follows: PIP 0.023 mol/L, TMC 0.0057 mol/L, air blowing rate 2.7 m/s for 30 min after aqueous coating, aqueous coating pressure 0.1 MPa, organic solution flowing rate 0.32 m/s, and heat treating time 3 min. The resultant HFC membrane showed a high selectivity of divalent ion and monovalent ion. Salt rejections of $MgSO_4$ and NaCl were 98.13 and 18.6% with the permeate flux of 32.6 and 40.2 L m^{-2} h^{-1} at 0.7 MPa, respectively. Field emission scanning electron microscopy images indicated that composite membrane prepared by TWC technique had a uniform active layer from the upper end to the bottom of the hollow fiber. And the salt rejection and permeate flux showed almost no difference between different membrane sections. Stability results suggested that good reproducibility could be obtained by TWC technique for the preparation of high-performance HFC NF membrane. The resultant NF membrane showed a high removal rate of chemical oxygen demand and chroma of landfill leachate which were approximately 100%. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41187.

INTRODUCTION

Most of commercial composite membranes are thin-film composite (TFC) membranes prepared by interfacial polymerization (IP) of diamine and acyl chloride.[1–3] The active layer is formed on porous flat sheet membranes and rarely coated on hollow fiber substrates.[4,5] Due to high-packing density and self-support, hollow fiber used as substrates in the preparation of composite membrane has attracted more and more attention.[6,7] Most of researchers focus on the improvement of separation performance through monomers selection[8,9] and support properties enhancement such as mechanical properties, hydrophilicity, and so forth.[10,11] However, few studies about preparation methods are reported. Most use conventional immersion coating for outer-skinned composite membranes preparation[12,13] or pumping coating or gravity coating for inner-skinned composite membranes preparation.[14,15] And the experiments are generally carried out in a laboratory scale.

During module fabrication process of outer-skinned hollow fiber composite (HFC) membranes, external functional layers are vulnerable to stick and rub against each other. The coating layers would be ruptured and even stripped from the outer surface of the substrate. In addition, concentration polarization and foulants deposition are easy to emerge with the decline of filtration efficiency. Therefore, it is urgent to investigate inner-skinned HFC membrane. There are still some problems to be solved in the preparation of inner-skinned HFC membrane. The pumping coating process is complex and there are many man-made operations. Moreover, performance differences between different sections in each fiber are ignored, especially when a long fiber filament is used as the substrate. Monomer concentration gradient along substrate surface would appear in conventional single way coating method leading to an uneven thickness of the active layer. Once under high or unsteady pressure, the active layer might be collapsed.

Some researchers attempted to optimize the coating process. Veríssimo et al.[16] pointed out that the removal of the unabsorbed aqueous solution drops from support fiber surface with air or nitrogen was essential to obtain a thin film without pinholes on fiber bore side. The preparation procedure was optimized by introducing an inert liquid buffer between the
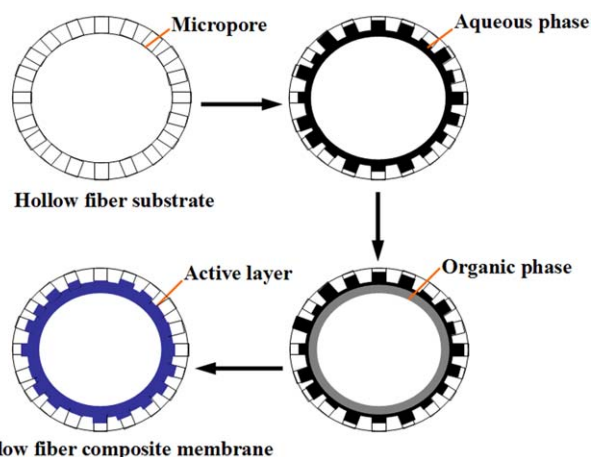
Scheme 1. Diagram of the process of inner-skinned HFC membrane preparation by IP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coatings of aqueous and organic solution. Yang et al.[17] reported that piperazine (PIP) aqueous solution was purged through the lumen side of the fibers under gravity and the acid accepter was used during IP process. However, important factors including air blowing time after aqueous coating, organic solution flowing rate, aqueous coating pressure, and fiber length were less mentioned in previous papers.

A novel coating technique, named as two-way coating (TWC), is applied into the preparation process of HFC membrane. TWC is improved from the two-way flow separation technique, which has been successfully applied in membrane separation operation. Valves of feed inlet and outlet are switched periodically so that the flow directions of raw solution and concentrated liquid could be periodically changed. Pollutants could be adsorbed uniformly along the whole fiber filament and thus membrane fouling and concentration polarization are greatly alleviated. The process of TWC technique was illustrated in Scheme 2. Different dimensions of HFC membrane can be prepared mechanically by this method.

This work aims to develop a novel technique to prepare high-performance HFC membrane with good reproducibility. In this study, HFC nanofiltration (NF) membrane was prepared by TWC technique via IP of PIP and trimesoyl chloride (TMC) on polysulfone (PSF) hollow fiber membrane. The effects of IP conditions on NF membrane separation performance were systematically discussed. The uniformity of functional layer was observed through field emission scanning electron microscopy (FESEM). The reproducibility of this novel coating technique for HFC NF membrane preparation was also studied. In addition, the effect of preservation conditions on separation performance of dried NF membrane was studied. Finally, the prepared NF membrane was applied in the treatment of landfill leachate.

EXPERIMENTAL

Materials

PIP was purchased from Shanghai TIANLIAN Fine Chemical (China). TMC was supplied by Beijing ODYSSEY Chemicals

(China) with recrystallization in petroleum ether. PSF hollow fiber membranes with an inner diameter of 0.75 mm (molecular weight cut-off 20,000 Da, porosity 68%) were obtained from Tianjin MOTiMO Membrane (China). Magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), and *n*-heptane were all analytical reagents and used without further purification from Tianjin Kermel Chemical Reagent (China). Landfill leachate was supplied by Tianjin Dahanzhuang landfill (China). The formation process of ultrathin active layer on the inner skin of porous hollow fiber substrate was illustrated in Scheme 1.

Preparation of HFC Membrane

Main components of TWC equipment were illustrated in Scheme 2. And specific procedure for the preparation of HFC membranes was as follows:

1. Membrane module fabrication. The effective membrane area for each module was around 0.4 m^2. Each module was composed of 150 fibers with a length of 125 cm and tied into one bundle. Both ends of the bundle were sealed with epoxy resin.
2. Membranes pretreatment. Membrane modules were firstly immersed in pure water for 24 h to remove protective liquid. Then modules were installed in TWC system and excessive liquid in fiber lumen was blown out with compressed air.
3. HFC membrane preparation. Switch on valves 1, 4 and close valves 2, 3 meantime. PIP aqueous solution was circulated for a certain time. Afterward, solution flow direction was changed by opening valves 2, 3 and closing valves 1, 4 to repeat the cycle process. Subsequently, turn off the pump and unscrew valves 7, 8. After excess aqueous solution was drained from the fiber lumen, compressed air was introduced through turning on valves 5 and 8 for a certain time, followed by changing the blowing direction through opening the valves 6 and 7. After the drying process was finished, TMC solution was poured into fiber lumen from the top of
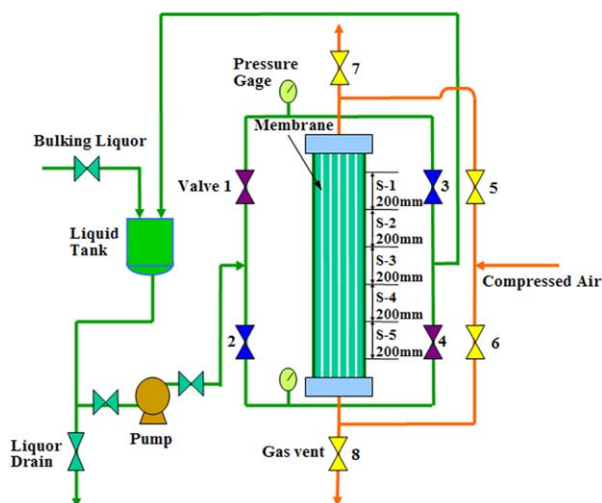
Scheme 2. Flow chart of the inner-skinned HFC membranes preparation by TWC technique. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
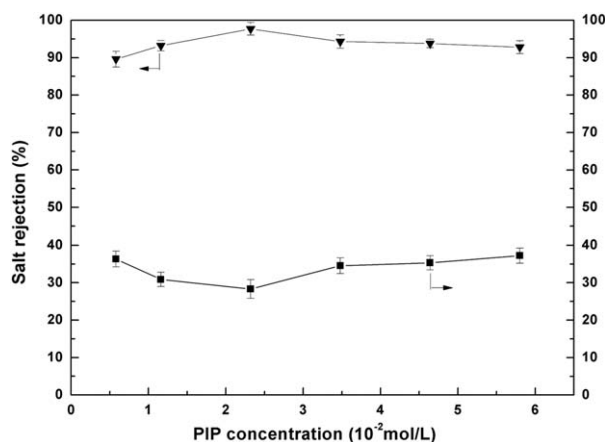
Figure 1. Effect of PIP concentration in aqueous phase on HFC membrane separation performance.

valve 7, while IP reaction occurred immediately and a thin active layer was formed on the inner surface of PSF substrate. Excess organic solution was blown out with compressed air which was similar to the drying step after aqueous coating above.

4. Post-treatment. HFC membranes were dried in an oven at 60°C for 1–15 min and then kept in pure water for the removal of residual solvent, monomers, and oligomers.[18]

In order to investigate the effect of TWC process on membrane structure and performance, HFC membranes prepared in this study were divided into five sections with an effective length of 200 mm, which were designated as S-1, S-2, S-3, S-4, and S-5, respectively, as shown in Scheme 2.

Membrane Characterization

Morphological Structure of Membranes. FESEM (Hitachi S-4800, Japan) was used to analyze surface morphology of different membrane sections. Samples were frozen in liquid nitrogen, fractured, and then sputtered with gold. Surface morphology of different membrane sections was also characterized by atomic force microscopy (AFM, Agilent AFM 5500). The observation was operated in tapping mode at room temperature in air. Roughness was obtained in terms of the mean roughness (R_m). The mean roughness was defined as the average value of the surface relative to the center plane for which the volumes above and below the plane were equal.

NF Permeation Tests. The permeation tests of NF membranes were carried out in a cross-flow filtration set-up at 25°C under 0.7 MPa. The feed was 1 g/L MgSO$_4$ or NaCl aqueous solution. Membrane was compacted at 0.8 MPa until the permeate volume was stable. Water permeate flux (F) was obtained as:

$$F = \frac{V}{A \cdot t} \qquad (1)$$

where F-water permeate flux (L m^{-2} h^{-1}); V-water permeation volume (L); A-the effective membrane area (m^2); and t-filtration time (h).

Salt rejection (R) was calculated as:

$$R(\%) = \ 1 - \frac{C_p}{C_f} \times \ 100\% \qquad (2)$$

where C_p and C_f are the salt concentrations of permeate and the feed, respectively. The salt concentrations were examined via a conductivity meter (DDS-11A, Shanghai Leici Instrument Works, China). If there was no special instruction, the rejection was referred to MgSO$_4$.

NF Membrane Preservation. The effects of different glycerol concentration on separation performance of dried NF membranes were investigated. Seven NF modules with similar separation performance were immersed in pure water or glycerol aqueous solutions with different concentration for 24 h followed by a shade drying in the atmosphere. Salt rejection and permeate flux were tested at an interval of 15 days. After each test, membrane modules were immersed into the corresponding glycerin aqueous solution and dried before the next performance test.

Landfill Leachate Treatment by NF Membrane. The product water of tubular membrane bioreactor (MBR) was using as raw water of NF membrane. Chemical oxygen demand (COD), total dissolved solids (TDS), total residue (TR), and chroma of raw water and permeate water were tested at an interval of 3 h. NF membrane was flushed with pure water through fiber lumen for 30 min. Then 0.2 wt % hydrochloric acid was used to clean NF membrane for 30 min followed by a flush of pure water to wash away the residual acid solution. The flux recovery ratio (F_{RR}) after chemical cleaning was calculated as follow.

$$F_{RR}(\%) \ = \ \frac{F_{ac}}{F_0} \times \ 100\% \qquad (3)$$

where F_0 and F_{ac} were the virgin permeate flux and the permeate flux after cleaning, respectively.

RESULTS AND DISCUSSION

Effects of Polymerization Conditions on NF Performance

PIP Concentration. Monomer concentration has an important influence on composite membrane performance and the influence may be different due to different coating area.[10,19,20] PIP concentration in aqueous solution and TMC in organic solution was optimized, respectively, as shown in Figures 1 and 2. When
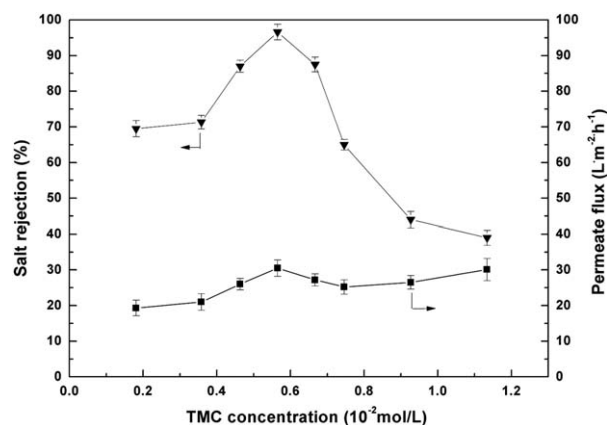

Figure 2. Effect of TMC concentration in organic phase on HFC membrane separation performance.

the effect of each monomer concentration on the performance of composite membranes was studied, other preparation parameters were fixed including aqueous phase coating pressure 0.1 MPa, air blowing rate 4.61 m/s for 30 min after coating PIP solution, organic solution passage time for 8 min with flowing rate 0.32 m/s, reaction time of 2 min, and heat treating for 3 min. It should be noted that the passage time of aqueous solution was kept at 30 min due to its little effect on membrane performance.[7]

The permeate flux and salt rejection of HFC membrane obtained under different concentration of PIP were illustrated in Figure 1. It could be seen from Figure 1 that permeate flux initially decreased and then kept stable with the increase of PIP concentration. At the same time, salt rejection firstly increased and then leveled off. This was because polyamide network structure could not be fully formed at low PIP concentration. Consequently, the separation performance of composite membrane was poor. When PIP concentration reached 0.023 mol/L, an integrated and dense network structure was formed so that both the rejection and flux achieved the maximum. With PIP concentration further increased, a dense cross-linking barrier was formed. It hindered PIP molecules diffusion onto the interface between nascent layer and organic phase leading to a stable thickness of functional layer. Therefore, the performance of composite membranes remained almost stable.[21] Similar results were obtained in other researches,[7,14] in which membrane modules with effective membrane area of 13.19 cm^2 or a length of 1/8 in were fabricated, respectively. In this study, PIP concentration was kept at 0.023 mol/L.

TMC Concentration. The permeate flux and salt rejection of HFC membrane obtained under different concentration of TMC were illustrated in Figure 2. Before TMC concentration reached 0.0057 mol/L, the rejection and flux both increased. However, when TMC concentration continued to increase from 0.0057 to 0.0074 mol/L, both of the flux and rejection declined. It should be noted that the optimum of TMC concentration here was lower than that reported in other literature[22,23] in which the effective membrane area and length of substrate membrane were much smaller. When TMC concentration slowly increased to 0.0057 mol/L, IP was gradually accomplished. A thin nascent active layer with dense network structure was formed leading to the increasing rejection. And meanwhile, the un-reacted chloride groups of TMC were converted into carboxylic acid groups through hydration which enhanced the hydrophilicity of the composite NF membrane. As a result, the flux also increased.[24]

When TMC concentration continued to increase from 0.0057 to 0.0074 mol/L, both of the flux and rejection declined. Maurya et al.[25] pointed that the network density and the rejection layer thickness were the two factors responsible for the higher rejection. During this stage, with the increasing of TMC concentration, the functional layer gradually became thick while excess TMC molecules initiated the conversion of acyl chloride to carboxylate contributing to the decline of network density. The combination of these two factors resulted in the decline of the rejection and flux.

When TMC concentration continued to increase in the range of 0.0074–0.011 mol/L, the flux slightly increased while the
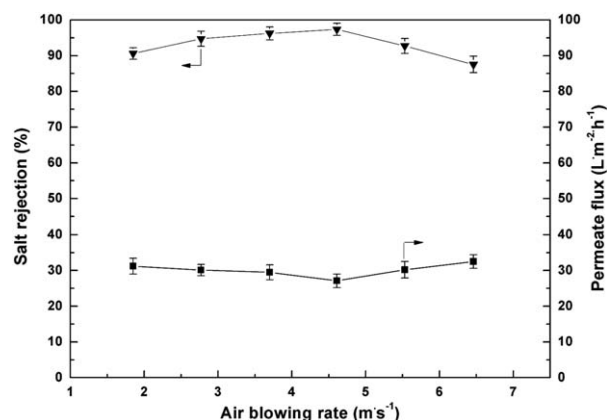

Figure 3. Effect of air blowing rate after PIP solution coating on HFC membrane separation performance.

rejection obviously declined. An et al.[24] explained that when TMC concentration was too high, the heavy cross-linking reaction occurred, making the diffusion rate of PIP decrease. And this resulted in the formation of somewhat loose and incomplete network polyamide skin layer. Meanwhile, the residual acid chloride groups could be converted into carboxylic acid groups, resulting in the surface morphology stability of the polyamide layer decrease. Consequently, the flux increased and the rejection obviously declined. Moreover, the by-product such as hydrogen chloride could not be excluded immediately from the network structure so that IP reaction was carried out in the opposite direction. This also resulted in a poor separation performance. Therefore, TMC concentration was kept at 0.0057 mol/L to prepare HFC membranes.

Air Blowing Rate in Fiber Lumen. As mentioned in previous literature,[17,26] the drop removal of aqueous solution from the surface of support fiber was essential to obtain a thin layer without pin-holes. Figure 3 showed the effect of air blowing rate after aqueous solution coating on membrane separation performance. The PIP and TMC concentration were fixed at 0.023 and 0.0057 mol/L, respectively. Other preparation conditions were the same as depicted in "PIP Concentration" section. It could be found that as air blowing rate increased, the rejection increased firstly and then gradually decreased. The variation of flux exhibited an opposite tendency. The blowing rate directly affected the adsorption amount of PIP monomer on fiber inner surface and the integrity of active layer. At the initial stage, the drops of unadsorbed amine solution in fiber lumen could be well drained out with compressed air. A dense network structure without pin-holes could be obtained. When the blowing rate increased over 4.61 m/s, PIP molecules attached on PSF inner surface gradually reduced, a few defects appeared in the water film derived from PIP aqueous solution. Therefore, the resultant composite membrane had an imperfect layer and showed a poor rejection.

Air Blowing Time in Fiber Lumen. The effect of air blowing time after aqueous solution coating on membrane separation performance was showed in Figure 4. Other preparation conditions were the same as described in "PIP Concentration" section. It should be noted that the blowing time here was a total
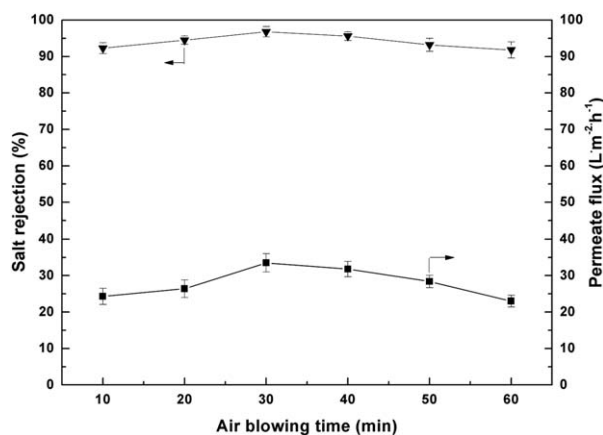
Figure 4. Effect of air blowing time after PIP solution coating on HFC membrane separation performance.

Figure 5. Effect of aqueous coating pressure on HFC membrane separation performance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value in two directions. That meant half time in each direction. Figure 4 showed that the flux increased firstly and then decreased. Salt rejection almost kept stable. Compared with TFC membrane, blowing time had smaller impact on HFC membranes performance.[17] This was because blowing rate was another factor affecting separation performance of polyamide membrane as depicted in "Air Blowing Rate in Fiber Lumen" section, which was generally ignored in the preparation process of TFC composite membrane. PIP monomer could not be uniformly distributed along substrate fiber for a short blowing time. However, long blowing time would induce pore shrinkage of support membrane and flux decline.[16] A thin and dense functional layer was formed only at appropriate blowing time.

Coating Pressure of Aqueous Solution. Each micropore of substrate membrane is a micro-reaction zone. The amount of aqueous monomer adsorbed in micropores has a great influence on active layer formation and HFC membrane separation performance.[7] So far, few researchers have investigated the effect of aqueous coating pressure on composite membranes performance probably due to the limitation of their coating method.

Figure 5 showed the effect of different aqueous coating pressure on membrane separation performance. Other preparation conditions were the same as depicted in "PIP Concentration" section. It could be seen that with the increase of coating pressure salt rejection firstly increased and then rapidly declined. At the same time, permeate flux exhibited the opposite trend. Best separation performance was reached when coating pressure was 0.1 MPa with the rejection of 97.5% and flux of 28.8 L m^{-2} h^{-1}.

An explanation was raised that the balance between the amounts of PIP molecules adsorbed on substrate inner surface and in membrane micropores determined the active layer formation and the separation performance. When coating pressure increased to 0.1 MPa, more PIP molecules was attached on micropores walls along with the permeation of aqueous solution, as shown in Scheme 3(a,b). Once IP reaction occurred, a thin layer could be quickly formed on PSF membrane surface [Scheme 3(c)]. With the proceeding of IP reaction, PIP molecules on the microporous walls diffused onto the newly generated layer surface [Scheme 3(d)] and reacted with TMC
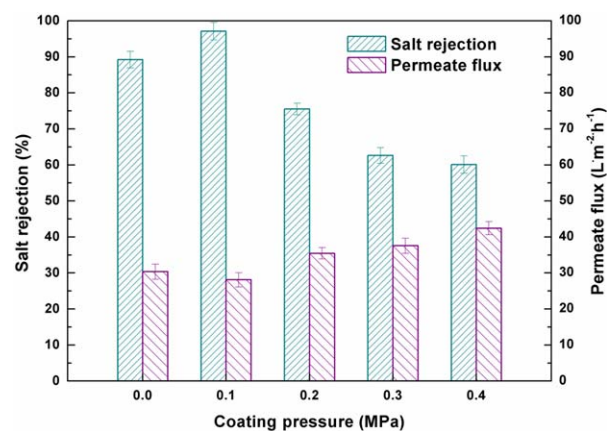
monomers. This covered the imperfections and thickened the functional layer leading to the formation of a thick and dense layer, as shown in [Scheme 3(e)]. When the pressure increased over 0.1 MPa, the amount of PIP molecules adsorbed on membrane surface decreased rapidly. The IP reaction was an instantaneous reaction, monomer diffusion onto nascent layer was relatively difficult and slow during the late stage, although more PIP molecules were attached in micropores.[7] Therefore, a thin and loose functional layer was formed resulting in a poor separation performance. Some PIP molecules were adsorbed on pore walls which could explain why the optimal concentration of aqueous phase in Figure 1 was lower than that reported in other literature.[7,14]

Flowing Rate of TMC Solution in Fiber Lumen. Generally, IP reaction between diamine and acid chloride occurs on the organic side of the aqueous-organic interface. The contact degree between organic phase and aqueous phase determines IP reaction rate and the dense degree of functional layer.[13] The contact degree was affected by TMC concentration, reaction time, and flowing rate of TMC solution in fiber lumen. Figure 6 showed the effect of TMC solution flowing rate on HFC membrane separation performance. It could be seen that with the increase of flowing rate, rejection increased firstly and then slightly decreased. The flux showed the opposite trend. IP reaction is an instantaneous process. Low flowing rate implies that there are not enough TMC monomers contacting with PIP monomers in a short time. This would result in a slow reaction rate and a thin layer with defects.[7] As flowing rate exceeded 0.32 m/s, excess TMC monomers would react with PIP monomers instantaneously. Acyl chloride and amide groups in cross-linking network structure was prone to be hydrolyzed resulting in a loose layer formation.

Reaction Time. Figure 7 showed the effect of reaction time on HFC membrane separation performance. It can be seen in Figure 7, during the first 30–60 s, the salt rejection gradually increased while the flux slowly decreased with the increase of reaction time. When the reaction time extended from 60 s to 120 s, the rejection exhibited an obvious increase from 70.5%
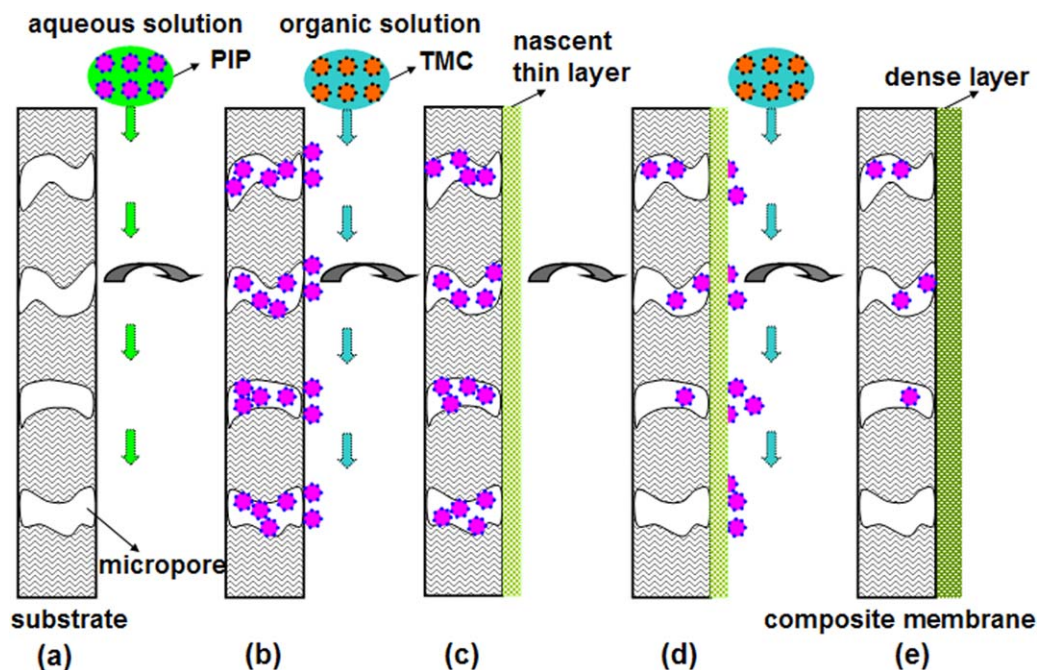
Scheme 3. Formation diagram of composite membrane at aqueous coating pressure of 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to 98.1% and the flux showed a significant decrease from 82.3 to 30.6 L m^{-2} h^{-1}. When further increasing the reaction time to 150 s, the rejection kept stable and the flux decreased slightly. The slow variations during the reaction time from 30 s to 60 s corresponded to the Scheme 3(b or c). At this stage, the nascent thin layer was gradually formed. The significant changes during the reaction time from 60 to 120 s corresponded to the Scheme 3(d or e). At this stage, the functional layer with highly cross-linked structure was gradually formed along with the diffusion of PIP molecules onto the surface of nascent thin layer. When the reaction time further extended from 120 to 150 s, the relatively thick functional layer was formed resulting in the further decrease of the water flux.

Heat Treating Time. Under an appropriate heat treatment, the cross-linking reaction could be well completed with the forma-

tion of a denser functional layer. Figure 8 showed the effect of heat treatment time at 60°C on separation performance. It could be observed that the rejection of composite membrane decreased first and then increased with the prolongation of heating time, while the flux variation appeared the opposite. On the one hand, IP reaction was an exothermic reaction. Heat treatment could induce the reverse reaction which generated polyamide hydrolysis. On the other hand, PIP molecules could diffuse more easily to the layer surface and react with TMC. The combined effects of these two aspects affected the resultant membrane performance. Obviously, the hydrolysis effect was the major factor at first, thus the rejection firstly decreased. As heat treatment time increased over 3 min, the diffusion of more PIP molecules as well as the pore shrinkage of support membrane resulted in the rejection improvement and flux decline.
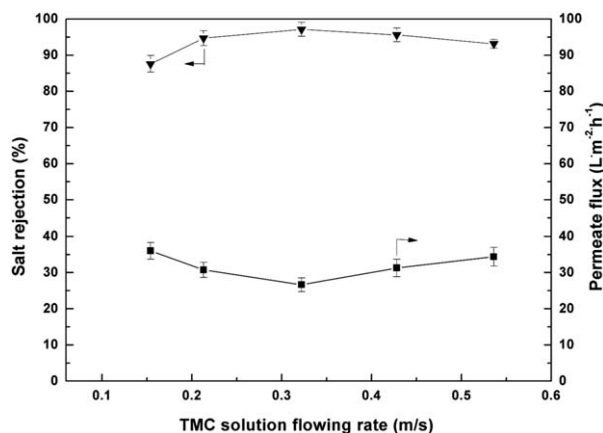

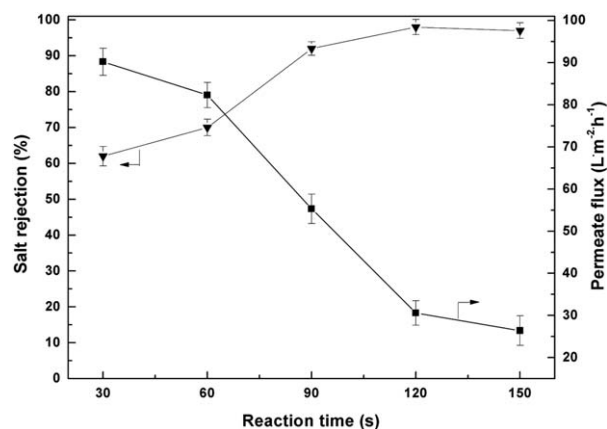**Figure 6.** Effect of TMC solution flowing rate on HFC membrane separation performance.

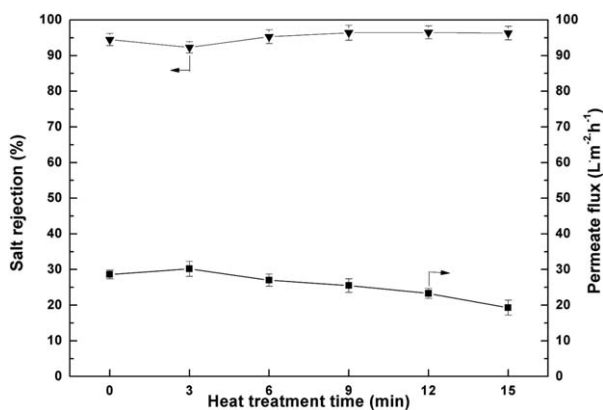**Figure 7.** Effect of reaction time on HFC membrane separation performance.

Figure 8. Effect of heat treatment time on HFC separation performance.

NF Properties Tests. The effects of NaCl and MgSO$_4$ concentration on HFC separation performance were shown in Figure 9. Obviously, the monovalent and divalent salt ions could be effectively separated by HFC NF membranes. The separation behavior was a typical characteristic of negatively charged NF membrane.[27] With the increase of salt concentration, the flux and rejection of two kinds of salt ions all slightly decreased. This phenomenon was due to Donnan balance and concentration polarization.[25,28]

Figure 10 showed the separation performance comparison of PIP-TMC NF membrane and a number of negatively charged NF membranes reported in the literature. It could be seen that most of the negatively charged NF membranes reported previously[2,4,13,28–33] exhibited a higher NaCl rejection between 30–50%. Whereas, NF membranes prepared by TWC technique [Figure 10(a)] showed a lower NaCl rejection of 18% and a higher MgSO$_4$ rejection of 98% simultaneously. This indicated that TWC technique was a perspective method to prepare desirable NF membranes with excellent separation performance. A perfect active layer was formed with charged groups distributing more uniformly in the network structure of polyamide layer during the TWC process.

The Stability of TWC Technique. The stability of a new explored technique is very important. Considering that membranes prepared without aqueous coating pressure exhibited a
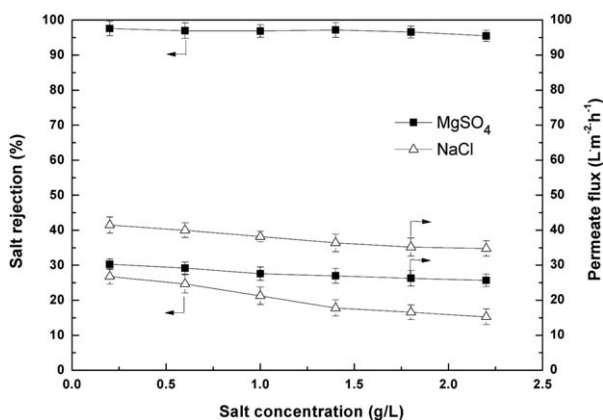

Figure 9. Effects of salt concentration on HFC membrane performance.
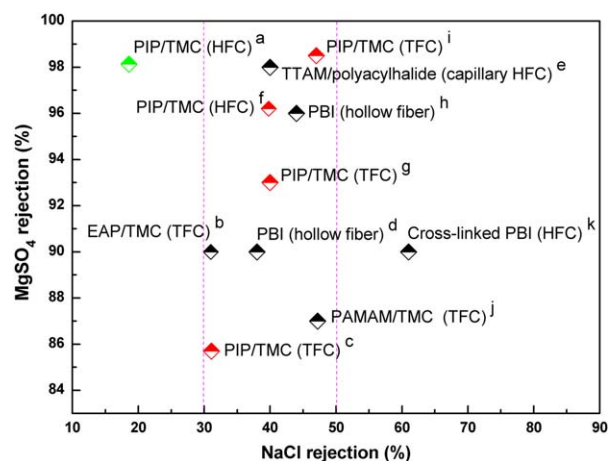

Figure 10. Separation performance comparison of the negatively charged NF membranes. (Data come from: a: this study, b: Ref. 28, c: Ref. 18, d: Ref. 4, e: Ref. 34, f: Ref. 35, g: Ref. 28, h: Ref. 36, i: Ref. 37, j: Ref. 38, and k: Ref. 31). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rejection of 89.2% and a flux of 30.4 L m^{-2} h^{-1} (as shown in "Coating Pressure of Aqueous Solution" section) which were acceptable in the actual operation, the stability testing of composite membrane prepared at aqueous coating pressure 0.1 MPa and 0.0 MPa were carried out as shown in Figure 11(a,b). It
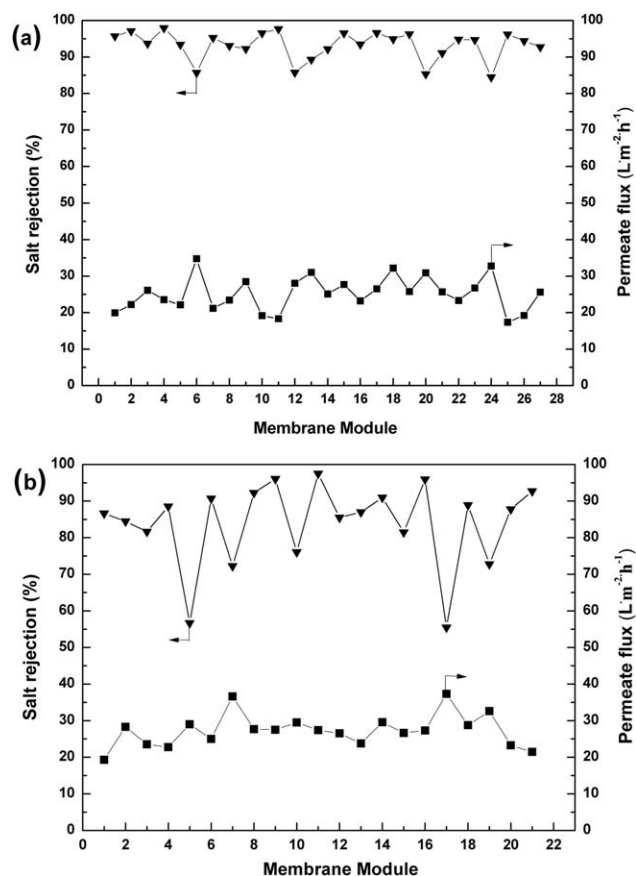

Figure 11. Stability of composite membrane performance at aqueous coating pressure of 0.1 MPa (a) and 0 MPa (b).
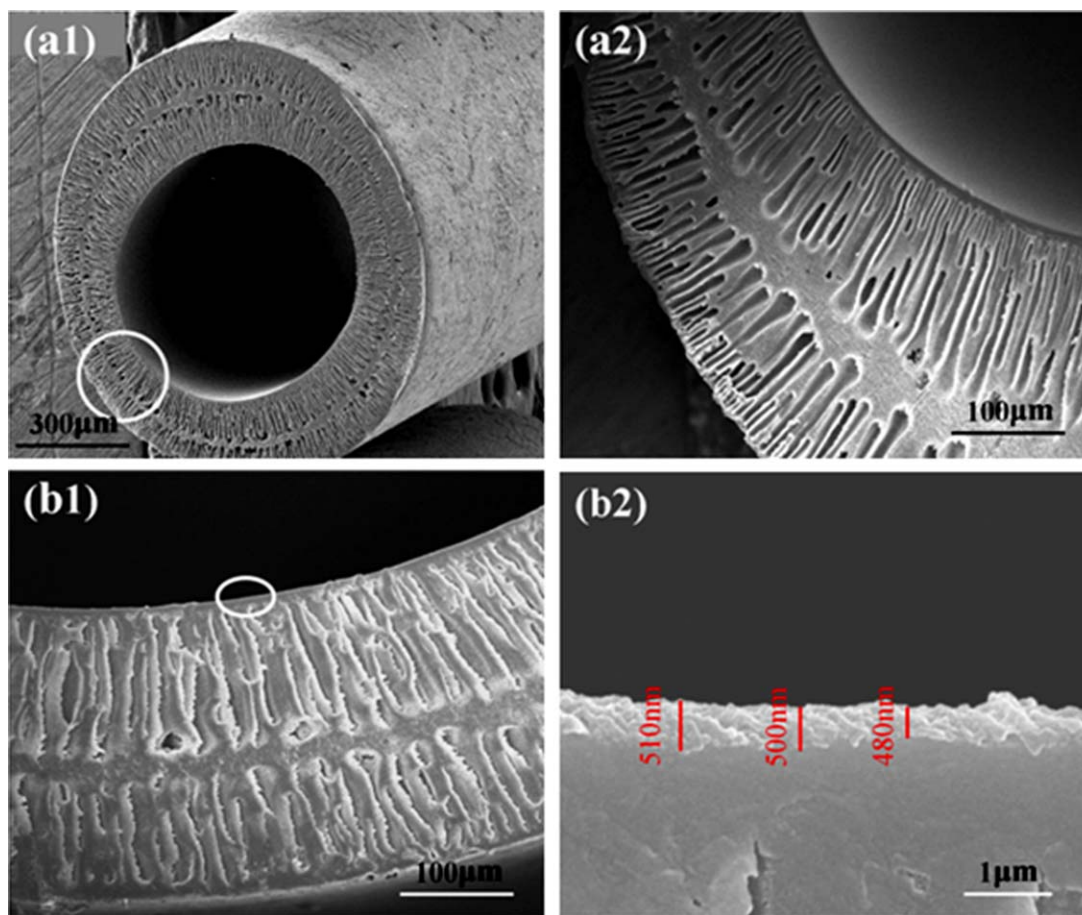
Figure 12. Cross section morphologies of PSF membrane (a1) (×70), composite membrane (b1) (×250). (a2) (×250) and (b2) (×20.0k) were the high resolution images of upper surface of (a1) and (b1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could be seen from Figure 11 that more high-performance NF membrane modules were obtained by TWC at aqueous coating pressure 0.1 MPa.

Cross Section Morphologies of Composite Membranes. Figure 12 showed cross section morphologies of PSF membranes and composite membrane (S-5). It could be clearly seen that PSF substrate exhibited a typical double finger-like pore structure. Generally, membranes with this structure had the characteristics of high flux, large bursting pressure, and strong strength, which were particularly suitable to be used as substrates of HFC membranes[2] An ultrathin functional layer with a thickness of about 500 nm was formed on the inner surface of PSF fiber as shown in Figure 12(b). The layer was tightly attached on PSF membrane surface. Active layer thickness of different membrane sections were characterized by FESEM analysis and the specific values of S-1, S-2, S-3, S-4, and S-5 were 470, 485, 430, 450, and 500 nm, respectively. It indicated that composite membrane

prepared by TWC technique had a uniform active layer from the upper end to the bottom of the hollow fiber.

Comparison of Separation Performance of Different Membrane Sections. Table I showed the separation performance of different membrane sections. It should be noted that the overall rejection and flux of composite membranes prepared by these two coating methods were both 96% and 26 L m^{-2} h^{-1}, respectively. It could be seen that the salt rejection and permeate flux showed almost no difference between different membrane sections which indicated that TWC was a relatively effective method to obtain a uniform separation performance in the preparation of HFC membrane with a long fiber length.

Effect of Preserving Conditions on NF Membrane Performance. It is necessary to maintain good stability of membrane performance during a long-term preservation. Additionally, membrane modules should be convenient for long-distance

Table I. Comparison of Separation Performance of Different Membrane Sections

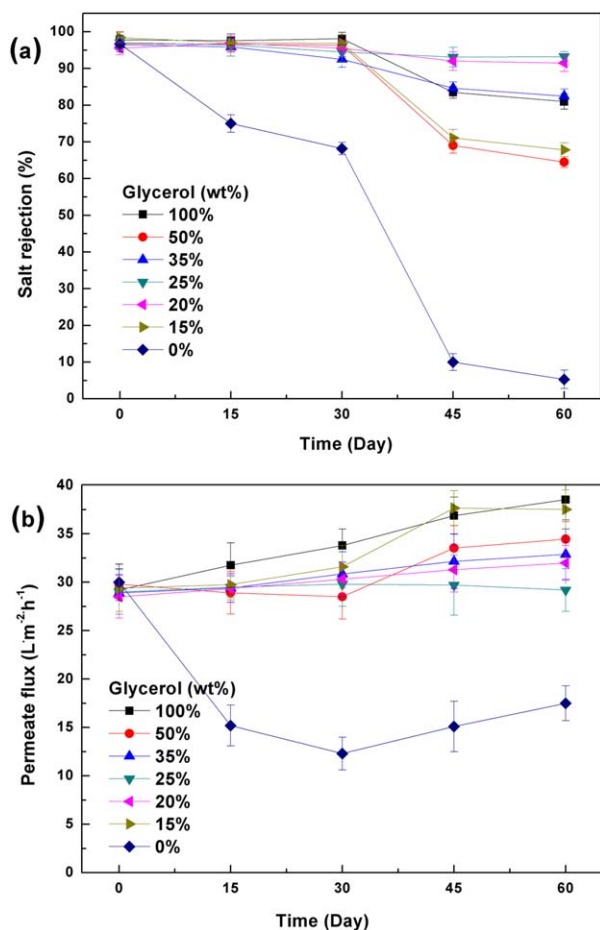| Section	S-1	S-2	S-3	S-4	S-5
Permeate flux (L m^{-2} h^{-1})	24.5 ± 2.5	27.3 ± 2.2	28.1 ± 1.3	29.5 ± 1.8	27.2 ± 2.4
Salt rejection (%)	96.24 ± 1.31	97.13 ± 1.82	94.35 ± 1.61	96.71 ± 2.05	96.96 ± 1.62

Figure 13. Effect of glycerol concentration on NF membrane performance. (a) rejection and (b) flux. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transportation. Generally, membrane modules are always preserved in the antiseptic solution to protect membrane surface from bacteria contamination.[34] However, the modules must be thoroughly cleaned before being used especially in drinking water treatment. Thus looking for an appropriate condition for composite membrane preservation under dry state is particularly important. Membrane preservation under wet state with different antibacterial agent has been investigated in previous literature.[34] Few studies were centered on dry state preservation of membrane modules. Glycerol was always employed as a protective solution due to its good wettability and environment harmlessness. Changes of NF membrane separation performance with preservation time and glycerol concentration were shown in Figure 13(a,b). It could be seen that the rejection and flux of composite membrane had not changed much in glycerin aqueous solution before 30 days. Thirty days later, great changes took place in the separation performance. The rejection and flux of NF membranes kept in 20 wt % and 25 wt % glycerol aqueous solutions remained almost unchanged during 60 days. However, NF membrane immersed in pure water showed a poor separation performance. Higher glycerol concentration was prone to breed bacteria, causing the degradation of NF separation performance.[34] Whereas, glycerol solution with lower concentration could not act as a wetting agent, resulting in the
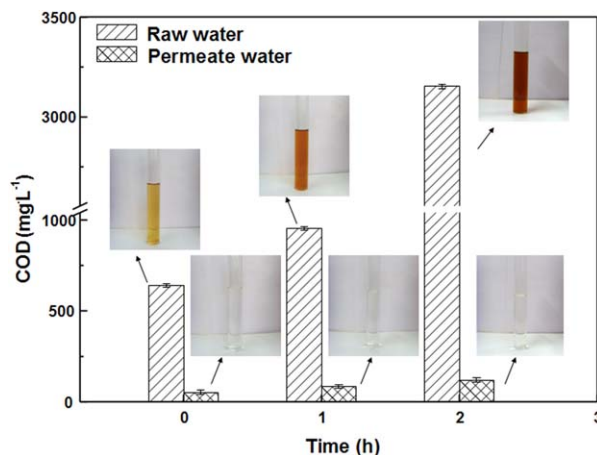

Figure 14. Variations of COD and chroma of landfill leachate with NF time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

serious shrink of membrane pores and dehydration of functional layer during long-term preservation in dry state. Therefore, 20 wt % glycerin aqueous solution was chosen as the protective liquid of HFC NF membranes.

Landfill Leachate Treatment by HFC NF Membrane. Landfill leachate is a kind of complex, high strength wastewater with lots of heavy metals, toxic materials, and organic matter, such as xenobiotic organic compounds which are difficult to degrade using conventional biological process.[35] MBR has proven to be a promising alternative. The product water of MBR always showed a high concentration of organic compounds and a deep color which could not be directly discharged into the surrounding environment. NF has been successfully applied in the COD and color removal of landfill leachate.[36–38] However, most of NF membrane modules used in the literature were flat-sheet or spiral-wound modules supplied by Dow-Film-tech, Millipore, etc. In this study, landfill leachate was treated by the combination technique of MBR and NF. NF membrane was fabricated by TWC technique. The variations of COD and chroma of landfill leachate filtrated by NF membrane was showed in Figure 14 and the pollutants removal rates were listed in Table II. It could be seen that NF membrane exhibited high removal rates of COD and chroma, which were above 90% and 98%.

Table II. Pollutants Removal of Landfill Leachate by NF Membrane at Different Operating Time

Pollutants removal rate (%)	0 h	3 h	6 h
COD[a]	92.2 ± 2.1	91.8 ± 1.3	96.5 ± 2.4
Chroma	98.00 ± 1.6	98.00 ± 2.1	99.00 ± 1.0
TDS[b]	17.4 ± 3.2	17.45 ± 5.2	10.9 ± 4.0
TR[c]	26.08 ± 4.42	29.63 ± 4.31	49.65 ± 3.82

[a] Chemical oxygen demand.
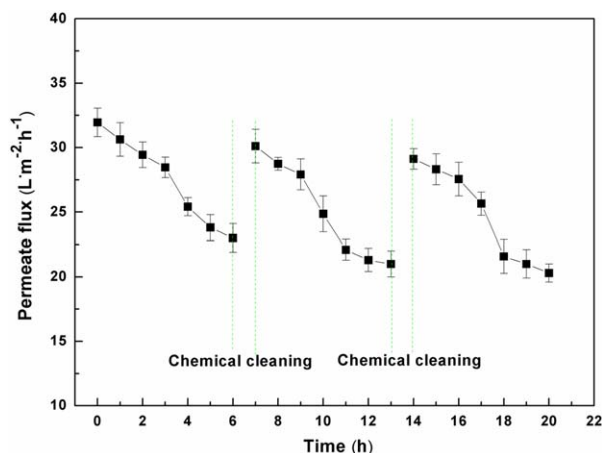[b] Total dissolved solids.
[c] Total residues.

Figure 15. Effect of chemical cleaning on NF membrane flux. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Chemical cleaning using caustic solution such as hydrochloric acid was effective in the removal of organic foulants. The strong caustic solution could emulsify the foulants and hydrolyze proteins and polysaccharides which resulted in a high flux recovery ratio.[39] In this study, NF membrane cleaning was carried out with 0.2 wt % hydrochloric acid at an interval of 6 h. It was found from Figure 15 that the flux decreased from 32 to 23 L m^{-2} h^{-1} during the first 6 h which was mainly caused by organic fouling. Two separate stages occurred in filtration operation, which were similar with the previous study.[40] The initial phase showed a rapid decline flux which was attributed to the pore blocking and organic pollutants stacking. During the second phase, permeate flux declined slowly, which was derived from the formation of an organic fouling layer on NF membrane surface. After filtration of 6 h and 12 h, the flux recovery ratio was 94.2 and 91.1%, respectively.

CONCLUSIONS

HFC NF membrane was prepared by TWC technique via IP of PIP and TMC on the inner surface of PSF membrane. The preparation conditions including PIP and TMC concentration, PIP solution coating pressure, air blowing rate, and time after aqueous coating, TMC solution flowing rate and heat treatment time had great effects on separation performance of NF membrane. Functional layer thickness remained almost unchanged from the upper end to the bottom of the hollow fiber. High-performance HFC membrane with good reproducibility could be obtained when aqueous solution coating pressure was 0.1 MPa. This was due to the adsorption balance of PIP monomers between inner skin surface and microporous on the fiber lumen. Based on the above analysis, TWC technique was proven to be a promising method for preparing high-performance HFC membrane.

ACKNOWLEDGMENTS

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