



Development of antifouling thin-film-composite membranes for seawater desalination

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ABSTRACT

The present contribution provides detailed information about the development of antifouling novel thin-film-composite (TFC) membranes for mostly water purification with special emphasis on seawater desalination in particular. The novel membranes were prepared by incorporating in-situ hydrophilic surface modifying macromolecules (iLSMM) into the TFC membranes, rendering the surface of the TFC membranes significantly more hydrophilic. The prepared membranes were then subjected to long term fouling studies using model foulants, including sodium humate (SH), silica particles (SPs), and chloroform (CF) spiked in the feed NaCl solution. The biofouling effect of silver salts was also studied by incorporating some silver salts (silver citrate hydrate, SCH; silver lactate, SL; and silver nitrate, SN) simultaneously with iLSMM into the TFC membranes. Halo test was conducted with *Escherichia coli* to examine the antibiofouling performance of the silver incorporated TFC membranes. It can be concluded by this work that iLSMM incorporated TFC membranes have performed excellently for the desalination of salty water (3.5 wt% NaCl), especially when the solution was spiked with typical foulants such as SH, SPs, and CF. The flux reduction was reduced significantly when iLSMM was incorporated in the TFC membranes by a newly developed technique. The antimicrobial fouling intensity of the studied membrane was in the order of: SN (ring width 0.55 mm) > SL (0.27 mm) > SCH (0.19 mm).

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1. Introduction

The ancient root of the saline water desalination can be traced back to the fourth century BC when Aristotle and Hippocrates extracted fresh water from saline water using the process of evaporation [1]. In the twentieth century, Reid and Breton observed that the cellulose acetate (CA) film rejected sodium chloride from aqueous solution [2]. However, commercialization of membrane desalination started after the development of the high flux asymmetric CA membrane by Loeb and Sourirajan [3]. Afterwards, the aromatic polyamide (PA) thin-film-composite (TFC) membrane of even higher flux was developed by Cadotte and coworkers by interfacial polymerization (IFP) between diamine in water phase and acyl chloride in organic phase on a porous polysulfone (PS) membrane as a support [4].

Nowadays, the world population lives in water stress condition. Researchers are more focused on the production of drinking water from the seawater applying membrane technologies [5–21], such as the reverse osmosis (RO) process using CA or TFC membranes. Our group has attempted to fabricate TFC membranes of

reduced fouling by adding LSMM (hydrophilic surface modifying macromolecule, polyurethane end-capped with polyethylene glycol). It was expected that the LSMM migrates to the surface of the synthesized PA layer while IFP is proceeding, rendering the surface more hydrophilic and thus making the membrane less susceptible to fouling [22]. Later, a new technique was developed to incorporate LSMM in the skin layer of TFC membrane. According to the method, LSMM was synthesized simultaneously with IFP by adding the monomers for LSMM synthesis (4,4'-diphenylmethane diisocyanate (MDI) and poly(ethylene glycol) (PEG)) into the organic phase of interfacial polymerization. The synthesized LSMM was called in-situ LSMM (iLSMM). The iLSMM incorporated membranes were subjected to a long term stability test using 3.5 wt% sodium chloride (NaCl) solution as the feed and their improved stability was confirmed [23].

The present contribution provides more detailed information on the fouling resistance of the iLSMM incorporated TFC membranes prepared by varying aqueous diamine concentration and heat curing time. Long term fouling studies were conducted using model foulants, including sodium humate (SH), silica particles (SPs), and chloroform (CF) in the feed NaCl solution. These foulants represent natural organic matters, inorganic, and organic foulants, respectively. Moreover, the effect of membrane compaction was investigated for all the studied membranes.

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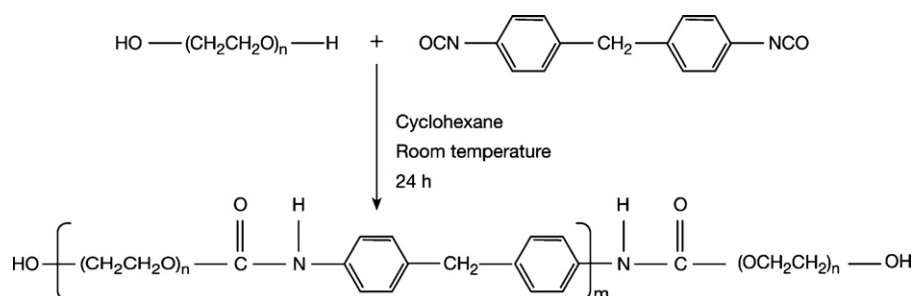


Fig. 1. The schematic presentation of LSMM synthesis reaction.

Silver or silver containing compound is used for antimicrobial purpose [24–28]. Incorporation of silver nanoparticles in TFC membrane greatly improves antibiofouling performance for *Pseudomonas* colonies [29]. It was also noticed that most of the silver nanoparticles stayed on the surface of prepared membranes. In this study, the biofouling effect of silver salts was also studied by incorporating some silver salts (silver citrate hydrate, SCH; silver lactate, SL; and silver nitrate, SN) simultaneously with iLSMM into the TFC membranes. Halo test was conducted with *Escherichia coli* (*E. coli*) to examine the antibiofouling performance of the silver incorporated TFC membranes.

2. Experimental

2.1. Materials

Commercial ultrafiltration (UF) polysulfone (PS) membrane of molecular weight cut-off 5×10^5 g/mol (500 kDa) used as the support membrane was obtained from the TriSep Corporation (Goleta, CA). 4,4'-Methylene bis(phenyl isocyanate) (4,4'-diphenylmethane diisocyanate, MDI, purity 98%), 1,3,5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC), 1,3-phenylenediamine (*m*-phenylenediamine, MPD, Flakes, purity 99+%) and poly(ethylene glycol) (PEG, typical average molecular weight 200Da), were received from Sigma–Aldrich Inc. (St. Louis, MO) and were used without further purification. Cyclohexane (purity 99.9+%) was received from Aldrich Chemicals Co., Inc. (Milwaukee, WI) and was also used without further purification. Sodium salt of humic acid, also known as sodium humate (SH, technical grade, Sigma–Aldrich Chemie GmbH, Steinheim, Germany); silica particles (SPs, silica fumed, powder size $0.007 \mu\text{m}$ and surface area $390 \pm 40 \text{ m}^2/\text{g}$, Sigma–Aldrich, St. Louis, MO); and chloroform (CF, OmniSolv of purity 99.9% from EMD Chemicals Inc., Gibbstown, NJ) were used for foulants. Sodium chloride (NaCl, ACS reagent grade of purity 99.99%) was received from Fisher Scientific Company (Fair Lawn, NJ). Silver nitrate (SN, 99+%), silver lactate (SL, 97%), silver citrate hydrate (SCH) were all purchased from Sigma–Aldrich, Inc. (St. Louis, MO). For the microbial part of the experiments, *E. coli* (American Type Culture Collection, ATCC # 33456) were obtained from ATCC, Manassas, VA, and Luria–Bertani (LB) broth and LB agar, respectively, both purchased from Sigma–Aldrich, Inc. (St. Louis, MO) were used for the preparation of liquid and solid media.

2.2. Preparation of thin-film-composite (TFC) membrane

TFC membrane preparation technique is based on inter-facial polymerization (IFP) between the di-amine (*m*-phenylenediamine, MPD) in the aqueous phase (2 and 3.4 wt%) and tri-acid chloride (trimesoyl chloride, TMC) in the organic phase (in cyclohexane 0.2 wt%). While 0.25 (w/v) (MDI + PEG, molar ratio 1:2) of MDI and

PEG monomers for the synthesis of iLSMM was added to the organic phase to prepare iLSMM incorporated TFC membranes, no MDI and PEG monomers were added to prepare the control TFC membranes. The scheme of the reaction for LSMM synthesis is shown in Fig. 1.

At first, the PS UF support membrane was dipped into an aqueous MPD solution for 2 h. The membrane saturated with aqueous MPD solution was held in a vertical position for 6 min to drain the excess MPD solution. The membrane surface was further blotted by Kimwipes tissue paper. The saturated membrane was then immersed in the cyclohexane solution of TMC, without or with MDI and PEG for 2 min, which resulted in the formation of a thin film of polyamide (PA) on top of the PS support. Then, the resulting composite membranes were heat-cured at 90°C in three different timeframes: i.e., 3, 5, and 8 min. The membranes were kept at ambient temperature for 24 h. Then, they were washed with the DI water and finally stored in the DI water at ambient temperature. It is highly noted that commercial PS membrane is hydrophilic from the contact angle data, and the roughness of the PA layer is lower than the roughness of composite (PA + iLSMM) layer. The preparation conditions of twelve TFC membranes so fabricated are summarized in Table 1.

2.3. Preparation of TFC membrane containing silver salt

The method of preparing silver bound iLSMM membranes is similar to iLSMM containing TFC membranes above described. This time, however, the aqueous phase contained 3.4 wt% of MPD and 0.25 wt% of silver salt (silver nitrate, SN, or silver citrate hydrate, SCH, or silver lactate, SL). It should be noted that all the silver salts were insoluble in cyclohexane. All the resulting composite membranes were heat-cured at 90°C for 5 min. The membranes were kept under ambient temperature for 24 h before they were washed with the DI water. Finally, the membranes were stored in the DI water at ambient temperature.

Table 1
The preparation condition of TFC membranes.

Membrane	Aqueous MPD solution (wt%)	Total (MDI + PEG) conc. in cyclohexane (wt%) ^a	Heat-cured time (min)
A0	2	0	3
A1	2	0.25	3
B0	2	0	5
B1	2	0.25	5
C0	2	0	8
C1	2	0.25	8
D0	3.4	0	3
D1	3.4	0.25	3
E0	3.4	0	5
E1	3.4	0.25	5
F0	3.4	0	8
F1	3.4	0.25	8

^a MDI:PEG molar ratio = 1:2.

2.4. Study on iLSMM

As LSMM (LSMM is a code used when it is synthesized separately from IFP) is supposed to be formed during the TFC membrane preparation, LSMM was synthesized independently under a similar condition in order to find out the structural nature of the iLSMM (iLSMM is a code used when it is synthesized during IFP).

2.4.1. Preparation of LSMM

The LSMM was synthesized by condensation polymerization [30–32]. 0.01 moles (2.5 g) of MDI and 0.02 moles (4 g) of degassed PEG of average molecular weight 200 Da were added to 988.5 mL of cyclohexane in a 1 L bottle under vigorous stirring. PEG and MDI were allowed to react for 24 h at room temperature, resulting in a solution of LSMM, which was precipitated by pouring the solution into distilled water. The LSMM was dried in an air circulation oven at 50 °C for 5 days until a constant weight of approximately 4.2 g was obtained.

2.4.2. Characterization of LSMM

The chemical name of the LSMM is poly(4,4'-diphenylenemethylene ethylene-urethane) with both ends capped by poly(ethylene glycol). The chemical structure of the LSMM used in this study is shown in Fig. 1. The solubility of the LSMM was studied on nine different solvents at room temperature. The LSMM was soluble in DMAc, NMP, dimethylformamide, dimethylsulfoxide, and tetrahydrofuran, whereas LSMM was insoluble in acetone, cyclohexane, n-hexane, and toluene.

The structure of LSMM was identified by NMR. All spectra were acquired on a Bruker AVANCE II 300 NMR spectrometer. The ^1H NMR spectrum was acquired in 16 scans using a 30° pulse. The acquisition time was 3.6 s and the recycle delay was 10 s. The ^1H gradient enhanced COSY-45 spectrum was acquired using 4 scans for each of 256 slices. The recycle delay was set at 1 s and the acquisition time was 167 ms (millisecond). The ^1H - ^{13}C gradient enhanced HMQC spectrum was acquired using 8 scans for each of 256 slices. The recycle delay was set at 1 s and the acquisition time was 167 ms. The spectral width in the ^{13}C domain was set at 170 ppm. The ^1H - ^{13}C gradient enhanced HMBC spectrum was acquired using 32 scans for each of 256 slices. The recycle delay was set at 1.5 s and the acquisition time was 167 ms. The spectral width in the ^{13}C domain was set at 230 ppm. The ^{13}C NMR spectrum was acquired using WALTZ 16 proton decoupling in 14,336 scans using a 30° excitation pulse. The acquisition time was 0.9 s and the recycle delay was 1 s. The ^{13}C DEPT-135 spectrum was in 5523 scans. The acquisition time was 0.9 s and the recycle delay was 2 s.

The ^1H spectrum of LSMM is shown in Fig. 2A. The presence of the hydroxyl group of the LSMM sample was confirmed by HMQC spectra in DMSO- d_6 solvent as peak was observed at about 4.64 ppm in the ^1H spectra but no signal appeared in the HMQC spectrum (Fig. 2B). The value of the n was calculated from the average molecular weight of PEG 200 Da which is 4.14. The value of m was calculated using the ^1H NMR. The ratio between the integrated peak area of the signals corresponding to all hydrogen (A_{H_T}) and the peak area of the aromatic signal ($A_{\text{H}_{\text{AR}}}$) is expressed as:

$$\frac{\sum A_{\text{H}_T}}{A_{\text{H}_{\text{AR}}}} = \frac{4nm + 11m + 4n + 3}{8m} \quad (1)$$

The right hand side of Eq. (1) is formulated from chemical structure of LSMM (Fig. 1). The left hand side of the equation is equal to 19.94/4.35 from ^1H NMR spectrum. The value of m for LSMM is calculated from Eq. (1) which is 2.15. Therefore, the molecular weight of LSMM is 1.1×10^3 Da.

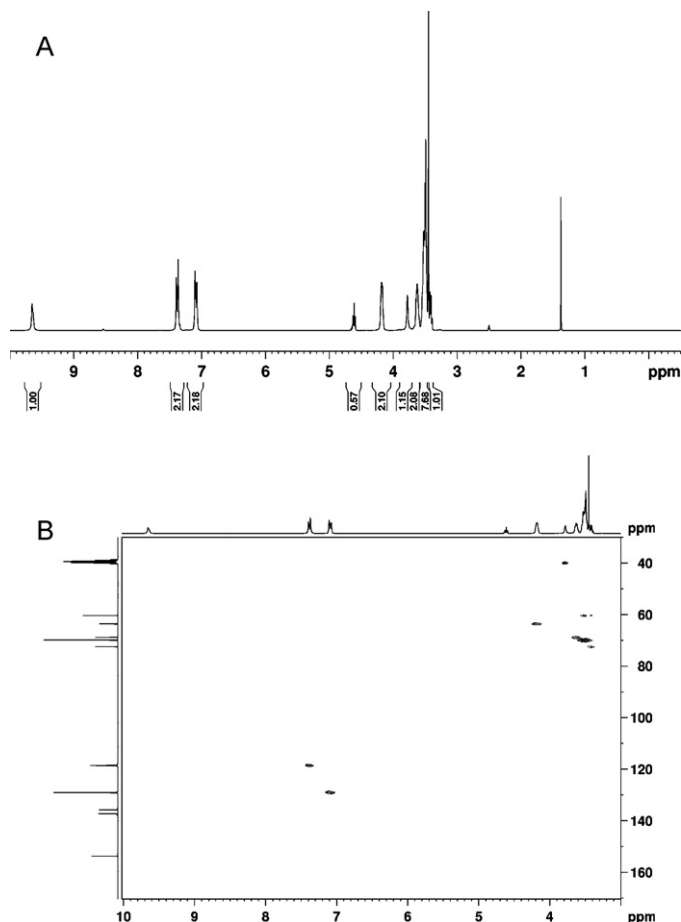


Fig. 2. (A) ^1H NMR and (B) HMQC NMR spectrum of LSMM.

2.5. Reverse osmosis

2.5.1. Reverse osmosis experiments with NaCl solution

Reverse osmosis (RO) experiments were conducted using a laboratory-scale system consisting of six small RO cross-flow cells connected in series [33–35]. The cells housed membrane coupons with an effective area of about 13.2 cm 2 and the feed flow rate was 36 L h $^{-1}$. All the experiments were performed using an operating pressure of 5520 kPa (800 psig). Each membrane was pre-compressed by filtering DI water at 6900 kPa (1000 psig) for 8 h and then for 4–5 h at 5520 kPa. Pure water permeation (PWP) rate was measured at 5520 kPa after the pressurization. The NaCl salt concentration in the feed aqueous solution was 3.5 wt%. The concentrations of the feed and the permeate solution were determined via a conductivity meter (model CON 110, Oakton Instruments, Vernon Hills, IL). The flux and rejection data were calculated from triplicate measurements.

For each sample, solute NaCl rejection (R) was calculated, it is defined as:

$$R = 1 - \frac{C_p - C_w}{C_f - C_w} \quad (2)$$

where C_p is the permeate conductivity, C_f is the feed solution conductivity, and C_w is the pure water conductivity. In order to ensure the accuracy, reliability, and reproducibility of the collected data, all measurements were performed at least triplicate, and then, the mean value were taken.

2.5.2. Fouling experiments

Eighteen TFC membranes were prepared to compare fouling of membranes without and with iLSMM. Sodium salt of humic acid (SH), silica particles (SPs), and chloroform (CF) were used for foulants, representing natural organic matters, inorganic particles and small organic solutes dissolved in water, respectively. Two hundred ppm of each foulant was either dissolved or dispersed in the 3.5 wt% NaCl solution to prepare the feed solution. The compositions of the feed and the permeate were determined by the following methods. The concentration of NaCl was determined by conductivity measurement, which is considered sufficiently precise since the amount of the foulant involved is very small.

The concentration of SH was determined by UV absorption using a spectrophotometer (model DU-40, Beckman Instruments Inc., Irvine, CA). Measurements were performed using a 1 cm quartz cell and at a wavelength of 254 nm. Pure water, 0.175 and 3.5 wt% NaCl aqueous solutions were used in the reference cell, but there was no change in the absorbance.

The concentration of the SPs was determined by the particle size analyzer (PSA) using Zitasizer instrument (model Nano-S, Malvern Instruments Ltd., Worcestershire, UK). Measurements were made using a 1 cm quartz cell. The pure water was used as a reference. The specific conditions were: measurement position 4.65, attenuator 11, and run number 20. It should be noted that the mean count rate (kcps) is the vital parameter to measure the concentration of SPs. The concentration of SPs was also measured, as a supplementary examination, with the help of a spectrophotometer (model DU-40, Beckman Instruments Inc., Irvine, CA). Measurements were performed using a 1 cm quartz cell at the wavelength of 530 nm. The pure water and 0.175 wt% NaCl aqueous solutions were used as references.

The concentration of chloroform (CF) was determined by a total organic carbon (TOC) analyzer with UV-persulfate method in total carbon (TC) mode (Phoenix 8000, Rosemount Analytical Inc., Tekmar Dohrmann Division, Santa Clara, CA). Calibration was made by using chloroform solutions of known concentrations (1.0–200.0 ppm).

Initially, PWP was measured; then flux (J_0) of aqueous 3.5 wt% NaCl was measured. Afterwards, flux (J_t) at various times (t) of aqueous 3.5 wt% NaCl with or without 200 ppm of foulant was measured. The flux reduction (FR) in percentage was calculated by using Eq. (3):

$$FR(\%) = \frac{J_0 - J_t}{J_0} \times 100 \quad (3)$$

2.5.3. Membrane compaction studies

Another series of six TFC membranes were prepared under the chosen membrane preparation conditions and characterized by NaCl rejection. Those membranes were then subjected to a long term (200 h) compaction test with the feed DI water, measuring the pure water permeation rate at different times. The flux reduction defined by $(1 - \text{PWP at 200 h}/\text{initial PWP})$ was then calculated in a range of 19.9–29.4% without any significant difference between without and with iLSMM incorporation. These values are close to the FR values displayed by the TFC membranes with iLSMM incorporation when the membranes were subjected to the long term test with 3.5 wt% NaCl solution. Hence it can be concluded that the FR of the membranes with iLSMM incorporation was primarily due to compaction, while FR is more than compaction for the TFC membranes without iLSMM incorporation.

Finally, the compaction effect on the substrate PS membrane was investigated by pressurization at 5520 kPa under pure water and measuring PWP (see Table S6). The FR in percentage was cal-

Table 2

Results from sodium chloride separation experiments by RO.

TFC	PWP (L/m ² h)	Flux (L/m ² h) ^a	NaCl rejection (%)
A0	68.50 ± 3.15 ^b	42.61 ± 6.33	86.19 ± 1.12
A1	46.99 ± 0.96	35.14 ± 0.46	93.44 ± 0.25
B0	78.12 ± 2.34	41.54 ± 3.47	94.09 ± 0.63
B1	57.16 ± 2.66	31.13 ± 1.70	96.49 ± 0.53
C0	58.70 ± 3.05	34.16 ± 3.44	82.56 ± 2.82
C1	44.41 ± 0.52	23.44 ± 0.58	94.39 ± 0.92
D0	56.97 ± 2.29	32.46 ± 1.93	92.00 ± 2.19
D1	47.70 ± 2.59	31.79 ± 1.34	96.01 ± 0.93
E0	69.46 ± 2.03	27.04 ± 1.22	95.81 ± 0.66
E1	55.49 ± 1.94	26.02 ± 0.83	97.93 ± 1.04
F0	49.34 ± 1.26	21.75 ± 0.10	87.62 ± 0.08
F1	39.92 ± 0.91	21.08 ± 0.89	94.70 ± 0.67

^a Feed, aqueous 3.5 wt% NaCl solution; operating pressure, 5520 kPa; operating temperature, room.

^b The ± sign is a standard deviation (s.d.) of independent measurements of membrane coupons: average of four coupons for A0, C0, and F0; average of two coupons for A1, C1, and F1; average of twelve coupons for B0, D0, and E0; average of ten coupons for B1, D1, and E1.

culated by using Eq. (4):

$$FR(\%) = \frac{PWP_{0h} - PWP_{200h}}{PWP_{0h}} \times 100 \quad (4)$$

FR values are in a range of 31.4–36.2%. Hence, compaction was much reduced by the skin layer formation of TFC membranes.

2.6. Biofouling experiment by *E. coli*

To evaluate the antibiofouling effect of the membrane, the Halo test was conducted with *E. coli* [36,37]. The *E. coli* was grown in a liquid LB media at 37 °C with a shaking speed of 150 rpm using a shaking incubator (Model: Lab-Line Orbit Environ-Shaker, Lab-Line Instruments Inc., Melrose park, IL). The *E. coli* solution was freshly prepared for each experiment and used within 12 h. In the present study, solid media of nutrient (LB) agar (called agar plate, hereafter) was prepared. The membrane was cut into pieces of 2 cm diameter disk. The *E. coli* was inoculated on an agar plate, and the membrane disk was placed. The prepared agar plate was incubated at 37 °C for 5 h. The thickness of the inhibition zone (IZ) that appeared around the membrane disk was then measured.

3. Results and discussion

The fluxes and salt rejections (in the presence of 3.5 wt% NaCl in the feed) of the twelve membranes listed in Table 1 are given in Table 2. The membrane performance was observed at an operating pressure of 5520 kPa and room temperature. From Table 2, it can be concluded that all the membranes prepared under the conditions given in Table 1 are in nanofiltration category with NaCl rejections ranging from 86.19 to 97.93%. On the basis of the above RO data; we have selected six types of membrane (Bi, Di and Ei, $i = 0$ and 1, where 0 and 1 denote absence and presence of iLSMM, respectively) for the fouling study.

The results of long term (200 h) tests are shown in Figs. 3–7. Fig. 3 shows the flux reduction (FR in %) at different operation times. The FR increased drastically during the initial 50 h of operation for all the TFC membranes without incorporation of iLSMM, and the rate of FR increase slowed down as operation time became longer. After 5 h of operation, the iLSMM incorporated membranes showed lower FR values than membranes without iLSMM. It is interesting to note that the flux of the B1 membrane was much lower than B0 at time zero but after 200 h of operation the order was reversed. Slight improvement in NaCl rejection was observed for all the membranes, with or without incorporation of iLSMM.

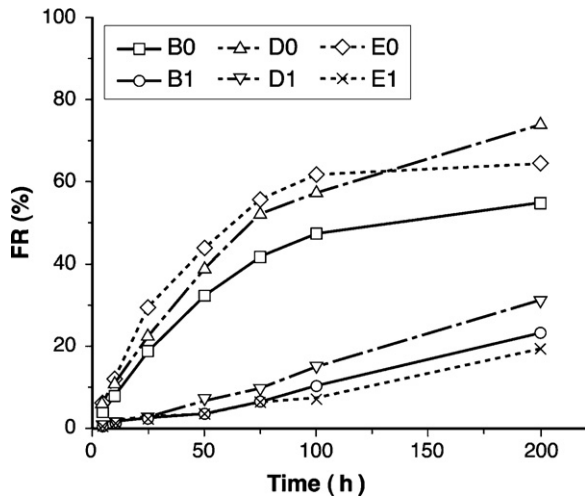


Fig. 3. The FR (%) versus operational time for aqueous 3.5 wt% NaCl solution.

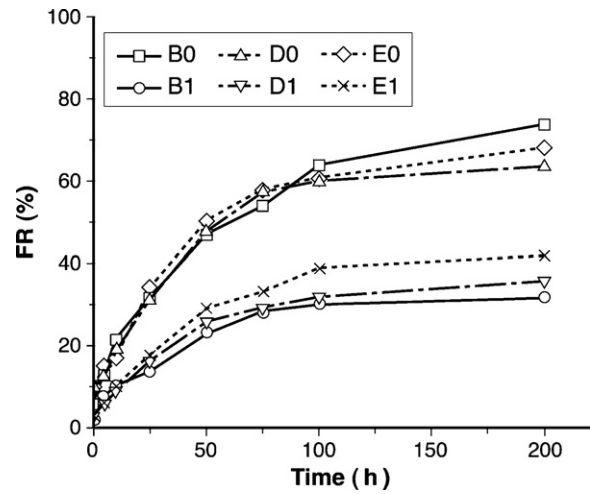


Fig. 6. The FR (%) versus operational time for aqueous 3.5 wt% NaCl solution spiked with 200 ppm of chloroform.

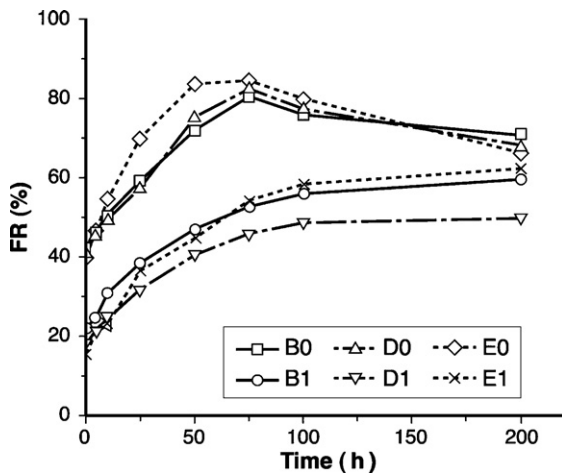


Fig. 4. The FR (%) versus operational time for aqueous 3.5 wt% NaCl solution spiked with 200 ppm of sodium salt of humic acid.

The long-term fouling test was conducted with the feed 3.5 wt% NaCl solution into which 200 ppm of SH was spiked (Fig. 4). Notably, all the permeate solutions contained less than 1 ppm of SH. It was further observed that the initial FR values were lower for the mem-

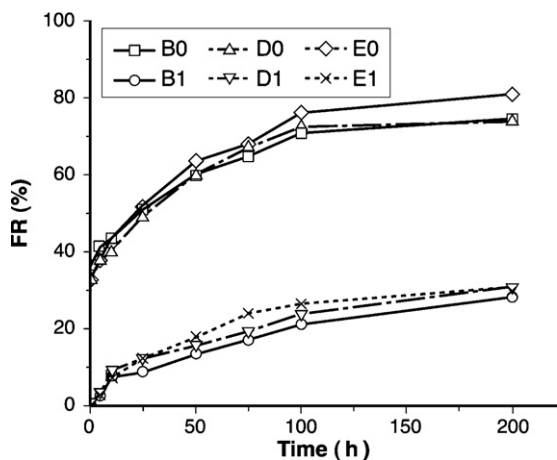


Fig. 5. The FR (%) versus operational time for aqueous 3.5 wt% NaCl solution spiked with 200 ppm of silica particles.

branes incorporated with iLSMM. After 75 h of operation, FR started to decrease, i.e., the flux increased for all the membranes without iLSMM whereas the flux continued to decrease for all the membranes with iLSMM incorporation (see Table 3(A)). As for NaCl rejection, it started to decrease at 75 h for all the membranes without iLSMM, while it kept increasing for all the membranes with iLSMM (see Table 4(A)). It is suggested that the PA linkage of the membranes without iLSMM is destroyed when they are exposed to alkaline environment for more than 75 h, resulting in increase in the flux and decrease in the NaCl rejection. In contrast, all the iLSMM incorporated TFC membranes showed much superior stability in the presence of SH. Generally, SH macromolecules are highly adsorbed to surface [38]. The rate and extent of FR depends upon ionic strength, pH, and concentration of SH [39].

The long term fouling test was performed by adding 200 ppm of SPs in to 3.5 wt% NaCl feed solution (Fig. 5). All the permeate solutions contained less than 1 ppm of SP. Initial FR was much lower for the membranes with iLSMM compared to without iLSMM. The FR continued to increase for both membranes without and with iLSMM incorporation. However, after 200 h of operation, the flux of the membranes with iLSMM became more than double the flux of the membranes without iLSMM (see Table 3(B)). The NaCl rejection remained almost constant for the membranes without

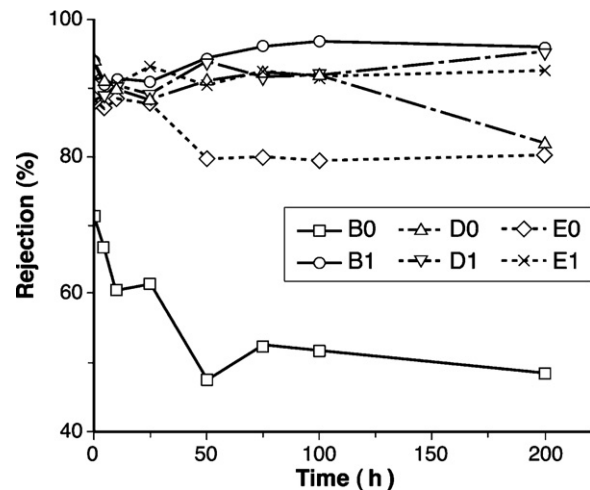


Fig. 7. The CF rejection (%) versus operational time for aqueous 3.5 wt% NaCl solution spiked with 200 ppm of chloroform.

Table 3
The flux results of the long-term (200 h) RO test of the six TFC membranes.

TFC	1 h	5 h	10 h	25 h	50 h	75 h	100 h	200 h
(A) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm SH ^a								
B0	25.55	24.29	22.02	18.03	12.39	8.57	10.51	12.50
B1	25.04	24.09	22.11	19.74	17.09	15.03	13.97	12.91
D0	19.43	17.84	16.62	14.02	8.07	5.66	7.20	10.47
D1	27.32	26.26	25.18	22.70	19.85	18.05	17.17	16.70
E0	16.23	14.30	12.34	8.04	4.32	4.06	5.41	9.01
E1	22.75	21.05	20.62	16.93	14.63	12.31	11.09	10.1
(B) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm SPs ^a								
B0	24.30	22.42	21.72	18.81	15.46	13.54	11.18	9.76
B1	31.08	30.45	29.07	28.61	27.10	25.95	24.71	22.43
D0	21.43	19.87	19.08	16.22	12.82	10.64	8.89	8.44
D1	32.66	31.70	29.72	28.81	27.64	26.43	25.00	22.72
E0	17.58	16.11	14.94	12.46	9.39	8.36	6.21	4.93
E1	26.14	25.75	24.64	23.20	21.72	20.08	19.45	18.60
(C) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm CF ^a								
B0	37.91	35.09	31.46	27.44	21.32	18.46	14.51	10.58
B1	32.56	30.63	29.76	28.68	25.56	23.86	23.23	22.72
D0	30.80	29.68	27.51	23.43	17.78	14.46	13.58	12.36
D1	29.69	28.79	27.78	25.53	22.66	21.71	20.81	19.77
E0	24.50	22.90	22.54	17.84	13.50	11.53	10.74	8.69
E1	25.76	24.89	23.79	21.78	18.80	17.75	16.25	15.45

^a Feed, aqueous 3.5 wt% NaCl solution spiked with 200 ppm SH, or SPs or CF; operating pressure, 5520 kPa; operating temperature, room.

iLSMM, whereas slight increase was observed for the membranes with iLSMM (see Table 4(B)). These results suggest that more SP are deposited on the skin layer of the membranes without iLSMM. The superior performance of iLSMM incorporated membranes is obvious. Deposition of SPs is referred to as particulate fouling [40].

The long term organic fouling test was investigated by adding 200 ppm of CF in to 3.5 wt% NaCl feed solution. The FR and CF rejection are summarized in Figs. 6 and 7, respectively. The FR values were much higher for the membranes without iLSMM than those with iLSMM. The separation CF tends to decrease for the membranes without iLSMM while it tends to increase for the membranes with iLSMM (Fig. 7). The same trend is observed for NaCl rejection (Table 4(C)). Among the three membranes without iLSMM, the flux (Table 3(C)) and separation decreased most significantly for the B0 membrane that contains the lowest amount of MPD. These results indicate that the stability of membranes was improved by the incorporation of iLSMM. It is especially noteworthy that separation of the membranes with iLSMM increased with increasing operational period. More than 95% removal of chloroform was

achieved in single stage RO desalination. Therefore a higher CF removal is expected while passing through more than one RO desalination stage. The possible mechanism of CF rejection using commercial membranes was explained by absorption/diffusion in the membrane/desorption processes [41]. Data from pilot plant of TFC RO membrane showed that the rejection of CF reached better than 96.8% using the aqueous conc. range 800–1100 $\mu\text{g}/\text{dm}^3$ [42]. However, the gradual increase of CF rejection with operation time suggests that CF rejection of the iLSMM incorporated membranes is not by the adsorption mechanism but by the sieving mechanism. The results of the compaction test with feed DI water is as follows. The flux reductions defined in the experimental Section 2.5.3 were in a range 19.9–29.4% for membranes both with and without iLSMM. There was no statistically significant difference between those two categories. These values are close to the FR values displayed by the TFC membranes with iLSMM incorporation, when the membranes were subjected to the long term test with 3.5 wt% NaCl solution (see Fig. 3). Therefore, it can be concluded that the FR of the membranes with iLSMM incorporation was pri-

Table 4
The rejection of NaCl in % results of the long-term (200 h) RO test of the six TFC membranes.

TFC	1 h	5 h	10 h	25 h	50 h	75 h	100 h	200 h
(A) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm SH ^a								
B0	94.74	94.91	95.11	95.34	95.50	95.71	94.12	93.37
B1	96.33	96.38	96.52	96.60	96.67	96.86	97.00	97.26
D0	92.76	92.97	93.18	93.42	93.62	93.73	92.45	91.16
D1	96.18	96.23	96.30	96.42	96.59	96.72	96.82	96.91
E0	95.36	95.54	95.68	95.79	95.87	95.92	94.22	92.95
E1	97.91	98.15	98.39	98.59	98.77	98.90	98.95	98.96
(B) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm SPs ^a								
B0	93.89	93.96	93.98	94.12	94.13	94.19	94.32	94.45
B1	96.85	97.00	97.18	97.34	97.52	97.68	97.81	97.92
D0	93.02	93.11	93.17	93.24	93.38	93.48	93.67	93.70
D1	96.96	97.09	97.18	97.32	97.43	97.52	97.73	97.89
E0	96.33	96.41	96.48	96.52	96.63	96.70	96.79	96.87
E1	98.42	98.57	98.64	98.77	98.84	98.91	98.96	99.20
(C) Aqueous 3.5 wt% NaCl solution spiked with 200 ppm CF ^a								
B0	94.84	94.39	94.01	92.86	90.82	89.45	87.84	86.85
B1	96.65	96.73	96.77	96.97	97.44	97.77	98.00	98.17
D0	94.04	93.74	93.41	92.72	91.17	90.92	90.00	88.90
D1	94.84	94.92	95.23	95.53	95.82	96.17	96.61	97.19
E0	95.63	95.00	94.59	94.24	92.93	91.99	91.11	90.88
E1	98.89	98.92	99.02	99.22	99.46	99.60	99.70	99.77

^a Feed, aqueous 3.5 wt% NaCl solution spiked with 200 ppm SH, or SPs or CF; operating pressure, 5520 kPa; operating temperature, room.

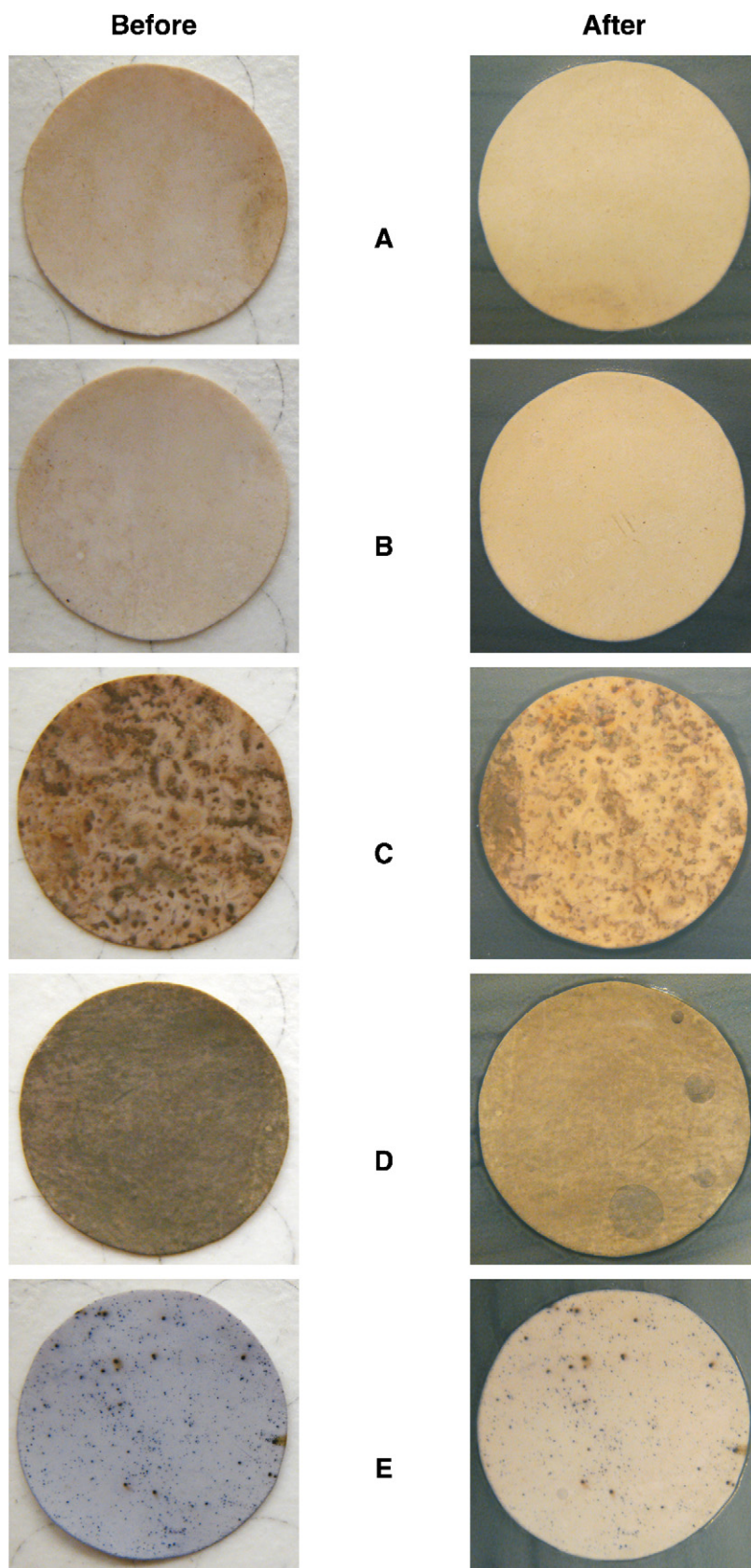


Fig. 8. TFC membrane coupons before and after the Halo test: (A) TFC without iLSMM, (B) TFC with iLSMM, (C) TFC with iLSMM and silver nitrate, (D) TFC with iLSMM and silver lactate, and (E) TFC with iLSMM and silver citrate hydrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

marily due to compaction, while FR was more than compaction for the membranes without iLSMM incorporation. When the substrate PS membrane was subjected to the compaction test, the flux reductions defined in Section 2.5.3 were in a range 31.4–36.2%. Hence, compaction was much reduced by the skin layer formation of TFC membrane.

The control membranes, with and without incorporation of iLSMM in TFC, did not show any Halo ring around the membrane (Fig. 8). Halo ring appeared when the silver salts were incorporated. The ring width of membranes with SN, SL and SCH were 0.55 ± 0.06 , 0.27 ± 0.02 , and 0.19 ± 0.03 mm, respectively. Thus, the TFC membrane with iLSMM and SN showed the highest antibacterial effect while other silver incorporated TFC membranes showed similar but lower effectiveness. In relation to this work, it is to be noted that PU foam coated with silver nanoparticles exhibited null *E. coli* in the permeate side during filtration [43].

4. Conclusions

It can be concluded by this work that iLSMM incorporated TFC membranes have performed excellently for the desalination of salty water (3.5 wt% NaCl), especially when the solution was spiked with typical foulants such as SH, SPs, and CF. The FR was reduced significantly when iLSMM was incorporated in the TFC membranes by a newly developed technique. It would be very interesting to test these novel membranes for chlorine resistance in the future work. It can also be concluded that silver salts incorporated in the TFC membranes have indeed antibiofouling effect. Future studies are designed to bind silver ions to the iLSMM either electrostatically or by complex formation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2010.10.050.

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