Physico-Chemical Pretreatment to Seawater Reverse Osmosis (SWRO):

Organic Characterization and Membrane Autopsy

H.K. Shon[a], S. Vigneswaran[a], M.H. Zareie[a], R. Ben Aim[b], E. Lee[c], J. Lee[c], J. Cho[c] and In S. Kim[c]

[a]Faculty of Engineering, University of Technology, Sydney, Australia (hkshon@eng.uts.edu.au; vigid@eng.uts.edu.au; hadi.zareie@uts.edu.au), [b] Institute National des Sciences Appliquees, Complexe Scientifique de Rangueil, 31077 Toulouse Cedex 4, France (email: benaim@insa-tlse.fr), [c]Environmental Science and Technology, Gwangju Institute of Science and Technology, Gwangju, Korea (ju0826@.gist.ac.kr; storyhil@gist.ac.kr; jwcho@gist.ac.kr; iskim@gist.ac.kr)

ABSTRACT

In this study, different pretreatment methods such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), powdered activated carbon (PAC) adsorption and ferric chloride ($FeCl_3$) flocculation were evaluated in terms of their capability in removing seawater organic matter (SWOM) and the characteristics of the foulants on the seawater reverse osmosis (SWRO) membranes. A detailed experiment with a crossflow SWRO filtration unit was conducted with SR membrane (MWCO 100 Da) at 60 bar with seawater (conductivity = 48.9 mS/cm) drawn from south-western Korea.

The SWOM removal by UF, NF, PAC adsorption and $FeCl_3$ flocculation was 20.3%, 28.9%, 46% and 23.3%, respectively. SWOM used in this study predominantly consisted of small size organic matter (< 1000 Da). A large amount of the hydrophobic fraction present in SWOM was removed by PAC adsorption. The SDI_{5min} significantly decreased from 12.7 (without any pretreatment) to 3.2 (MF), 1.3 (UF), 1.0 (NF) and 4.4 (PAC adsorption). RO filtration of seawater with and without pretreatment showed significant flux decline (normalized flux decline (J/J_0) = 0.17±0.02) within 20-hr operation. The elemental analyses made on the RO surface after direct RO filtration showed that the relative fraction of the carbon decreased, while sodium (Na), magnesium (Mg), chlorine (Cl) and iron (Fe) elements were found in the foulants extracted from the fouled membrane surface. The average roughness of the clean membrane surface was 41.5 nm. After MF and UF pretreatment, the roughness slightly increased to 54.8 and 55.6 nm, respectively. On the other hand, without any pretreatment, with PAC adsorption and with $FeCl_3$ flocculation, the roughness increased up to 69.7, 66.4 and 110 nm, respectively. It can be concluded that the pretreatment by MF and UF could relatively preserve the RO membrane surface.

Keywords: Pretreatment; Seawater desalination; Reverse osmosis; Membrane autopsy; organic matter

INTRODUCTION

Global water shortage can be solved by alternative water sources i.e. desalination and wastewater reclamation. Even if desalination has been developed, the operation is costly due to the requirement of high energy and membrane fouling. The membrane fouling of seawater reverse osmosis (SWRO) has a significant impact on operation of desalination plants. The SWRO foulants consist of i) biofouling (48%), ii) inorganic colloids (18%), iii) organic compounds (15%), iv) silicites/silicates (13%), v) mineral deposits (6%) and vi) coagulants (5%) [1]. Although the concentration of the organic matter in seawater is relatively low and consequently the portion of organic foulant is small in comparison with inorganic constituents, seawater organic matter (SWOM) is a more difficult problem to be solved in the desalination processes. Dudley et al. [2] reported that membranes with severe biofouling were found with 60%

organic foulant. However, SWRO is difficult to predict membrane fouling in terms of filtration flux as it is nonporous membrane.

Membrane autopsy is one of the most effective techniques to determine SWRO fouling [3-7]. To identify the fouling on SWRO surface, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), atomic force microscopy (AFM), zeta potential, contact angle, pyrolysis-gas chromatography/mass spectrometry (GC/MS) and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) have been used [8]. The zeta potential detects the electrokinetic value associating a realistic magnitude of surface charge on SWRO. ATR-FTIR confirms a detailed screen of the molecular functional groups contributing to membrane fouling. SEM/EDX is used for visual investigation of membrane fouling and elemental analysis on foulants. AFM provides information on membrane roughness. Contact angle represents hydrophobicity on membrane surface.

SWOM can be removed by applying different pretreatment processes to SWRO. Conventional pretreatment includes coagulation, filtration and activated carbon, whereas microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are recently used as advanced pretreatment. In this study, different physico-chemical pretreatment methods were evaluated in terms of their capability in removing SWOM. Membrane autopsy was also investigated on the SWRO membrane surface after various pretreatments.

MATERIALS AND METHODS

Seawater. This study was conducted with seawater drawn from south-western Korea (approx. N35º4'56'', E126º26'26''). The typical seawater characteristics were found (pH = 8.10; conductivity = 48.9 mS/cm; total dissolved solid = 32827 mg/L; turbidity = 0.4 NTU; specific UV absorbance (SUVA) = 1.28, SWOM = 1.56 mg/L; and alkalinity = 78 mg/L as $CaCO_3$).

Pretreatment Methods. Flocculation was carried out using an optimum dose of ferric chloride ($FeCl_3$ = 20 mg/L) predetermined by standard jar tests. The seawater was placed in a 1 L container and an optimum dose of ferric chloride was added. The sample was stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The characteristics of the PAC (James Cumming & Sons Pty Ltd., Australia) are given elsewhere [8]. For the adsorption experiments, one gram of PAC was added to 1 L of seawater and stirred with a mechanical stirrer at 100 rpm for one hour. Membrane filtration used in this study as pretreatment was a dead-end cell type. MF (cellulose ester, Advantec MFA, Inc., USA) with 0.45 μm pore size using a vacuum pump was employed to filter seawater. A stirred batch cell (8400, Amicon, Millport, USA) with UF (10 kDa, YM10, regenerated cellulose, Millipore, USA) and NF (1 kDa, YM1, regenerated cellulose, Millipore, USA) membranes was used at 4.5 bar, 41.8 cm^2 effective surface area and 20 ºC.

SWRO Set-up. A crossflow SWRO filtration unit was used to study the effect of pretreatment on the membrane performance. The schematic diagram of crossflow SWRO filter experimental setup is shown in Figure 1. The concentrate was recycled back to the feed tank except for the sample withdrawn for DOC measurement. Each experiment was conducted over a period of 20 hours. New membranes were used in each experiment to avoid the effect of residual fouling and to compare the results obtained under different conditions. Seawater, with and without pretreatment, was pumped into a flat sheet membrane module (effective membrane area of 0.0057 m^2). The operating transmembrane pressure and cross-flow velocity were controlled at 60 bar and 0.5 m/s by means of by-pass and regulating valves. The Reynold's number was approximately 750 (laminar flow). The RO membrane used in this study was SR (Saehan, Korea) (Table 1).

Table 1 Characteristics of RO membrane used

	Material	MWCO* (dalton)	Contact angle(°)	Zeta potential at pH 7 (mV)	PWP**at 60 bar (m/d)
SR	Aromatic polyamides	100	35	- 21	2.04

* MWCO: molecular weight cut-off. ** PWP: pure water permeability

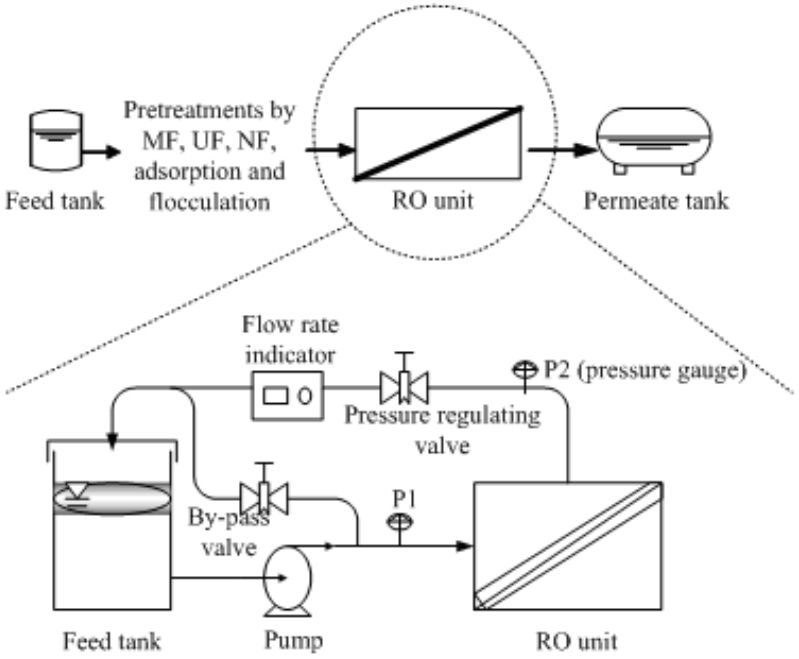


Figure 1 Schematic drawing of cross-flow SWRO unit used in this study

SWOM Characterization. Dissolved organic carbon (DOC) was measured by a carbon analyser (TOC-V, Shimadzu, Japan). The non-purgeable organic carbon (NPOC) method was employed. All samples were filtered through 0.45 μm membrane prior to the DOC measurement and were acidified with the addition of 2 N HCl to remove inorganic carbon by sparging with hydrocarbon free air prior to DOC measurement. XAD-8 and XAD-4 resins were used for fractionating organic matter into hydrophobic (XAD-8 adsorbable; mostly hydrophobic acids with some hydrophobic neutrals) and transphilic (XAD-4 adsorbable; hydrophilic bases and neutrals) components. The remaining fraction escaping the XAD 4 is the hydrophilic component.

Membrane Characterization. The clean and fouled membrane surfaces were analyzed for functional groups using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The fouled membranes were examined by FTIR (460 plus, Jasco, Japan) equipped with an ATR accessory. Contact angle measurements using the sessile drop method with a contact angle meter (Tantec, Co., USA) were used to determine an index of membrane hydrophobicity; 20 μL of Milli-Q water was dropped onto the dried membrane surface and the contact angle was measured within approximately 10 seconds. SEM/EDX (FE-SEM S-4700, Hitachi Corp., Japan) was used to investigate membrane structure and element on membrane fouling. The voltage was 5 kV and the working distance was 12 mm. The magnification was 20,000 times. The top and side views of the membranes were analyzed. A Digital Instruments Multimode Nanoscope III scanning force microscope was used. Each imaging was conducted in tapping mode, with 512 × 512 data acquisitions at a scan speed of 1.4 Hz at room temperature in air. Oxide-sharpened silicon nitride tips with integrated cantilevers with a nominal

spring constant of 0.38 N/m were used for atomic force microscopy (AFM). The roughness of the membrane surface was assessed by measuring the roughness parameters.

RESULTS AND DISCUSSION

Removal of DOC and Hydrophobic Fraction. The effect of different pretreatments was investigated in terms of DOC removal (Figure 2). The DOC removal by UF (10,000, MWCO), NF (1,000, MWCO), PAC adsorption and $FeCl_3$ flocculation was 20.3%, 28.9%, 46% and 23.3%, respectively. This result suggests that the majority of organic matter in SWOM was smaller than 1000 Da. PAC adsorption led to the highest DOC removal of 46% of SWOM. This may be due to the fact that the majority of organic size in SWOM is small as adsorption removes small size of organic matter [9]. The effluent obtained after different pretreatments was fractionated in terms of hydrophobic, transphilic and hydrophilic fraction (Figure 3). The large amount of the hydrophobic fraction was removed by pretreatment of PAC adsorption. This may be due to hydrophobic nature of PAC. In other words, hydrophobic nature of PAC preferentially absorbs hydrophobic SWOM as they are of same nature.

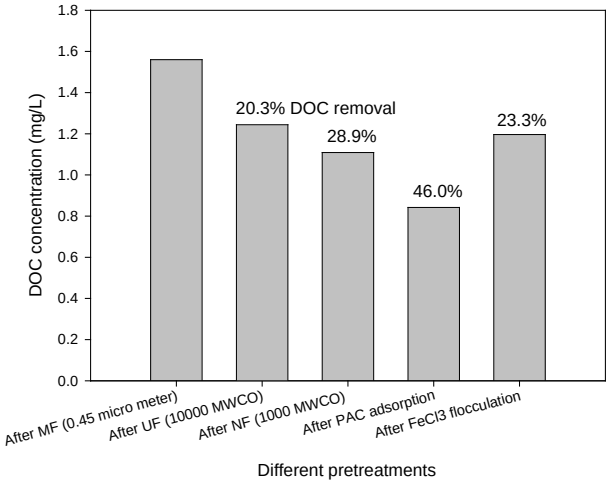


Figure 2 SWOM removal by different pretreatments in seawater

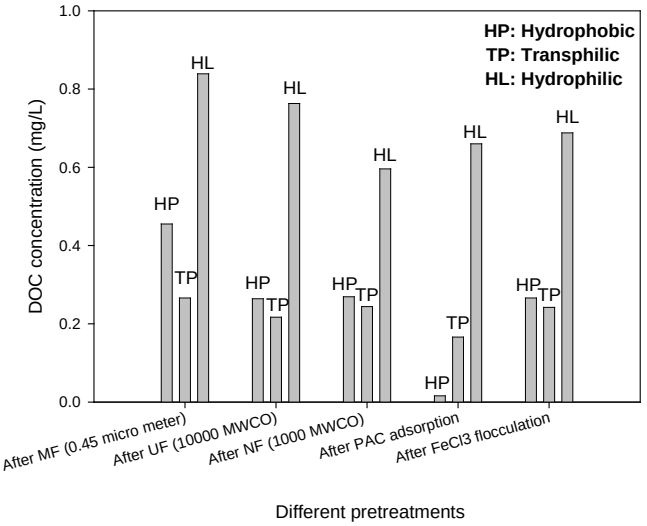


Figure 3 Hydrophobic, transphilic and hydrophilic fraction of seawater after different pretreatments

SDI_{5min} and SWRO Flux Decline with Different Pretreatments. SDI_{5min} after different pretreatments was measured using a dead end cell with 0.45 μm membrane filter at 2 bar (Figure 4). The turbidity of seawater taken from Hampyeong was 0.4 NTU and the SDI_{5min} was 12.7. After MF, UF, NF and PAC adsorption pretreatment, the SDI_{5min} significantly decreased to 3.2, 1.3, 1.0 and 4.4, respectively. However, the SDI_{5min} reduction after pretreatment of $FeCl_3$ flocculation was marginal. The performance of RO membranes in treating seawater was studied in terms of permeate flux (J/J_0). Here, J is filtration flux at a given time and J_0 is pure water filtration flux. All the results of RO filtration of seawater both with and without pretreatment indicated significant flux decline. The filtration flux was very similar up to 0.17±0.02 (J/J_0) at 20-hr operation.

Membrane Autopsy

i) Contact Angle and ATR-FTIR Spectroscopy. Contact angle on the clean and fouled membranes after different pretreatments was measured. A higher contact angle indicates higher hydrophobicity of the membrane surface. The result of the contact angle shows the following order: clean (38º)> NF (34º)> MF (33º) > UF (31º)> flocculation (30º)> adsorption (28º)> without any pretreatment (22º). The fouled membrane without any pretreatment indicated low contact angle, suggesting that pretreatment

could preserve the membrane surface. ATR-FTIR analysis was conducted to investigate the functional groups in the foulants on the clean and fouled membrane surfaces (Figure 6). Only a marginal change of functional groups was observed on the fouled membranes. Without any pretreatment, the band observed at wave number of 1520 cm^{-1} was due to the carboxyl group (-COO-). The transmittance intensity without any pretreatment and after $FeCl_3$ flocculation pretreatment was low with a lot of noise. The peaks with low transmittance intensity on the membrane surface were too difficult to be analyzed for functional groups. On the other hand, the peaks observed for the membranes with PAC adsorption, MF, UF and NF as pretreatment were similar to the clean one.

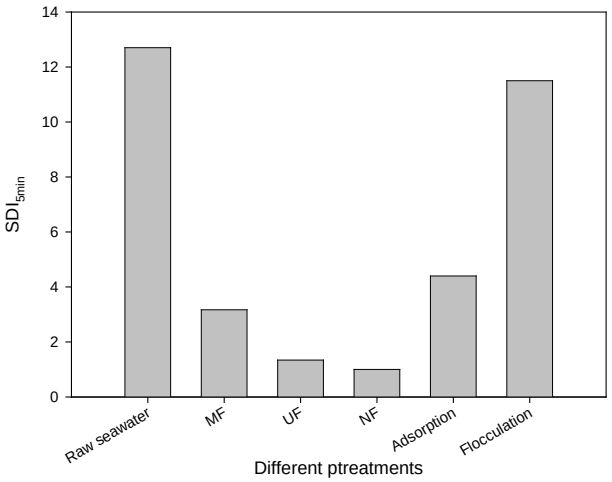


Figure 4 SDI_{5min} profile after different pretreatments (membrane pore size = 0.45 µm; pressure with nitrogen gas = 2 bar; dead end cell type)

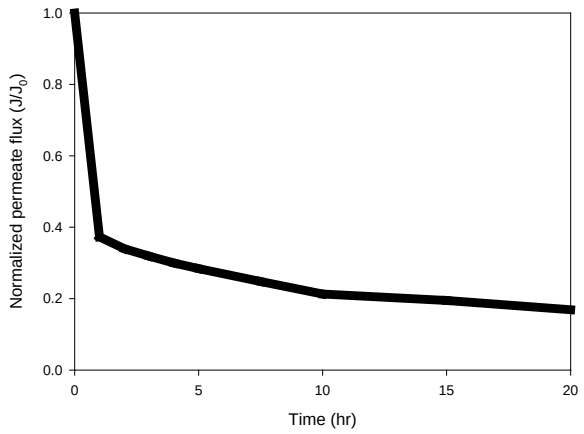


Figure 5 Temporal variation trend of filtration flux with and without pretreatment (membrane = SR; crossflow velocity = 0.5 m/s; initial pure water flux = 2.04 m/d at 60 bar)

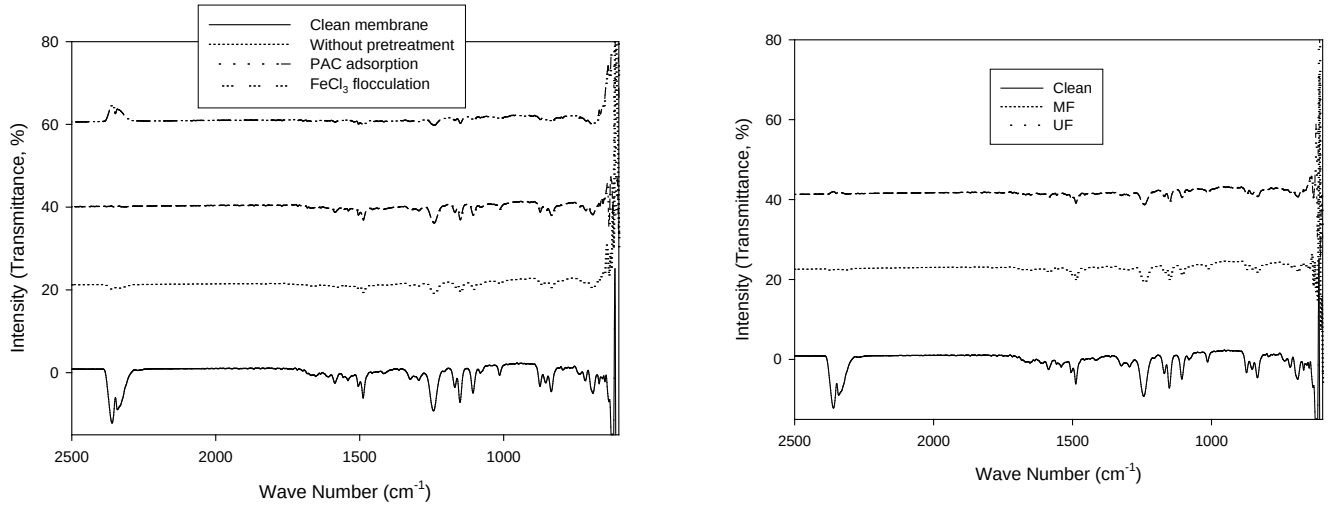
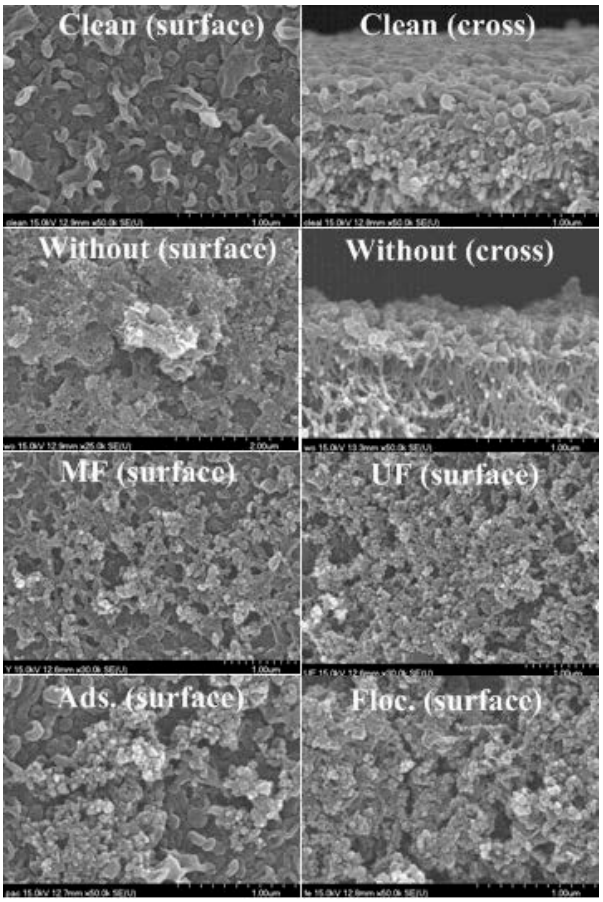


Figure 6 ATR-FTIR spectra with clean RO membrane and after different pretreatments

ii) SEM/EDX. SEM/EDX results on the RO membrane surfaces after different pretreatments in the range of 2.5 µm x 2.5 µm are shown in Figure 7. The foulants on the RO surfaces were found to be amorphous. The RO membrane experienced a severe fouling with naked eyes when seawater was filtered without any pretreatment. The SEM image of the RO cross-section without any pretreatment and with flocculation pretreatment indicated a fouling thickness of approximately 0.1 µm. On the other hand, the other pretreatments did not consist of notable cake layer. Further, the detailed elemental results are shown in Figure 7. The clean membrane consisted of carbon (C), oxygen (O) and sulfur (S)

originating from building components of polyamide membrane polymer and polysulfone support. However, the EDX results of the direct RO filtration showed quite different elements on the fouled membrane surface. The relative fraction of the carbon decreased, while new sodium (Na), magnesium (Mg), chlorine (Cl) and iron (Fe) elements were found in the foulants. Wilf et al. [10] reported that the decrease of carbon peaks is due to low penetration of electron beam into membrane because of the foulant layer. The increase of oxygen peak is due to a component of oxides (Si, Al) and iron hydroxides. After flocculation pretreatment, iron content increased up to 3% of atomic percentage. After the other physico-chemical pretreatments, no significant elemental change was observed.



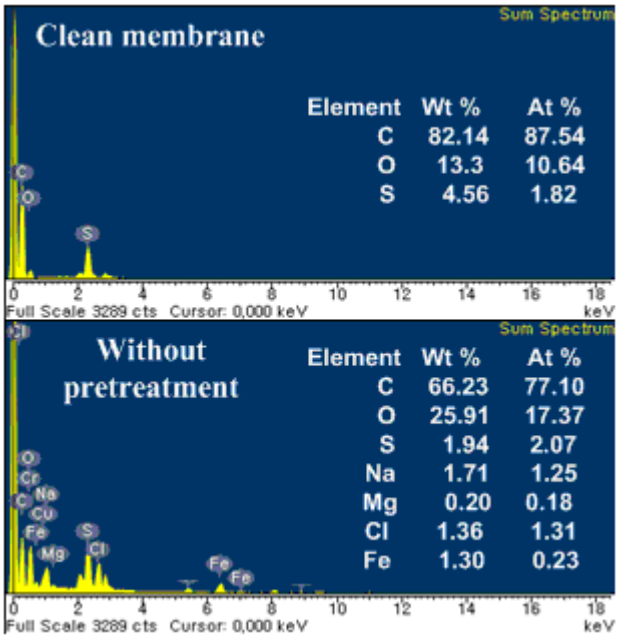


Figure 7 SEM/EDX results on the RO membrane surfaces after different pretreatments (clean = clean membrane; without = without pretreatment; Ads. = PAC adsorption pretreatment; Floc. = $FeCl_3$ flocculation pretreatment)

iii) AFM. AFM images of the RO membrane surfaces were investigated after different pretreatments (Figure 8). Surface morphology on the RO membrane surfaces was determined using tapping mode AFM. The unique ridge and valley structure with doughnut shape features was found on the clean membrane. The inner diameter of the doughnut shape was 80-150 nm as measured by line profile from the AFM image. The higher resolution of this image is given in the inset with scan area of 500 x 500 nm. The RO membrane surface without any pretreatment showed more irregularities with new protuberances which were not observed in the clean membrane surface. The particle shape features had a diameter in the range of 30 to 40 nm. The foulants indicated a similar result after pretreatments of PAC adsorption and $FeCl_3$ flocculation. However, the foulants after the physical pretreatments by MF and UF showed the disk-type feature. The grain size was estimated from AFM line profile to be 300 to 800 nm. For more detailed information, the AFM roughness was measured.

Table 2 shows roughness values on the RO membrane surfaces after different pretreatments. They were measured in terms of average roughness (S_a), root-mean-square roughness (S_q), surface area (S_{dr}), peak-peak count (S_y) and ten point height (S_z). Here, the peak-peak count is an estimate of the shape of the overall distribution of z-values which is short or wide and tall or narrow. The ten point height is defined as the average height of the five highest local maximums plus the average height of the five lowest local minimums. The average roughness (S_a) of the clean membrane surface was 41.5 nm. After MF and UF pretreatment, the roughness slightly increased up to 54.8 and 55.6 nm, respectively. On the other hand, without any pretreatment, with PAC adsorption and with $FeCl_3$ flocculation, the roughness increased up to 69.7, 66.4 and 110 nm, respectively. It can be concluded that the pretreatment by MF and UF could better preserve the membrane surface.

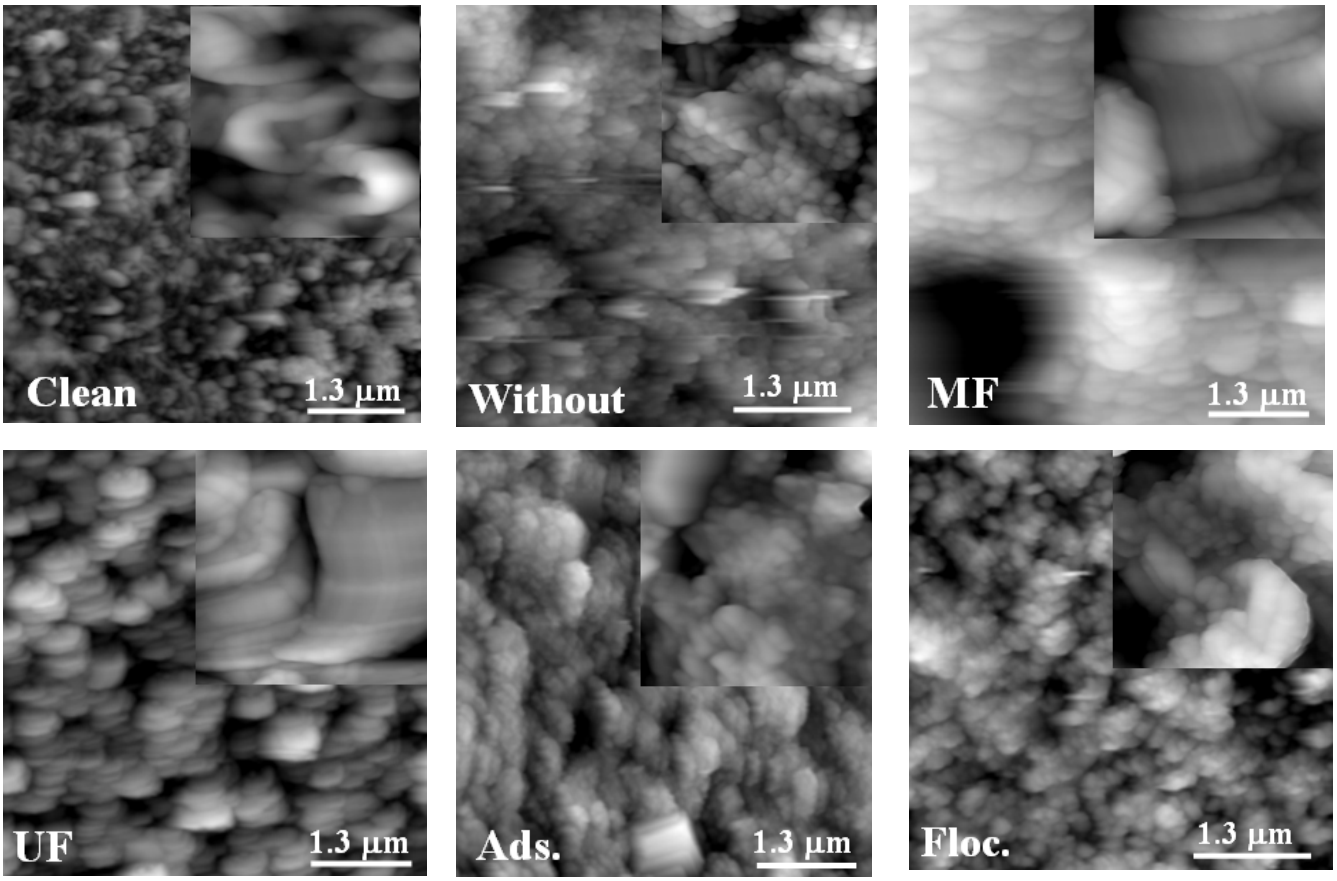


Figure 8 AFM images on the RO membrane surfaces after different pretreatments. All images are 5 x 5 μm and the insets in all images are 500 x 500 nm. (clean = clean membrane; without = without pretreatment; Ads. = PAC adsorption pretreatment; Floc. = $FeCl_3$ flocculation pretreatment)

Table 2 Roughness measurements on the RO membrane surfaces after different pretreatments (Average roughness (S_a), root-mean-square roughness (S_q), surface area (S_{dr}), peak-peak count (S_y) and ten point height (S_z))

	S_a (nm)	S_q (nm)	S_{dr} (%)	S_y (nm)	S_z (nm)
Clean	41.5	52.1	47.3	456	348
Without pretreatment	69.7	86.9	67.1	550	529
MF pretreatment	54.8	65.4	35.6	461	445

UF pretreatment	55.6	69.1	38.1	457	419
PAC adsorption pretreatment	66.4	83.2	57.7	570	545
$FeCl_3$ flocculation pretreatment	110	140	121	1025	979

CONCLUSIONS

The effect of different physico-chemical pretreatment methods to SWRO was evaluated in terms of their capability in removing SWOM and membrane autopsy on the membrane surface. The results led to the following conclusions:

1. The DOC removal by UF, NF, PAC adsorption and $FeCl_3$ flocculation was 20.3%, 28.9%, 46% and 23.3%, respectively.
2. The large amount of the hydrophobic fraction was removed by pretreatment of PAC adsorption.
3. SDI_{5min} after MF, UF, NF and PAC adsorption pretreatment decreased from 12.7 up to 3.2, 1.3, 1.0 and 4.4, respectively. RO filtration of seawater with and without pretreatment indicated significant flux decline (normalized flux decline (J/J_0) = 0.17±0.02).
4. The result of the contact angle shows the following order: clean (38º)> NF (34º)> MF (33º) > UF (31º)> flocculation (30º)> adsorption (28º)> without any pretreatment (22º).
5. The SEM image of the RO cross-section without any pretreatment and with flocculation pretreatment indicated a fouling thickness of approximately 0.1 μm. On the other hand, the other pretreatments did not form cake layer of significant thickness.
6. The clean membrane consisted of carbon (C), oxygen (O) and sulfur (S) originating from building components of polyamide membrane and polysulfone support. However, the EDX result of the direct RO filtration showed quite different elements on the fouled membrane surface. The relative fraction of the carbon decreased, while new sodium (Na), magnesium (Mg), chlorine (Cl) and iron (Fe) elements were found in the foulants on the fouled membrane surface.
7. The average roughness of the clean membrane surface was 41.5 nm. After MF and UF pretreatment, the roughness slightly increased up to 54.8 and 55.6 nm, respectively. On the other hand, without any pretreatment, with PAC adsorption and with $FeCl_3$ flocculation, the roughness increased up to 69.7, 66.4 and 110 nm, respectively. It can be concluded that the pretreatment by MF and UF could better preserve the membrane surface.

ACKNOWLEDGEMENT

This research was funded by ARC discovery and Linkage International grants. The first author appreciates a UTS Chancellor's postdoctoral fellowship grant.

REFERENCES

[1] M.G. Khedr. Desalination & Water Reuse. 10 (2000) 3-10.
[2] L.Y. Dudley, U.A. Annunziata, J.S. Robinson and L.J. Latham. Proc. IDA World Congress on Desalination and Water Sciences, Abu Dhabi, 4 (1996) 45-52.
[3] A.S. Al-Amoudi and A.M. Farooque. Desal. 178 (2005) 261-271.
[4] M.G. Khedr. Desal. 153 (2003) 295-304.
[5] S. Bouguecha and M. Dhahbi. Desal.151 (2003) 75-86.
[6] F.H. Butt, F. Rahman and U. Baduruthamal. Desal. 114 (1997) 51-64.
[7] J.S. Baker, S.J. Judd and S.A. Parsons. Desal. 110 (1997) 151-165.
[8] H.K. Shon, S. Vigneswaran, In S. Kim, J. Cho and H. H. Ngo. J. Membr. Sci. 234 (2004) 111-120.

[9] H.K. Shon, S. Vigneswaran and S.A. Snyder. Cri. Rev. Env. Sci. Tec. 36 (2006) 327-374.
[10] Wilf M. The guide book to membrane desalination technology. Balaban Desalination Publications, Italy, 2007.