



Comparison of media and membrane filtrations for seawater desalination pretreatment

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ABSTRACT

We compared microfiltration (pressurized and submerged) and media filtration as pretreatment to increase the removal of organics and to reduce reverse osmosis (RO) membrane fouling. The studied plant (feed rate = 2,500 m³/d, production rate = 1,000 m³/d) was taking seawater from East Sea of Korea and originally consisted of strainers, coagulation, dissolved air flotation, dual media filters (DMF), and RO membrane processes. A pressurized microfiltration (MF) and a submerged microfiltration (SMF) were installed and compared with DMF as pretreatment to the RO process. Upon pilot test results over one year, MF exhibited higher removal of dissolved organic materials. Average removals of UVA₂₅₄ were 23, 19, and 13% at MF, SMF, and DMF, respectively. These results were confirmed with molecular weight distribution, and compositions of humic and fulvic acids. Silt density index (SDI) values were lower in membrane processed waters, and the SDI results correlated with transparent exopolymer particles ($r = 0.73$). The results indicated that MF can be an effective pretreatment to reduce RO membrane fouling with higher removal of organic materials.

Keywords: Reverse osmosis; Desalination; Pretreatment; Media filtration; Microfiltration

1. Introduction

Due to the recent rapid economic growth and industrialization, global water shortage has been intensified. Thirty-five percent (%) of the world population and 20% of the entire countries might be suffering from severe water shortage in 2025, and in recent years numerous large-scale seawater desalination plants have been built in those water-stressed countries to overcome the water shortage issues [1,2]. Over

50% of desalination plants larger than 50,000 m³/d have adopted reverse osmosis (RO) processes since 2000 because RO has better energy efficiency, thus reducing energy costs than multi-stage flash and multi-effect distillation [2,3].

However, there have been several issues to overcome for RO membranes to desalt seawater, such as flux decline, short membrane life, increased cleaning and maintenance cost, and membrane fouling [4]. Membrane fouling can occur as gel layers that form due to increased salinity, particles and/or

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micro-organisms [5]. Organic matters with different physical and chemical properties can cause severe membrane fouling even at low concentrations by adsorbing on the membrane surface and/or into the membrane pores [6]. Extra-cellular polymeric substances (EPS) from micro-organisms can also accelerate membrane biofouling in seawater desalination processes [7]. Silt density index (SDI) and/or modified fouling index (MFI) have been used to monitor the fouling issues on RO membranes and to predict the efficiency of pretreatment processes prior to RO. In general, higher the SDI or MFI, higher is the RO fouling potential [8].

Several pretreatment processes such as media filters and dissolved air floatation (DAF) have been applied, and in most cases coagulants such as FeCl_3 or cationic polymers were added prior to those pretreatment processes to remove dissolved organic matters [9]. However, those multi-stage pretreatment processes have experienced complex maintenance and management issues, and microfiltration and/or ultrafiltration have recently been considered for desalination pretreatment [10,11]. In this study, we compared microfiltration and media filtration to pretreat seawater from East Sea of Korea and to reduce RO membrane fouling thus increasing the performance of a seawater desalination plant equipped with 16-inch RO membranes (a production capacity of $1,000 \text{ m}^3/\text{d}$).

2. Materials and methods

2.1. Materials

The desalination plant we studied was in Busan, Korea taking seawater from East Sea of Korea. The raw seawater in average exhibited pH 8.2, conductivity (EC) of $53.2 \text{ mS}/\text{cm}$, total dissolved solids (TDS) of $37,971 \text{ mg}/\text{L}$, dissolved organic carbon (DOC) of $1.3 \text{ mg}/\text{L}$, and UVA at 254 nm (UVA_{254}) of 0.010 cm^{-1} . Fig. 1 exhibits a schematic of the plant. The plant originally consisted of strainers, DAF, dual media filters (DMF), and RO membranes. Maximum production capacity of the desalination plant was $1,000 \text{ m}^3/\text{d}$ with a feed rate of $2,500 \text{ m}^3/\text{d}$. DAF and DMF were operated at $2,400 \text{ m}^3/\text{d}$. Pressurized microfiltration (MF) and submerged microfiltration (SMF) were added to the original plant and operated at 100 and $200 \text{ m}^3/\text{d}$, respectively. MF was made by polyvinylidene fluoride (PVDF) and has a pore size of $0.1 \mu\text{m}$. SMF was made by high density polyethylene (HDPE) and has a pore size of $0.4 \mu\text{m}$. Both membranes were provided by Eonity Co., Ltd (Korea). Chemically enhanced backwash was used for cleaning each microfiltration membrane during operation.

2.2. Experimental and analytical methods

To investigate characteristics of water quality treated by each process, we measured pH, EC, TDS, UVA_{254} , DOC, size exclusion chromatography (SEC), fluorescence excitation emission matrix (FEEM), transparent exopolymer particles (TEPs), and other typical water quality parameters.

DOC was measured by a TOC analyzer (TOC-VCPH, SIMADZU, Japan). Samples were pre-filtered by GF/F filters ($0.7 \mu\text{m}$), and non-purgeable organic carbon method was used to measure DOC. UVA_{254} was measured at 254 nm wavelength by a UV spectrophotometer (HS3300, HUMAS, Korea) after filtered by GF/F filters. SEC was measured by high-performance liquid chromatography using a column (Protein-Pak 125 column, $10 \mu\text{m}$, $7.8 \times 300 \text{ mm}$, Waters, USA); mobile phase was made with Na_2HPO_4 (1.135671 g), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (1.103938 g), NaCl (23.37899 g) in 4 L distilled water. Samples were detected by UV730D (YOUNGIN, Korea). FEEM analysis was conducted by a fluorometer (RF5301, SHIMADZU, Japan) equipped with xenon lamps (slit interval: 10 nm , excitation range: $220\text{--}400 \text{ nm}$, and emission range: $250\text{--}600 \text{ nm}$).

TEP was measured using alcian blue 8GX (Fluka, USA) staining solution. The staining solution (0.02%) was made by dissolving 20 mg alcian blue to 0.06% acetic acid in 100 mL volume flask. A calibration curve for TEP was made with xanthan gum. Two hundred (200) mg Xanthan gum (Sigma Aldrich, USA) was dissolved in 200 mL distilled water, then filtered through a polycarbonate filter (pore size $0.4 \mu\text{m}$, diameter 47 mm , Whatman, USA) by increasing the amount from 0.1 to 3.0 mL (in this study, we filtered $0.1, 0.5, 1.0, 2.0,$ and 3.0 mL). Next, 1 mL of alcian blue staining solution was dropped on the filter. After waiting for 10 seconds for the reaction, the filter was rinsed with 1 mL ultrapure distilled water and was transferred to 200 mL beaker; 6 mL of 80% sulfonic acid was added to the beaker. After 2 hours of reaction/soaking, we measured UV-vis spectrophotometer at 787 nm wavelength. Samples (200 mL) followed the same procedures as standards.

To estimate the membrane fouling potential, SDI was calculated by Eq. (1):

$$\text{SDI} = \frac{\left[1 - \left(\frac{t_i}{t_f}\right)\right]}{T} \times 100 \quad (1)$$

where T is total elapsed flow time, min (typically 15 min); t_i is the initial time required to collect 500 mL of sample (s); t_f is the time required to collect 500 mL of sample after test time T .

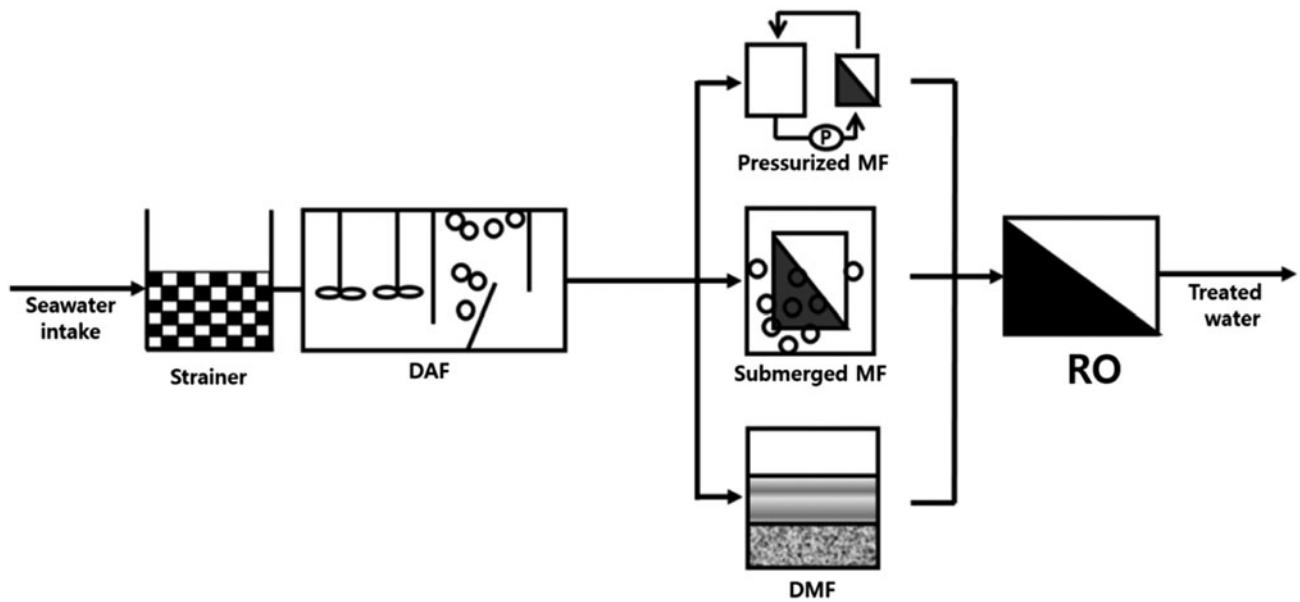


Fig. 1. Schematics of the desalination plant studied.

3. Results and discussion

3.1. Removal of ionic, particulate, and organic materials

No pretreatment process in this study (DAF, DMF, MF, and SMF) achieved significant reductions (<5% reduction, data not shown) in EC, TDS, and other ionic substances (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , B, Al, Cr, Mn, Fe, Ni, Cu, An, Sr, Cd, Ba, etc.) as expected. Most of those values decreased through the RO membrane process to >99%. The RO process showed the average recovery of

40% with the feed and production rates of 50 and 20 m³/h, respectively, over one year of operation.

Each pretreatment process could achieve a decent removal of particulate materials. Turbidities of raw, DAF treated, DMF treated, SMF treated, and MF treated waters averaged 0.42, 0.35, 0.22, 0.09, and 0.06 NTU, respectively, over one year of operation. Monitoring results of the turbidity values in raw water and pretreated waters revealed higher removal efficiency of particulate materials can be achieved with a membrane filtration (MF and SMF) rather than DMF.

Dissolved organic materials were also removed through each pretreatment process. Fig. 2 shows the

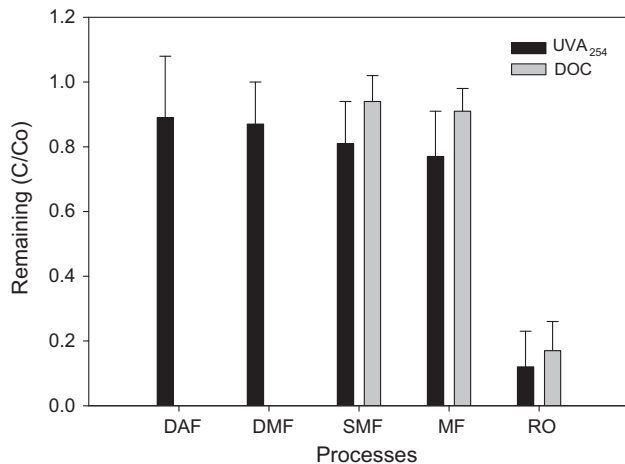


Fig. 2. Variation in organic materials (as UVA₂₅₄ and DOC) through each process (average values and standard deviations presented).

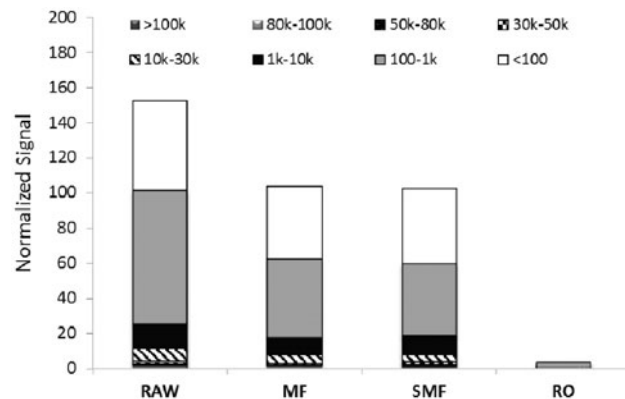


Fig. 3. Molecular weight distributions of treated water by each process.

results of UVA_{254} and DOC in each processed water. UVA_{254} and DOC of raw seawater averaged 0.010 cm^{-1} and 1.3 mg/L , respectively. Average removals of UVA_{254} were 23, 19, and 13% at MF, SMF, and DMF, respectively. Removal of DOC was lower than that of UVA_{254} . Average removals of DOC were 9 and 6% at MF and SMF, respectively. Upon the results, MF could achieve slightly higher removals of

dissolved organic materials than SMF. This was possibly due to smaller nominal pore size of MF ($0.1 \mu\text{m}$) than SMF ($0.4 \mu\text{m}$), rather than operational conditions. Regardless of the membrane pore size, hydrophobic materials (presented as UVA_{254}) were relatively readily removed through the pretreatment processes. Through the RO process, the average removals of UVA_{254} and DOC increased to $>80\%$. Removals of

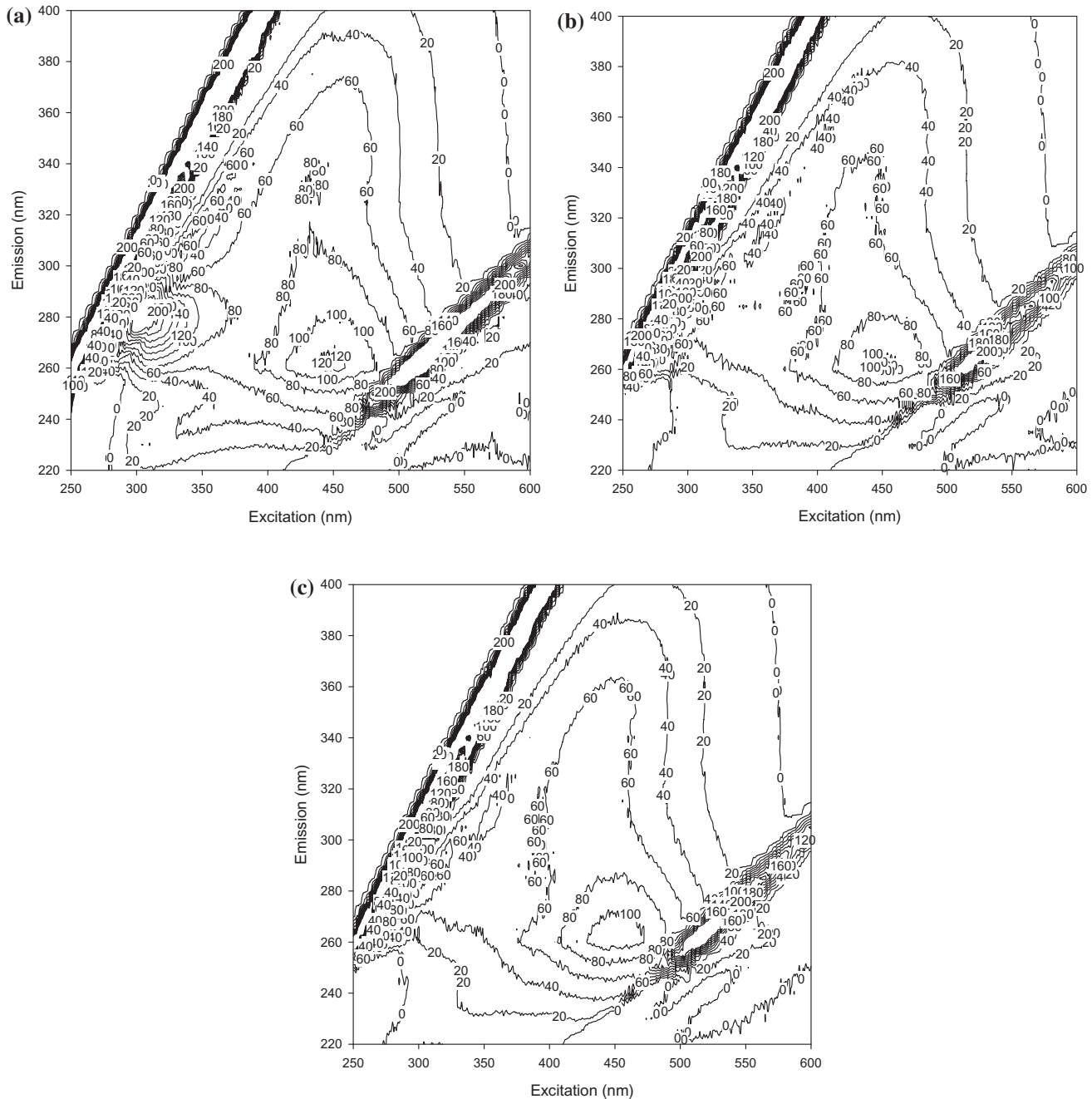


Fig. 4. FEEM results of raw and treated water by each process: (a) raw water, (b) MT treated water, and (c) SMF treated water.

dissolved organic materials through the pretreatment processes were not significant compared with RO process.

3.2. Membrane fouling and dissolved organic materials

SDI and MFI have been used to predict the efficiency of pretreatment processes prior to RO [8], and SDI was monitored several times during this study. SDI averaged 4.6 in raw water ($n = 15$), 4.4 in DAF-treated water ($n = 20$), 3.4 in DMF-treated water ($n = 20$), 3.0 in SMF-treated water ($n = 12$), and 1.2 in MF-treated water ($n = 24$). SDI values decreased through the pretreatment processes, especially by MF. This was possibly due to lower concentrations of turbidity and dissolved organic materials in the MF-treated water than other pretreatment treated waters. Lower SDI is generally due to lower organics and particulates contents [8]. However, this could not be the only reason because the difference of those parameters of MF- and SMF-treated waters was not significant. To better understand the difference in SDI between MF- and SMF-treated waters, characteristics of organic materials were further investigated.

Molecular weight distributions of organic materials in water samples were compared as shown in Fig. 3. Raw water contained higher portion (83%) of <1,000 Dalton (Da) size organic materials and some (17%) over 1,000 Da. Through the pretreatment (MF and SMF) all the sizes of colloids were somewhat removed, and, especially 100–1,000 Da size colloids exhibited more removals (~40%) than other sizes of colloids. This was probably because the smaller size of colloids formed flocs during coagulation and were removed through the pretreatment. Without coagulant addition, the colloidal size of organic materials could pass through the tested MF and SMF processes.

FEEM was also analyzed to assess types of organic materials in the water samples (Fig. 4). Polyaromatic humic acid peaks (emission 260 nm and excitation 450 nm [12,13]) were appeared in raw, MF-treated and SMF-treated waters. Polyaromatic humic acid peak in raw water was reduced by 20% in MF- and SMF-treated waters, but the difference between MF and SMF were minimal.

Fibrillar and acidic polysaccharides from bacterioplankton, represented as TEP [14], were also compared. TEP can enhance viscosity of water by particles and frequent collision between each particles, thus can influence membrane fouling [15,16]. TEP larger than 0.4 μm did not show significant difference between samples, averaging 37, 36, and 34 $\mu\text{g Xn/L}$ in raw, SMF, and MF waters, respectively. However, TEP sized 0.1–0.4 μm were in average 384, 378, and

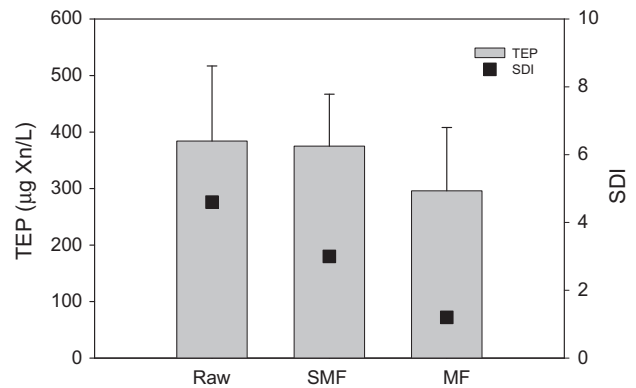


Fig. 5. TEP (0.1–0.4 μm) and SDI of treated water by each process.

296 $\mu\text{g Xn/L}$ in raw, SMF, and MF waters, respectively. MF with relatively smaller pores had higher TEP removals than SMF. This can support why SMF-treated water had relatively higher fouling potentials than MF-treated water. Although it is not a strong correlation, SDI decreased as TEP decreased in this study as shown in Fig. 5.

4. Conclusions

- (1) Removal of dissolved organic materials was higher with MF than media filtration, and hydrophobic materials (presented as UVA_{254}) were readily removed regardless of the pretreatment process types (DMF, SMF, and MF).
- (2) SMF-treated water had relatively higher fouling potentials than MF-treated water, and this was explained by TEP contents. As the contents of organic materials decreased, SDI value decreased.
- (3) This study found that MF can be more effective pretreatment than media filtration to pretreat seawater and to reduce RO membrane fouling. However, operations and maintenance costs and issues were also considered prior to application.

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