Characteristics of membrane fouling by consecutive chemical cleaning in pressurized ultrafiltration as pre-treatment of seawater desalination

Yun Chul Woo[a,b], Jeong Jun Lee[a], Leonard D. Tijing[b], Ho Kyong Shon[b], Minwei Yao[b] and Han-Seung Kim[a,*]

[a]Department of Environmental Engineering and Energy, Myongji University, 116 Myongji-Ro, Cheoin-Gu, Yongin-Si, Gyeounggi-Do 449-728, Republic of Korea

[b]Centre for Technology in Water and Wastewater (CTWW), School of Civil and Environmental Engineering, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia

*Corresponding author: H.-S. Kim, Tel: +82(31)330-6695, Fax: +82(31)336-6336, Email: kimhs210@mju.ac.kr

Abstract

In the present study, the effect of consecutive chemical cleaning on the fouling control of pressurized ultrafiltration (UF) as a pre-treatment process for desalination was investigated. Oxalic acid and sodium hypochlorite were chosen as chemical agents for the cleaning methods. Initial tests showed that the cleaning in series of oxalic acid-sodium hypochlorite-oxalic acid had the optimal cleaning efficiency. A flux recovery of over 91.0 % via continuous chemical cleaning experiments for UF process using real seawater as feed was obtained. However, the decrease in flux recovery was observed with the increase of the number of cleaning cycles due to continuous fouling formation on the membrane. It was found that hydrophobic organic foulants were relatively easier to be removed from the membrane surface by using the chemicals in this study, while hydrophilic inorganic foulants such as Na^+ and Cl^- were found to adhere more on the membrane surface after cleaning. The

presence of foulants on the membrane has reduced its tensile strength but it was retrieved near its initial tensile strength after chemical cleaning. The consecutive chemical cleaning has recovered about 96.8% in the first cleaning, but more rapid fouling was observed thereafter. This was attributed to the presence of inorganic scales, which were not fully removed during the cleaning process, thus it combined with organic foulants over time, resulting to faster fouling and lesser cleaning efficiency with the increase of cleaning cycles. Thus, it is important the inorganic foulants should be thoroughly removed so as to minimize the extent of fouling formation after each chemical cleaning.

Keywords: Chemical cleaning; desalination; membrane fouling; ultrafiltration; pre-treatment.

1. Introduction

Nowadays, many regions of the world suffer from the scarcity of fresh water resources for potable, industrial and agricultural purposes. The main problem is the difficulty to supply potable water in water shortage areas. Several illnesses are associated with contaminated drinking water. One of the alternative and sustainable ways to produce fresh water is through seawater desalination. Desalination processes include multi stage flash (MSF) and multi-effect distillation (MED), and reverse osmosis (RO) [1-3]. The RO process is derived from a membrane technology that only allows water to pass through a semi-permeable membrane, and reject the solute (i.e., salt). Seawater is fed to the RO system by applying high pressure to get drinking water. Compared to the distillation processes, RO has three times lower specific energy consumption, and has easier construction and system operation [4].

However, seawater cannot be fed directly to RO due to some reasons: first, seawater has inorganic and organic compounds, which can contribute to membrane fouling; and second, if

seawater recorded a silt density index (SDI) value of over 5, this could strain the RO membrane. For these reasons, it is necessary to incorporate a pre-treatment method such as coagulation, flocculation, media filtration, multi-media filtration (MMF) and microfiltration/ultrafiltration (MF/UF) in desalination process prior to RO process [5].

There are several advantages in using MF/UF as pre-treatment of RO process. (1) SDI values between 2 to 4 are possible to obtain using this membrane-based pre-treatment, which is more stable compared to other methods; (2) MF/UF is more compact compared to other processes, thus requiring less-footprint; (3) MF/UF has a stable flux, and; (4) it can be automated. However, there are also some drawbacks with the use of MF/UF, which include the need for high electrical energy consumption, operating cost and higher initial capital cost [6-9]. Additionally, similar with the RO process, membrane fouling can happen to MF/UF process in a long-term operation, which deters its performance. To combat fouling, physical cleaning is needed to be carried out periodically such as backwashing, aeration, air-scrubbing, and chemical enhanced backwashing (CEB). However, physical cleaning and CEB are limited for long-term operation so as not to disrupt the operation [10]. Usually, operation for more than 6 months requires chemical cleaning with various chemical agents. It takes almost one day to perform cleaning in place (CIP) every 6 months operation.

As you can see **Table 1**, many researchers used various chemical agents for a wide range of filtration process. The membrane surfaces are exposed to high concentrations of chemical agents for the cleaning process. Different concentrations of chemicals for CIP have been suggested such as 0.5% nitric acid [11], 2% nitric acid [12], 2% sodium hypochlorite, and 1 % sodium hydroxide. Kwon et al [13]., used 500 ppm sodium hypochlorite, 250 ppm sodium hydroxide, 2500 ppm citric acid and 250 ppm sodium hypochlorite. Our previous work [14] utilized 0.1 %, 0.5 %, 1 %, 2 % and 5 % sodium hydroxide in addition to various concentrations (1, 2, and 3%) of nitric acid. However, based from our review of literature, no

one has yet investigated the use of chemical cleaning for pressurized hollow fiber ultrafiltration as pre-treatment of desalination by real seawater.

In the present study, fouling of membrane was generated using seawater as feed. The recovery rate was measured after chemical cleaning using various chemical agents at different concentrations, in addition to recovery rates for alkaline and acid. The most efficient chemical agents based on recovery rate were used for combination chemical cleaning. Flux recovery rate was measured and the membrane performance was evaluated after chemical cleaning. In addition, foulant characteristics were evaluated using different analytical methods such as SDI test, Fourier transform infrared spectroscopy (FT-IR), contact angle, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and tensile strength. To our knowledge, this is the first report of chemical cleaning for pressurized hollow fiber ultrafiltration as pre-treatment of desalination using real seawater, as well as the analysis of fouling characteristics on the ultrafiltration membrane.

[Table 1]

2. Materials & methods

2.1 Specification of UF membrane

Polyvinylidene fluoride (PVDF) hollow fiber membrane was used in this study, which is widely employed in microfiltration and ultrafiltration. The advantages of PVDF membrane include high mechanical strength, high thermal stability, low cost and high chemical resistance [36, 37]. The hollow fiber membranes had a pore size of 0.038 μm. Each fiber has an internal diameter (I.D) of 0.8 mm, an outer diameter (O.D) of 1.2 mm, a length of 15 cm and a membrane area of 2.26×10^{-3} m^2. Specifications of the hollow fiber membrane are summarized in **Table 2**.

[Table 2]

2.2 Filtration system

A dead-end filtration set-up was used in the present study as shown schematically in **Fig. 1**. The feed flows perpendicularly to the membrane surface. Dead-end filtration experiment was conducted at constant pressure of 0.5 bars. The virgin membrane recorded an initial flux of 140 LMH. The flux of the fouled membrane was observed to decrease obtaining only 35 LMH [9, 14, 38]. The schematic diagram of the lab-scale MF/UF system is shown in Figure 1. Seawater from the southern sea (location: Kijang-gun, Busan, South Korea), was used as feed without any initial pre-treatment. The seawater was first passed through the MF/UF membrane for a specific duration until fouling is observed. After which, Chemical cleaning was started by pumping chemical cleaning agents through the membrane in a recirculating mode The applied pressure was set at 0.5 bar measured by a pressure gauge [9, 14]

[Figure 1]

2.3 Batch test

Batch tests were performed in two cleaning modes: (1) by single chemical cleaning and (2) by chemical cleaning in series. Chemical cleaning in series was conducted based on the results from the single chemical cleaning. The results here indicated a need for a continuous chemical cleaning experiment.

128 2.3.1 Single chemical cleaning

129

130 Three types of chemical cleaning agents were tested in this study: alkaline (sodium hydroxide
131 (NaOH) and sodium hypochlorite (NaOCl)), organic acid (citric acid ($C_6H_8O_7$) and oxalic
132 acid ($C_2H_2O_4$)), and inorganic acid (sulfuric acid (H_2SO_4) and nitric acid (HNO_3)). The
133 chemical cleaning agents were diluted to obtain different concentrations: 0.1 %, 1 %, 3 % and
134 5 %. To determine the effectiveness of each chemical agent on the flux recovery during a
135 single cleaning mode, each chemical was passed on the surface of the MF/UF mini-module
136 system for 30 minutes followed by 10 minutes rinsing with de-ionized water. Thereafter, flux
137 recovery was measured using seawater as feed for 10 minutes. The experiment was repeated
138 at different contact times – 1 hour and 2 hours. The flux (L/m^2h or LMH) was calculated
139 using the equation

$$\text{Flux (LMH)} = \frac{Q}{A} \times \frac{\eta_T}{\eta_{25}} \qquad (Eq.1)$$

140 where Q is the filtration flow rate (L/h), A is the effective surface area of the membrane
141 (m^2), η_T is the viscosity at actual temperature, and η_{25} is the viscosity at 25 ºC. The equation
142 used to calculate the recovery rate is as follows,

$$\text{Recovery rate (\%)} = \frac{Flux_C\ (LMH)}{Flux_I\ (LMH)} \times 100\ (\%) \qquad (Eq.2)$$

143 $$\text{Recovery efficiency (\%)} = \frac{Flux_C\ (LMH)}{Flux_P\ (LMH)} \times 100\ (\%) \qquad (Eq.3)$$

144 where $Flux_C$ is the flux after chemical cleaning, $Flux_I$ is the initial pure water flux and
145 $Flux_P$ is the flux previous chemical cleaning.

146

147 2.3.2 Chemical cleaning in series

148

149 Chemical cleaning of the membranes was also conducted by subjecting the fouled membrane

with different chemical agents in series. Two sequences were tested: (1) acid – alkaline – acid, and; (2) alkaline – acid – alkaline. First, the initial flux of the hollow fiber membrane in a mini-module was measured using seawater. This was followed by chemical cleaning for 30 minutes using either acid or alkaline agent. After which, cleaning was conducted for 1 hour, then followed by another cleaning for 30 minutes. Immediately after the chemical cleaning, the flux of the cleaning membrane was measured using de-ionized water, and the percent recovery rate was calculated. The total duration of the chemical cleaning was 2 hours, with cleaning sequence of 30 minutes – 1 hour – 30 minutes [39, 40].

2.4 Method of the consecutive chemical cleaning on fouling mitigation

Alkaline and acid agents were chosen for single chemical cleaning, and chemical cleaning in series experiments. Flux of the fouled membrane was found to decreased by 75% compared to the initial flux. Chemical cleaning was repeated four times and the cleaning duration was maintained for 2 hours, with cleaning sequence of 30 minutes – 1 hour – 30 minutes.

2.5 Analytical methods

In order to determine the degree of wettability, the hollow fiber membranes were subjected to a contact angle measurement test using a tension meter (Sigma 701, Biolin Scientific). The morphology of the hollow fiber membrane and the foulants was examined by scanning electron microscopy (SEM) (Hitachi S-3500N) and energy dispersive X-ray spectroscopy (EDS) attached to SEM. Hollow fiber membranes were mounted in a universal testing machine (LF Plus, Lloyd Instruments, AMETEK) to evaluate their mechanical properties. A gauge length of 5 cm and a speed of 50 mm/min were maintained for all tests. The outer

diameter of the membranes was determined using a digital micro-caliper. A Varian 2000 Fourier transform infrared spectroscope (FT-IR) was used to obtain the spectra of the membranes. All spectra were acquired by signal averaging 32 scans at a resolution of 8 cm^{-1} in ATR mode. The SDI_{15} and PF factor were analyzed by GE Osmonics auto SDI tester. Turbidity was measured by HACH 2100N from HACH company. Shimadzu UV spectrophotometer UV-1800 and TOC-5000 were used to measure UV_{254} and DOC concentration, respectively. Total dissolved solids (TDS) and pH were analyzed by Orion 4-star plus pH/conductivity meter from Thermo Scientific.

3. Results and discussion

3.1 Results of the single chemical cleaning

[Figure 2]

Six chemical cleaning agents divided into alkaline and acid agents were used in the present study: sodium hydroxide, sodium hypochlorite, sulfuric acid, nitric acid, citric acid and oxalic acid. Each chemical agent was prepared at different concentrations of 0.1 %, 1 %, 3 % and 5 %. The pH of each solution is listed in **Table 3**. **Fig. 3** shows the results of cleaning at different durations of 30 min, 1 h and 2 h. The results showed consistently better cleaning effect by the acid agents compared to the alkaline agents regardless of the cleaning time. The alkaline sodium hypochlorite showed better cleaning compared to sodium hydroxide at different concentrations. The use of sodium hydroxide showed increasing flux recovery as its concentration increased from 0.1 to 5%. On the other hand, sodium hypochlorite showed increasing cleaning effectiveness up to 3% concentration, but declined its efficiency at >3%. The pH of the alkaline solutions showed very high value of around 12, which is considered a

harsh condition for the membrane [41, 42]. The photographic images in **Fig. 2** showed browning of the mini-module after exposure to pH 12, which is attributed to the partial dissolution of the epoxy on the potting site making it undesirable to use. Thus, to minimize the effect of very high pH, a much lower pH was preceded for the cleaning test. For the alkaline agent, the 1% sodium hypochlorite treatment showed the optimum result as there was not a big gap in effectiveness between 1 and 3% concentrations.

The acid cleaning showed varying trends for each cleaning agent. The highest flux recovery was obtained by oxalic acid, followed by citric acid then nitric acid and sulfuric acid. The increase of acid concentration has also resulted to better cleaning efficiency, however, decreased recovery was observed for sulfuric acid, nitric acid and citric acid at concentration >3%. The best result among all cleaning agents was obtained using oxalic acid. Furthermore, the results also indicated that longer cleaning duration has resulted to increased flux recovery. From among all agents, the oxalic acid at 1% showed the best result considering that there was not big difference in flux recovery for 1, 3 and 5% oxalic acid cleaning. Thus, for further cleaning tests, the 1% oxalic acid was chosen.

[Figure 3]

[Table 3]

3.2 Results of the chemical cleaning in series

Based from our initial results, 1% sodium hypochlorite and 1% oxalic acid as cleaning agents were chosen for chemical cleaning in series experiments. Since the pH of sodium hypochlorite is around 12, it would be wise to use lower concentration for cleaning, thus 1% concentration is selected. The chemical cleaning in series tests were carried out by

conducting interval cleaning using both 1% sodium hypochlorite (NaOCl) and 1% oxalic acid. Two sets of tests were carried out at two different cleaning durations. The first set (Series 1) was cleaning with oxalic acid, then NaOCl, then oxalic acid for a time of 15-30-15 min, respectively. The other set (Series 2) was NaOCl first, then oxalic, then NaOCl for the same time duration of 15-30-15 min, respectively. Another two sets (Series 3 and 4) were carried for the same series of experiments but at longer duration of 30-60-30 min. **Fig. 4** shows the results of the different cleaning in series experiments. The cleaning Series 1 (oxalic acid-NaOCl-oxalic acid) at a shorter time duration showed better flux recovery of 77% compared to Series 2 at 65%. The same trend was observed when the cleaning duration was increased to 30-60-30 min, obtaining around 94% recovery for oxalic acid-sodium hypochlorite-oxalic acid cleaning. In general, acid agents are known to treat inorganic foulants, while alkaline agents are best at cleaning organic foulants [43]. During filtration, inorganic foulants such as Na^+ and Cl^- were observed to have more serious effect than organic foulants to the membrane in desalination process, because salt ions can interact strongly with organic foulants [44]. For this reason, an acid chemical should be used first to remove theinorganic foulants and then a base chemical should follow to enhance the removal efficiency.

[Figure 4]

3.4 Effect of the consecutive chemical cleaning on fouling mitigation

Continuous fouling and cleaning tests were carried out for more than 2 days (**Fig. 5**). In the first 20 h, the flux declined steadily from an initial flux of 142 LMH to 36 LMH, or a decline of around 25% due to the fouling formation. Using the series cleaning of oxalic acid-NaOCl-

oxalic acid for 30-60-30 min interval, the first cleaning was carried out to the fouled membrane and recovered 96.8% of the initial flux (137.4 LMH). However, as soon as cleaning was finished, the flux again drastically declined in the next 12 h until a decrease to 75% from the initial flux value. Three more cleaning cycles were carried out at different intervals, resulting to 92.7, 91.1, and 91.0% of initial flux for each cleaning, respectively. The third and fourth chemical cleaning showed very similar flux recovery, which indicates a critical point for cleaning after three cleaning cycles. This means that after second cleaning time, the flux can be recovered to the previously recovered flux. As shown in the Fig. 5c, the recovery efficiency of the after first, second, third and fourth cleaning were 96.8, 95.8, 98.3 and 99.9%, respectively. It showed that the flux was almost fully recovered to the previous recovered value as cleaning times increased. After each cleaning, the fouling tendency tends to be higher. This could be due to the pore blocking of some foulants especially inorganic salts that could not be successfully removed by chemical cleaning. Additionally, the cleaning process could have roughened the surfaces of the membrane, which could provide additional sites for fouling to occur and develop. The fouling rate was found to increase with the increase in the number of cleaning cycles (**Table 4**), which could be attributed to the incomplete cleaning of the inorganic foulants in the previous cleanings, which eventually served as attachment sites for other foulants to adhere and form rapidly.

[Figure 5]

[Table 4]

3.5 Tensile strength

Tensile strength is a relatively new parameter investigated in autopsy studies. It presents the mechanical strength of the membrane fiber, and hence is directly related to the material

properties of the membrane [45, 46]. The tensile strengths of the virgin, fouled and cleaning membranes were evaluated using a universal testing machine, and was calculated using the following equation:

$$\sigma_\beta = l_\beta \times A_T \quad \text{(Eq. 4)}$$

where σ_β is the tensile strength (gf/mm^2), l_β is the maximum load (gf), and A_T is the membrane area (mm^2) [47, 48].

[Figure 6]

Tensile strength is commonly used in the structural material for stress and strain relationship. The tensile strength was measured by extending the hollow fiber strings until rupture at a rate of 5 mm/min. Triplicate tests were performed and the values were averaged. As shown in **Fig. 6**, the virgin membrane obtained a tensile strength of 256.76 gf/mm^2. However, in the fouled membrane, the tensile strength was found to decrease by 14% at a value of 220.05 gf/mm^2. After the first chemical cleaning, the membrane tensile strength recovered its tensile strength similar to the virgin membrane, which could indicate that most of the foulants were removed from the surface. However, after consecutive cleanings, the membrane showed decreasing tensile strengths as more cleanings progressed. This could be attributed to the possible presence of foulants inside and/or surface the membrane pores even after cleaning. This is in congruent to the results of the continuous cleaning and fouling tests in **Fig. 6.** Additionally, the exposure of the membrane surface to cleaning chemicals could have degraded a little bit of the membrane material, resulting to a slight decrease of tensile strength. However, even from several cleaning cycles, the cleaning membrane still showed higher tensile strength than the fouled membrane. This indicates the positive effect of cleaning in maintaining the mechanical properties of the membrane.

3.6 FT-IR

[Figure 7]

[Table 5]

To analyse the composition of foulants and the membrane surface, FTIR spectra were taken. **Fig. 7** and **Table 5** show the spectra and corresponding band vibrations of the virgin, fouled and cleaning membranes. All membranes showed the same wavelengths of the basic characteristic of a PVDF material at 841 cm^{-1}, 880 cm^{-1} and 1072 cm^{-1}, 1173 cm^{-1}, 1273 cm^{-1}, and 1404 cm^{-1}, which correspond to CH_2 rocking, m C-C asymmetric stretching, CF_2 symmetric stretching, CF out of plane deformation, and CH_2 wagging, respectively [49]. This signifies that the membranes did not change in their characteristics. However, transmittance intensity was observed to decrease after the chemical cleaning process. This could be due to the clogging of some pores of the membranes due to foulants that could have lessened the penetration of light, thus resulting to lower transmittance intensity. However, it can be deduced from the results that if chemical cleaning duration is increased, it could produce better cleaning efficiency thus more foulants will be removed, resulting to more pronounced transmittance intensity as with the virgin membrane [16, 19].

3.7 SEM & EDX

[Figure 8]

The morphological characteristics of the membrane surface and the inner pores were characterized by SEM (**Fig. 8**) and EDX (**Table 6**). **Fig. 8a** showed smooth and clean surface

of the virgin membrane, i.e., before the fouling process. However, after 20 h of test, the membrane surface was covered with a big mass of foulant (**Fig. 8b**). After the first cleaning (**Fig. 8c**), the membrane showed scattered small-sized particles, which seems to be inorganic particles [50]. The particles were confirmed to be inorganic salts after EDX analysis (**Table 6**). Similar observation was seen after 2-3 successive cleaning cycles (**Figs. 8d-e**). However, after 4^{th} cleaning cycle (**Fig. 8f**), the membrane showed an agglomeration of particles, which could be a mixture of organic and inorganic fouling. This illustrates that after several cleaning cycles, the efficiency of cleaning has decreased, which could be due to more pore blocking by foulants, as well as roughening of the surface due to many cleanings, which enhances the area for fouling to occur. Additional analysis by EDX (**Table 6**) showed mainly C and F elements in the virgin membrane, however new peaks (i.e., elements) were observed for the fouled and cleaning membrane. For the fouled membrane, numerous elements were observed on the membrane surface, which are usually present in seawater properties with high concentrations of Na^+ and Cl^-, indicating the presence of inorganic scales. The cleaning of the membranes resulted to decreased Na^+ content, but showed increasing Cl^- content with the increasing number of cleaning cycles. Mg element was also observed after the first cleaning. Increasing Na/F and Cl/F ratios (**Table 7**) were observed with the increase of cleaning cycles, which signifies that NaCl were adhered to the surface, and were not easy to remove most probably because of short chemical cleaning duration. The deposition of NaCl on the membrane has made the hydrophobic surface into hydrophilic because of the effect of hydrophilic properties of the inorganic NaCl. It was supposed that if membrane chemical cleaning duration is increased, higher cleaning efficiency is expected and could remove most of the inorganic scale deposits.

[Table 6]

[Table 7]

3.8 Water quality

[Table 8]

The effect of chemical cleaning can be determined by evaluating the water quality of the feed and permeate streams. Generally, total dissolved solids (TDS) cannot be removed by MF/UF process. However, as shown in **Table 8**, the TDS of the permeate water was much lower than that of the feed water, even after several cycles of cleaning. This indicate that some fouling matters especially inorganic NaCl, which consists the bulk of TDS, were still present in/on the membrane that resulted to constriction of the membrane pores (**Fig. 8**), thus more TDS were retained on the membrane resulting to the decreased TDS values. The silt density index or SDI_{15} is one of the commonly used parameters to predict membrane fouling. Normally, the SDI_{15} should be within 3 to 5 for efficient desalination process. If the SDI_{15} is more than 5 going through the RO process, the RO membrane will experience a lot of burden and will consume a lot of energy due to the deposition of big foulant particles. The SDI_{15} is a simple correlation of the decrease in filtration time of a known volume of the feed after a certain period of filtration time (usually 15 min). The SDI_{15} is calculated from the equation:

$$SDI_{15} = \frac{1 - (t_i/t_f)}{T_f} \times 100 \qquad (Eq. 5)$$

where t_i is initial filtration time (to filter a fixed volume), t_f the final filtration time (to filter the same fixed volume), and T_f is the elapsed time [51, 52] according ASTM D4189-95 [53, 54]. Unlike turbidity, which pertains to the amount of solids in a given sample, SDI_{15} determines the contaminants that could probably plug the membrane pores [55]. Thus,

plugging factor was also determined, which is considered as one of the frequently used terms in measuring the amount of suspended solids present in a water sample. PF can be calculated from the following equation:

$$\text{PF}\ (\%) = \ 1 - (\mathrm{t_i}/\mathrm{t_f}) \times 100 \ \approx \frac{\mathrm{SDI_{15}}}{\mathrm{T_f}} \qquad \text{(Eq. 6)}$$

where $\mathrm{t_i}$ is initial filtration time (to filter a fixed volume), $\mathrm{t_f}$ the final filtration time (to filter the same fixed volume), and $\mathrm{T_f}$ the elapsed time [51, 55, 56].

The initial SDI_{15} of the feed was 6.43, which was very high, but was reduced drastically to 0.39 ~ 1.01 after passing through the UF process even after many times of cleaning cycles. This has big implication to lessening the burden for the RO process, thus making the UF a good pre-treatment fit. Similarly, the turbidity and PF of the feed has steeply decreased after the UF process, though increasing trend could be seen with the increase of the number of cleaning cycles. This increase could be explained by the tendency of some foulants (especially the small molecular weight hydrophobic foulants) to deposit at the inner core of the membrane wherein through continuous consecutive cleaning, the adhered foulants are detached and are carried way with the permeate, thus increasing the SDI_{15}, PF and turbidity of the permeate.

All other parameters including UV_{254} and DOC also showed decreased values after passing through UF. DOC is often used in most membrane studies to evaluate NOM removal efficiency [57]. However, the SUVA values showed increasing trend with the increase of cleaning cycle. SUVA is the ratio of UV_{254} and DOC as shown in the following equation:

$$\mathrm{SUVA_{254}}\ (\mathrm{m^{-1}}\text{of absorbance per mg/l of DOC} = \mathrm{L/mg \cdot m}) = \frac{\mathrm{UV_{254}}}{\mathrm{DOC}} \qquad \text{(Eq. 7)}$$

This increasing trend of SUVA could be attributed to the increased presence of organic foulants (humic acid and fulvic acid) on/in the surface as determined by the increasing C/F ratio in **Table 7**. Fulvic acid particles are generally smaller than the UF membrane pore so

399 that it could pass through it easily. On the contrary, humic acid is a larger size particle that
400 could not easily pass through the UF membrane, thus it accumulates on the surface and attach
401 as foulants.
402
403 3.9 Contact angle
404
405 **[Figure 9]**
406
407 **Fig. 9** shows the contact angle (CA) measurements of the membranes. The virgin membrane
408 showed an initial CA of 83.8^{o}, indicating a slightly hydrophilic membrane. However, when
409 foulants were formed, the CA of the membrane surface increased to 131.8^{o}, which is
410 hydrophobic. This could be attributed to the presence of some suspended and total solids
411 present on the surface, which are known to be hydrophobic [13, 24, 58, 59]. After chemical
412 cleaning, the surface became more and more hydrophilic with the increase in cleaning cycles.
413 This signifies that many hydrophobic organic foulants were removed during the cleaning
414 process, thereby decreasing the hydrophobicity of the surface. Additionally, some hydrophilic
415 inorganic particles are still attached on/in the membrane surface even after several cleanings,
416 thus, they contributed to the decrease in CA.
417
418 **4. Conclusion**
419 In the present study, pressurized ultrafiltration (UF) was used as pre-treatment for
420 desalination, and the effect of different chemicals and cleaning modes on the removal of
421 fouling formation on UF membrane was investigated. Acid and alkali-based chemicals were
422 used as cleaning agents. Our initial tests showed that oxalic acid and sodium hypochlorite had
423 high efficiency in removing different types of foulants, thus they were applied for the

consecutive cleaning tests. Chemical in series cleaning consisting of either oxalic acid-sodium hypochlorite-oxalic acid series or sodium hypochlorite-oxalic acid- sodium hypochlorite were conducted at different cleaning times of 15-30-15 min or 30-60-30 min. The following are the summary and conclusions drawn from this study:

- Flux recovery by chemical cleaning was greatly affected by the kinds of chemicals and the sequence of dosage as well as contact time. The better efficiency was obtained by the sequence of acid-base-acid in series under the cleaning condition of same kinds of chemicals and contact time.
- The results of consecutive chemical cleaning showed that the flux was almost fully recovered to the previous recovered value as cleaning times increased; recovery efficiency of 96.8%, 95.8%, 98.3% and 99.9% after first, second, third and fourth time of cleaning, respectively. This implies that a stable flux could be maintained after several times of cleaning frequency; around 91% of initial flux was maintained after third chemical cleaning.
- However, the cleaning interval or filtration running time has been shortened due to the changes in the membrane surface structure by contact with chemical cleaning agents during every cleaning time. As seen from the analyses of contact angle and FTIR spectra, the surface of membrane has been gradually changed to hydrophilic nature due to the presence of hydrophilic inorganic foulants being not fully removed by chemical cleaning, which indicates that membrane fouling is progressed although apparent recovery efficiency seems to be high and stable.
- In terms of long-term operation and maintenance of membrane pre-treatment using MF/UF in desalination processes, it will be necessary that an enhanced chemical cleaning strategy on treating hydrophilic inorganic foulants as well as hydrophobic organic ones for the efficient management of desalination plants.

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603

Figure list

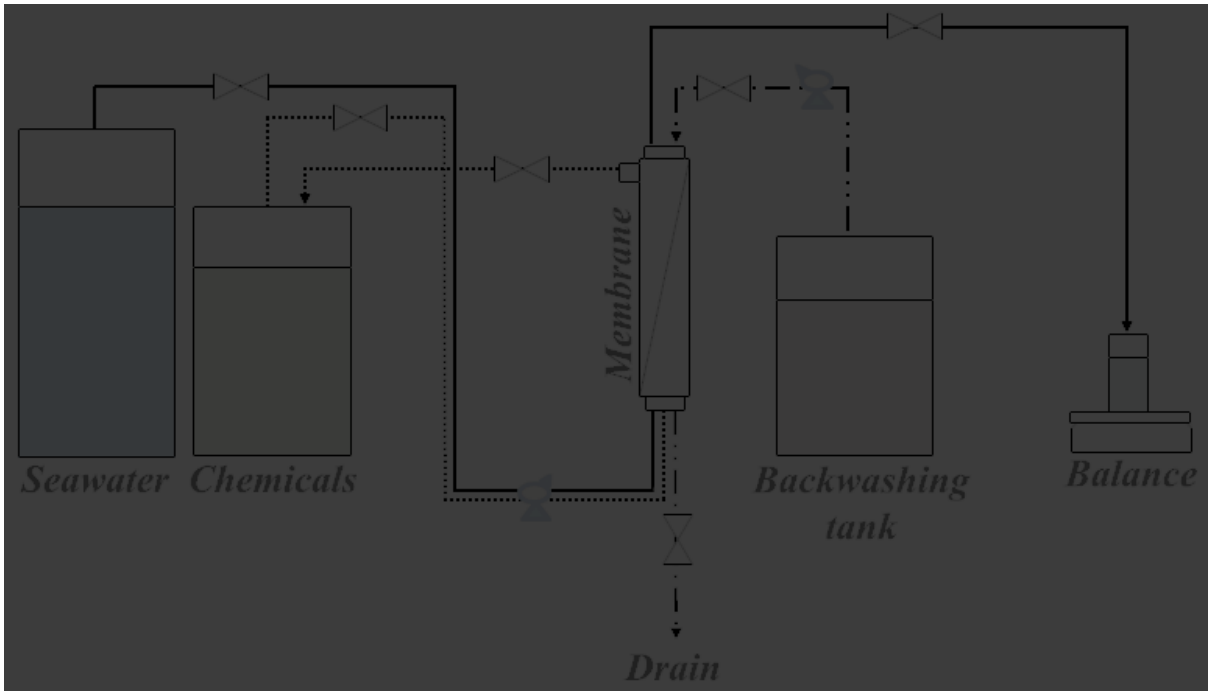

Figure 1. Schematic diagram of the pressurized hollow fiber UF system

Figure 2. Hollow fiber membrane before and after chemical cleaning (pH≥12)

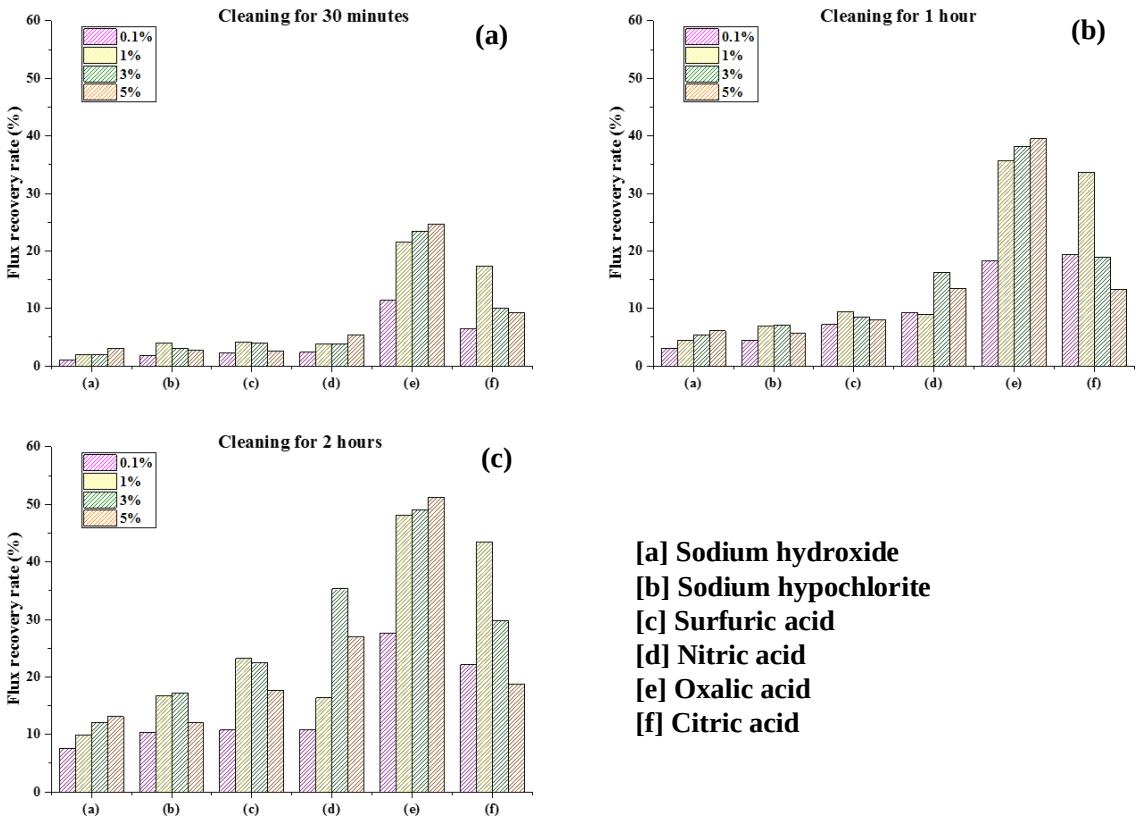

Figure 3. Recovery rate for single chemical cleaning using various cleaning agents at different cleaning durations: (a) 30 minutes, (b) 1 hour and (c) 2 hours

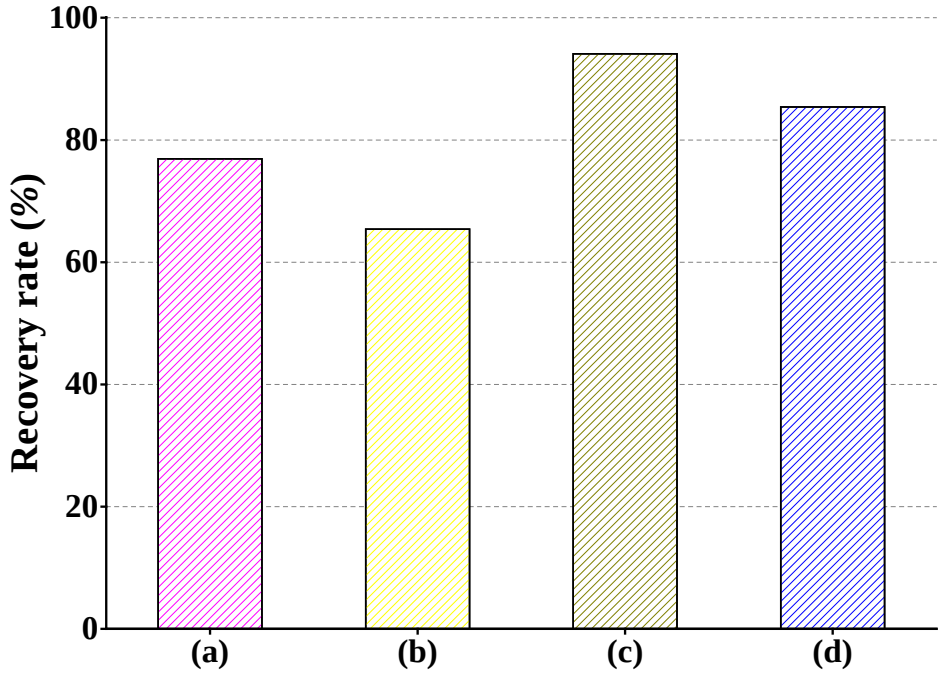

Figure 4. Recovery rates for chemical cleaning in series: (a, c) oxalic acid-sodium hypochlorite-oxalic acid, and (b, d) sodium hypochlorite-oxalic acid-sodium hypochlorite for (a, b) 15min-30min-15min, and (c, d) 30min-60min-30min

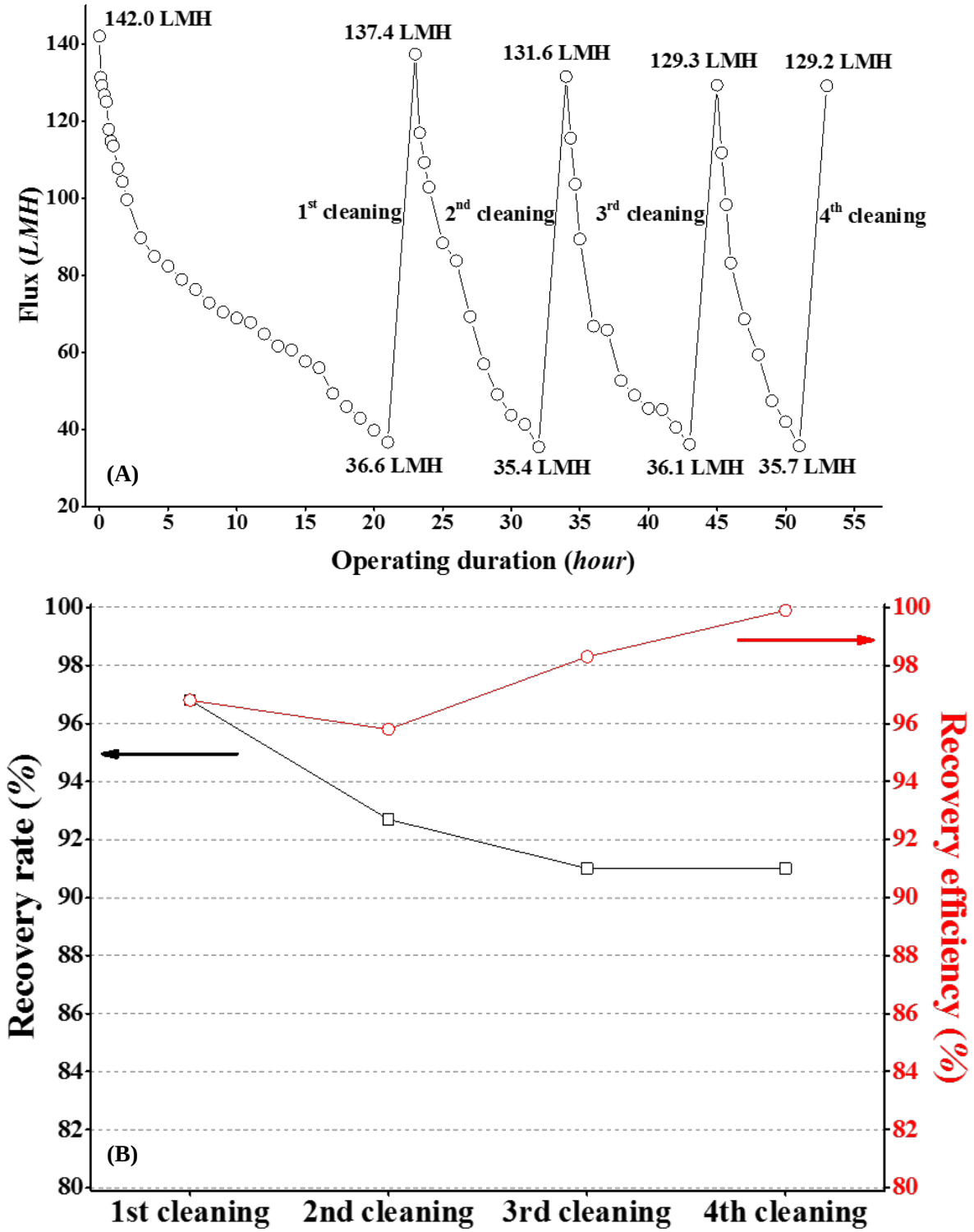

Figure 5. (A) Flux and (B) recovery rate and efficiency using chemical cleaning process

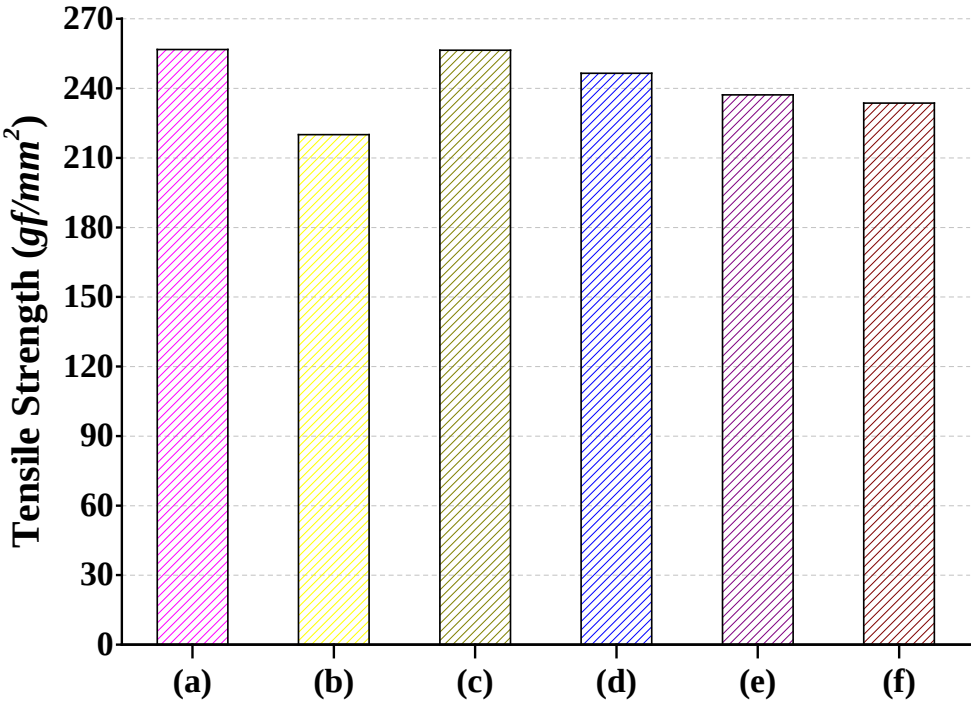

Figure 6. Tensile strength of the hollow fiber membranes: (a) virgin membrane, (b) fouled membrane and membranes after (c) 1st cleaning, (d) 2nd cleaning, (e) 3rd cleaning, and (f) 4th cleaning

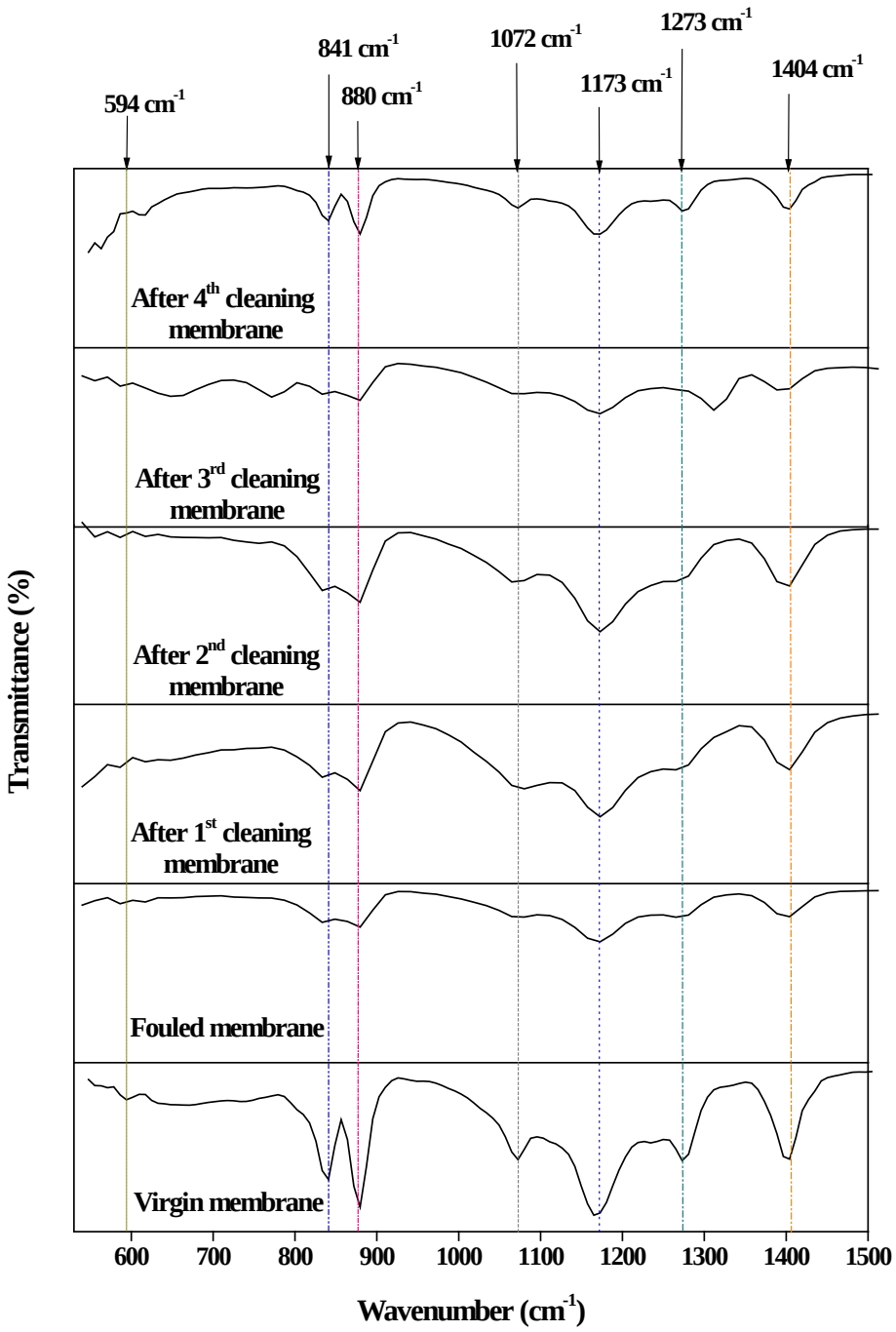

Figure 7 FT-IR spectra of the different membrane conditions

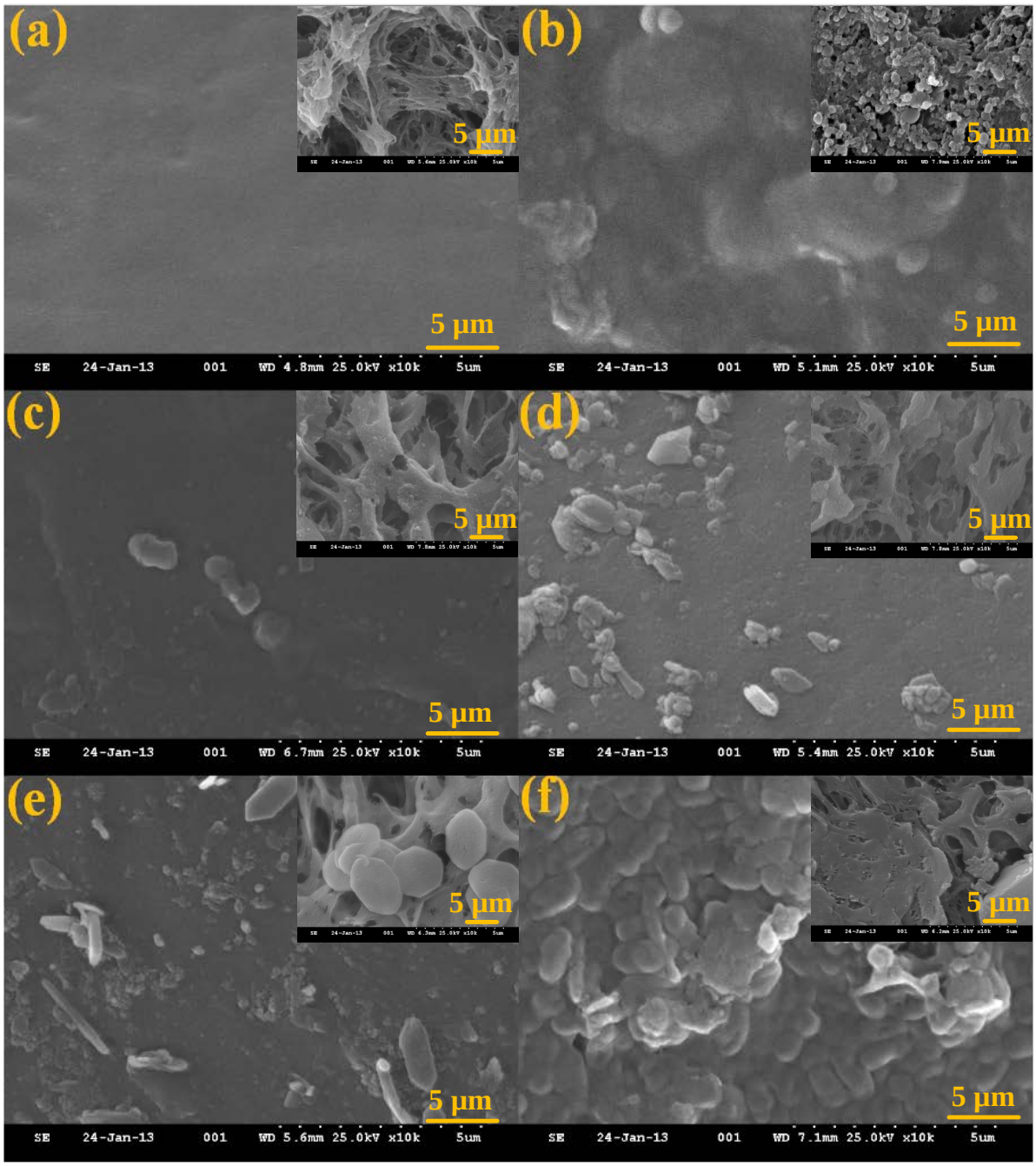

Figure 8. Surface SEM images of the (a) virgin membrane, (b) fouled membrane, and membranes after (c) 1st cleaning, (d) 2nd cleaning, (e) 3rd cleaning and (f) 4th cleaning. Insets: SEM corresponding SEM images of the inner pores

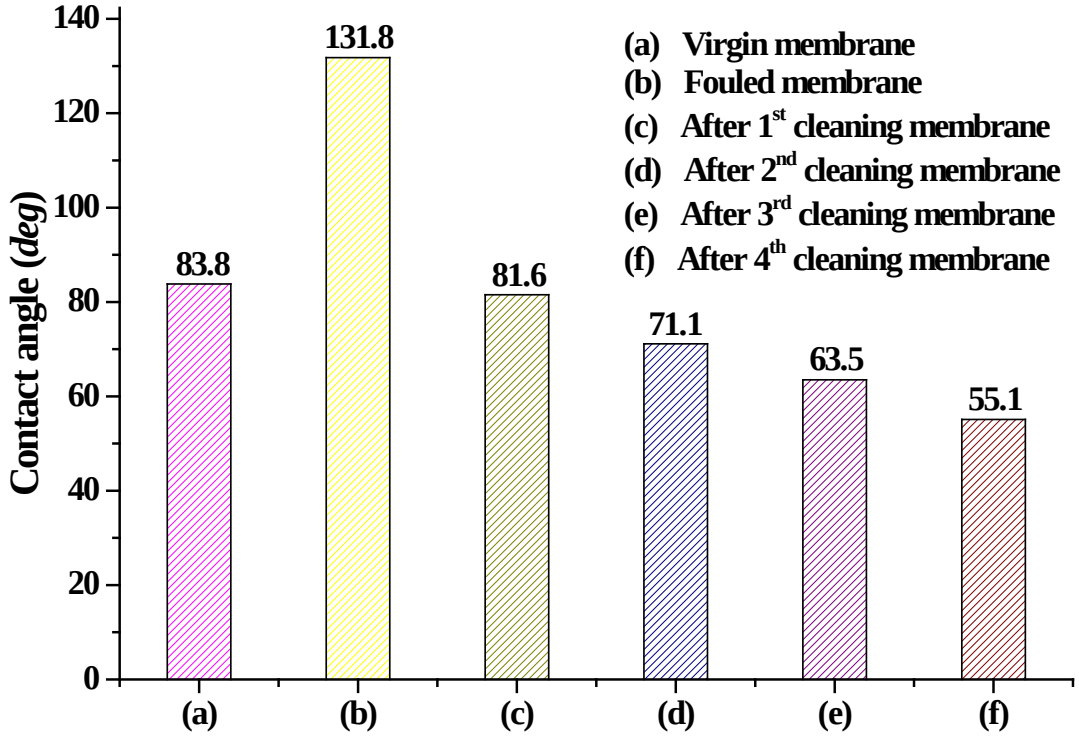

Figure 9. Contact angle measurement of different hollow fiber membranes: (a) virgin membrane, (b) fouled membrane and membranes after (c) 1st cleaning, (d) 2nd cleaning, (e) 3rd cleaning and (f) 4th cleaning

Table list:

Table 1. Published reports in literature using different cleaning agents for various processes

Filtration process	Feed solution	Chemical agents	Reference Number
Pressurized MF	Synthetic water (humic acid, Fe, Mn and Ca^{2+})	HNO_3, NaOH	[14]
Ceramic MF	3.5 wt % whey protein	NaOH	[11]
Ceramic MF	0.1 g/L of yeast in 10 g/L sugar solution	HNO_3, NaOCl, NaOH	[12]
Submerged MF	Stream water and secondary water from plant	$C_6H_8O_7$, NaOCl, NaOH	[13]
Spiral-wound UF	Skimmed milk (11 g/L proteins, 16 g/L lactose and 3 g/L salts)	NaOH, Tween 20, Ultrasil 10	[15]
Submerged UF	Algal-rich water	EDTA, HCl, NaOCl, NaOH	[16]
Submerged MF and UF	Potable water	$C_6H_8O_7$, NaOCl, NaOH	[17]
RO and NF	Licorice aqueous solutions	EDTA, NaOH, HNO_3, H_2SO_4, $CH_3(CH_2)_{10}CH_2OSO_3Na$	[18]
Flat-sheet MF	3.5 g/L of sodium alginate and 2 g/L of BSA	NaOCl	[19]
UF	Algae	$C_6H_8O_7$, NaOCl, NaOH	[20]
UF	Proteins	NaOCl, NH_4OH, Machine powder	[21]
UF	Surface water and ground water	$C_6H_8O_7$, NaCl, NaOH, $CH_3(CH_2)_{10}CH_2OSO_3Na$	[22]
UF	proteins	NaOCl, NaOH, Tween 20	[23]
Submerged UF	Surface water	$C_6H_8O_7$, Ethanol, NaOH	[24]
UF	Whey protein isolate	HCl, NaOH	[25]
UF	Surface water	$C_6H_8O_7$, H_2O_2, HCl, Kleen MTC 411, P3 Ultrasil 115, P3 Ultrasil 70, P3 Aquadean Sal, 4AquacleanFer 12	[26]
Capillary UF and MF	Reservoir water	$C_6H_8O_7$, H_2O_2, HCl, NaOCl, NaOH	[27]
Submerged MF	Micro-polluted raw water	HCl, NaOCl	[28]
NF	NOM with ionic compounds	NaOH, $CH_3(CH_2)_{10}CH_2OSO_3Na$	[29]
RO	Alginic acid with 32 g/L of synthetic seawater	De-Ionized water, EDTA, NaCl	[30]
Hollow fiber UF	20, 10 and 10 mg/L of humic acid, sodium alginate and BSA	Milli-Q, NaOCl	[31]
Submerged hollow fiber UF	Seawater	NaOCl	[32]
NF and RO	Oil sands process-affected water	HCl, NaOH	[33]
Flat-sheet MF	1 % of milk solution	EDTA	[34]
Flat-sheet UF and MF	Whey protein concentrate	NaOH	[35]

Table 2. Specification of the hollow fiber UF membrane

Shape	Hollow fiber pressurized module
Pore size, μm	0.038
Material	PVDF (Polyvinylidene fluoride)
Filtration flux, L/m^2h	130 ± 15
Membrane area, m^2	2.26×10^{-3}
Dimension ($\pi \times D \times l \times$ units)	$\pi \times 150$ mm $\times 1.2$ mm $\times 4$ units
Operating pressure, bar	0.5

Table 3. pH of cleaning solutions at different percent concentrations

Chemical	0.1 %	1 %	3 %	5 %
Sodium hypochlorite	11.10	11.76	12.10	12.23
Sodium hydroxide	12.82	13.13	13.44	13.89
Sulfuric acid	1.72	0.78	0.56	0.34
Nitric acid	1.59	0.75	0.34	0.12
Citric acid	2.41	2.24	2.12	1.90
Oxalic acid	2.29	1.48	1.22	1.08

Table 4. Time elapsed for membrane fouling at different stages

	1st fouling	2nd fouling	3rd fouling	4th fouling
Total fouled time (min)	1260	540	540	360
$\left(\frac{C_F}{C_I}\right) \times 100$ %	100.0	42.9	42.9	28.6

Table 5. Different bands of the FT-IR analysis

IR band (cm^{-1})	Range given in the literature (cm^{-1})	Type of vibration
841	839 ~ 845	CH_2 rocking CF_2 stretching CC stretching
880	880	C-C (asymmetric stretch)
1072	1074	C-C (asymmetric stretch)
1173	1184	CF_2 (symmetric stretch)
1273	1279	CF (out of plane deformation)
1404	1401-1406	CH_2 wagging

Table 6. EDX of hollow fiber membrane surface

Element	Initial	Fouled	After 1st	After 2nd	After 3rd	After 4th

		membrane	cleaning membrane	cleaning membrane	cleaning membrane	cleaning membrane
	Weight (%)	Weight (%)	Weight (%)	Weight (%)	Weight (%)	Weight (%)
C	40.95	42.11	37.99	39.09	39.12	39.14
F	59.05	47.70	57.66	52.68	52.68	52.58
O	-	2.79	1.97	3.30	2.90	2.56
Cl	-	3.98	1.35	3.00	3.10	3.29
Na	-	2.66	1.02	1.62	1.93	2.15
Mg	-	0.49	-	0.31	0.27	0.28
Al	-	0.10	-	-	-	-
K	-	0.10	-	-	-	-
Ca	-	0.08	-	-	-	-
Totals	100.00	100.00	100.00	100.00	100.00	100.00

Table 7. Ratio of the element divided by fluorine

$Element/F$	Initial	Fouled	After 1st	After 2nd	After 3rd	After 4th

		membrane	cleaning membrane	cleaning membrane	cleaning membrane	cleaning membrane
C/F	0.693	0.883	0.659	0.742	0.743	0.744
F/F	1.000	1.000	1.000	1.000	1.000	1.000
O/F		0.058	0.034	0.063	0.055	0.049
Cl/F		0.083	0.023	0.057	0.059	0.063
Na/F		0.056	0.018	0.031	0.037	0.041
Mg/F		0.010		0.006	0.005	0.005
Al/F		0.002				
K/F		0.002				
Ca/F		0.002				

Table 8. Water quality of feed and permeate before and after chemical cleaning

	Feed	Initial	After 1st cleaning	After 2nd cleaning	After 3rd cleaning	After 4th cleaning
TDS (ppm)	35557	26693	26942	27540	27650	27956
SDI_{15}	6.43	0.39	0.54	0.71	0.89	1.01
PF (%)	76.0	5.0	7.0	11.0	14.0	17.0
Turbidity (NTU)	49.6	0.079	0.171	0.269	0.344	0.356
DOC (ppm)	14.07	7.894	7.658	6.982	6.498	6.355
UV_{254} (cm^{-1})	0.104	0.051	0.057	0.058	0.061	0.064
$SUVA_{254}$ ($L/mg \cdot m$)	0.739	0.646	0.744	0.831	0.939	1.007