Ultrasonic-assisted removal of inorganic scales in high-salinity wastewater treatment using membrane distillation

Hyeongrak Cho, Jihyeok Choi, Yongjun Choi, Sangho Lee*

School of Civil and Environmental Engineering, Kookmin University, Jeongneung-Dong, Seongbuk-Gu, Seoul, 02707, Republic of Korea, Tel. +82-2-910-4529; Fax: 82-2-910-4939; emails: sanghlee@kookmin.ac.kr (S. Lee), rhino@kookmin.ac.kr (H. Cho), cj66563@gmail.com (J. Choi), choiyj1041@gmail.com (Y. Choi)

Received 18 October 2018; Accepted 28 February 2019

A B S T R A C T

This study focuses on ultrasonic-assisted cleaning of MD membranes for the treatment of high-TDS feed waters. The conditions for the ultrasonic application were explored to increase the cleaning efficiency and to minimize physical damage to the membrane. MD fouling tests were performed using synthetic feed waters with high scaling potential. After the fouling tests, cleaning experiments were performed by immersing the membrane cell in an ultrasonic generator and operated with a citric acid solution. The recovery of membrane permeability, liquid entry pressure, and ion rejection were measured, and scanning electron microscopy was used to visually analyze the membrane surface. Results indicated that the ultrasonic irradiation at low frequencies (28 and 45 kHz) led to either structural damage or wetting of the MD membranes. However, the ultrasonic irradiation at a higher frequency (72 kHz) exhibited a high cleaning efficiency without the structural damage and wetting. Compared with physical and chemical cleaning techniques, the ultrasonic-assisted cleaning resulted in higher flux recovery and foulant removal with a reduction in cleaning chemical consumption.

Keywords: Membrane distillation; Scale; Fouling; Cleaning; Ultrasonic irradiation

1. Introduction

Membrane distillation (MD) has become an important emerging water treatment technology and has the potential to replace conventional desalination techniques such as conventional desalination (MED, MSF) and reverse osmosis (RO) [1–3]. The MD has several advantages over conventional desalination technologies such as reverse osmosis (RO), multi-stage flash (MSF), multi effect distillation (MED), including low operating temperature and low hydraulic pressure, high salt rejection, and performance independent of high osmotic pressure for the feed water [1,3–14]. For these reasons, MD is considered for various applications including sweater desalination to produce freshwater [1,3,5–8,13,14]. MD can also be used to treat the concentrated brine by RO because of its ability to treat high-salinity feed water.

However, there are challenges to be overcome for effective application of MD technology. One of them is wetting of MD membranes. During long-term MD operation, water vapor evaporation occurs at the surface of the wetted crystal, and a crystal growth potential is generated. As a result, the new area of pores becomes wet with water, and the total area of the pores increases [13–16]. The hydrophobicity of the MD membrane is one of the important factors associated with these problems. There are several methods for measuring the degree of hydrophobicity of the membrane, such as contact angle (CA) and liquid entry pressure (LEP) [9,17].

Another challenge in MD technology is membrane fouling, which influences the efficiency of the MD process. The mechanism of fouling in MD is different from that in pressure-driven membranes such as microfiltration, ultrafiltration, and RO [18,19]. While fouling of an MD membrane is caused by the deposition of organic or inorganic pollutants,
the characteristics of the foulant layers may differ due to the lack of hydraulic pressure in MD. Nevertheless, it is difficult to control membrane fouling in MD systems because periodic backwash cannot be applied. Currently, offline physical and chemical cleaning is generally accepted as a method to recover the performance of fouled MD membranes [20–22]. However, this requires substantial amounts of chemicals consumed and may lead to membrane damage, frequent replacement of membranes, increased chemical costs, and production of chemical waste [23–25].

Recently, ultrasonic irradiation for membrane cleaning has received an increasing amount of attention from researchers as an alternative technique to conventional chemical cleaning [23,26]. Ultrasound can increase the efficiency of removing both organic foulants and inorganic scales via acoustic streaming and turbulence [27–29]. However, ultrasound must be used carefully because it may damage the membranes [30,31]. Ultrasonic irradiation has been used for cleaning of microfiltration (MF) and ultrafiltration (UF) membranes and found to be cost-effective [23,24,27,32–35]. However, relatively little information is available on the effectiveness of ultrasonic-assisted cleaning technique for MD membranes [36].

Accordingly, the objective of this study was to apply an ultrasonic-assisted cleaning technique to recover the permeability of MD membranes. Synthetic feed solution containing inorganic scale-forming ions was used to cause severe fouling of MD membranes. The conditions for ultrasonic irradiation such as frequency and output were varied and their effect on membrane properties and cleaning efficiency was evaluated. The cleaning efficiencies by the ultrasonic irradiation were compared with those by conventional physical and chemical cleaning methods. The novelty of this study lies in its systematic approach to explore appropriate conditions for ultrasonic-assisted cleaning of fouled MD membranes.

2. Materials and methods

2.1. Materials

The membranes used in this study were made of polyvinylidene fluoride (PVDF) (Millipore, USA). According to the manufacturers, the nominal pore size of the PVDF membranes was 0.22 μm, and the porosity was 75%. Membrane cells were made with membranes that had an effective area of 12.2 cm².

2.2. Experiment set-up

All fouling and cleaning experiments were conducted on a laboratory scale based on direct contact membrane distillation (DCMD) configuration. The experimental set-up comprises an electronic scale connected to a personal computer, two gear pumps, a feed tank, and a condenser. The conductivity and turbidity were measured to confirm water flux and scale formation during the process. During the experiments, the temperatures for the feed side and distillate side were fixed at 60°C and 20°C, respectively. After the fouling experiment, the membranes were examined to evaluate the effectiveness of different cleaning methods, including physical cleaning, chemical cleaning, and ultrasonic cleaning. An ultrasonic device with adjustable ultrasonic output (30 and 300 W) from the Mirae ultrasonic Tech (Republic of Korea) was used with a frequency range of 28–72 kHz. Fig. 1 shows a schematic diagram of the laboratory scale DCMD and ultrasonic cleaning procedure. The operating conditions for MD experiments are summarized in Table 1.

2.3. Membrane damage experiments

Prior to DCMD experiments, the pristine membranes were examined under various conditions for ultrasonic irradiations to check whether they were damaged or not. The ultrasonic frequencies were 25, 45, and 72 kHz, respectively, and the powers were 10, 50, and 100 W, respectively. The membranes were exposed to the ultrasound for 10 s in each test. Ultrasonic wave transducers with tips of 5.0 cm in diameter were placed directly on the lower outer surface of the ultrasonic cleaning tank, and the contaminated membrane

---

**Fig. 1.** Schematic of the laboratory-scale DCMD and ultrasonic cleaning device.
was located at the center of the tank containing distilled water. The membranes were examined using scanning electron microscopy (SEM). The CA and LEP were also measured.

2.4. DCMD experiments

2.4.1. Fouling experiments

Fouling experiments of the MD membrane were conducted at a synthetic feed water cross flow rate of 0.7 L min\(^{-1}\) (Table 1) and 0.4 L min\(^{-1}\) of distilled water, and the temperature of the feed water and distilled water were set at 60°C and 20°C, respectively. Each experiment was conducted until the water flux was completely reduced, and the membrane was cleaned to confirm the initial flux recovery ratio. The conductivity of the distillate was checked in real-time to evaluate the wetting phenomenon of the membrane during the fouling test.

2.4.2. Cleaning experiments

After fouling tests, the membrane was removed from the cell and cleaned using distilled water for 10 s. In the same way, hydrochloric acid with a pH of 3 was used to clean the membrane for 10 s. Moreover, ultrasonic waves were used for 10 s of cleaning for each condition, which were performed as a control test. The ultrasonic device used for the membrane damage experiments was also applied for the cleaning experiments. Flux recovery and salt removal were measured using cleaned membranes.

2.5. Analytical methods

2.5.1. Field emission scanning electron microscopy

An analytical field emission scanning electron microscope (FESEM; SUPRA SSVP, Carl Zeiss, Germany) was used to examine the surface of the pristine membrane and the fouling layer following experiments using energy dispersion spectrometry. All membrane samples were coated with a thin layer of platinum under vacuum prior to observation at an accelerating voltage of 15 kV.

2.5.2. Contact angle

CA was determined using a CA analyzer (SmartDrop, Femtobaf, Korea) with 2 μL droplets, with the values reported as an average of three measurements. The static CA was measured at the moment the drop was placed on the surface.

2.5.3. Liquid entry pressure

LEP is an important consideration when employing MD membranes to prevent pore wetting because the applied pressure must be lower than the LEP. In this study, the LEP was measured using the experimental device as shown in Fig. 2. The unit comprises a high-pressure nitrogen gas tank, a pressure regulator, a reservoir, a pressure sensor, and a membrane, which is to be tested. The LEP was measured by increasing the pressure applied on the membrane until water penetration was observed. The maximum pressure before water passes through the membrane is the membrane’s LEP. The LEP value for the PVDF membranes was 1.8 ± 0.3 bar. According to the Young–Laplace model, the pore radius \( r \) of the membrane is proportional to the surface tension \( \gamma \) and the inverse value of the LEP \( \Delta P \) \[37,38\]:

\[
r = \left( -\frac{2\gamma}{\Delta P} \right) \cos \theta
\]  

\[1\]
where $\theta$ is the intrinsic advancing CA between the liquid and the membrane material.

3. Results and discussion

3.1. Membrane damage effect of ultrasonic irradiation

The possibility of membrane damage by ultrasonic irradiation was investigated prior to conducting the cleaning tests. After applying the ultrasound under different frequencies and powers, the membrane surfaces were observed using SEM. If there were noticeable changes compared with the pristine membrane, it was concluded that the membrane was damaged by the ultrasonic irradiation. Fig. 3 shows the SEM images of the membranes after ultrasonic irradiation at 28 kHz. When the powers were 300 W (Fig. 3a) and 150 W (Fig. 3b), it was found that the membranes were significantly damaged. When the power was reduced to 30 W (Fig. 3c), the membrane did not show any significant difference compared with the pristine membrane (Fig. 3d). This implies that only the ultrasonic irradiation at 28 kHz and 30 W may be used for the membrane cleaning tests.

Similar results were obtained at 45 kHz as presented in Fig. 4. The membrane damage was clearly shown at 300 W (Fig. 4a) and 50 W (Fig. 4b), but it was not observed at 30 W (Fig. 4c). On the other hand, the ultrasonic irradiation at 72 kHz resulted in no membrane damage between 30 and 300 W, as shown in Fig. 5. Accordingly, the conditions necessary to avoid structural damage of the membrane were found to be 28 kHz and 30 W, 45 kHz and 30 W, and 72 kHz and 30–300 W based on results of the SEM analysis. The damage of PVDF hollow fiber membranes by ultrasonic irradiation was also reported in other study [36].

3.2. Changes in LEP and CA by ultrasonic irradiation

In addition to SEM analysis, LEP and CA were measured to examine the possibility of the changes in the membrane properties (i.e., hydrophobicity). Fig. 6 shows the effect of ultrasonic frequency on the CA. The ultrasonic frequencies were set to 28, 45, and 72 kHz, respectively, and the power settings were 300, 150, and 30 W, respectively. The most significant loss of hydrophobicity was observed at 28 kHz, leading to the wetting of the membrane. The LEP and the CA under these conditions were 0.1 bar and 80° ± 20°, respectively. The ultrasonic irradiation at 45 kHz also resulted in wetting, and the LEP and the CA were 0.1 bar and 100° ± 10°, respectively. Only the ultrasonic irradiation at 75 kHz showed a negligible impact on the membrane properties even when the power setting was higher than the other cases. Under this condition, the LEP and the CA were almost unchanged even after the application of ultrasound. This suggests that ultrasonic irradiation should be applied at 72 kHz to minimize MD membrane damage.

It should be noted that no macroscopic modification in the structures of the membrane surface was observed at 28 kHz and 30 W (Fig. 3c) and 45 kHz and 30 W (Fig. 4c). This further suggests that membrane surface properties

![Fig. 3. SEM images of membranes exposed to ultrasonic irradiation at different frequencies (a) 28 kHz, 300 W; (b) 28 kHz, 150 W; (c) 28 kHz, 30 W; and (d) pristine membrane.](image-url)
Fig. 4. SEM images of membranes exposed to ultrasonic irradiation at different frequencies (a) 45 kHz, 300 W; (b) 45 kHz, 150 W; (c) 45 kHz, 30 W; and (d) pristine membrane.

Fig. 5. SEM images of membranes exposed to ultrasonic irradiation at different frequencies (a) 72 kHz, 300 W; (b) 72 kHz, 150 W; (c) 72 kHz, 30 W; and (d) pristine membrane.
were changed by the application of ultrasound under these conditions, leading to a reduction in the LEP and the CA. Accordingly, it is possible to conclude that the ultrasonic frequency is more important than ultrasonic power with respect to damage inflicted on the membrane. In addition, it is recommended not only SEM analysis but also LEP and CA measurements should be done to confirm the ultrasound effect on MD membrane properties.

3.3. Changes in pure water flux by ultrasonic irradiation

Based on these results, DCMD experiments were conducted using deionized water to compare the pure water fluxes using membranes exposed under different ultrasonic irradiation conditions. The results are shown in Fig. 7. At 72 kHz, no flux changes were observed, which indicated that the membranes were intact. However, at 45 kHz, the flux was slightly lower than those at 72 kHz. Considering the results presented in Fig. 6b and its low LEP (0.1 bar), the flux was reduced due to the changes in the membrane structure or wetting. These results also confirmed that MD cleaning should be applied at 72 kHz to avoid the possibility of membrane damage.

3.4. Cleaning of fouled MD membranes by physical and chemical methods

To compare the cleaning efficiency, physical, physical/chemical, and ultrasonic cleaning methods were applied to the fouled MD membranes. Prior to the cleaning test, the membrane foul was induced using the synthetic feed water in Table 1. The flux profile with time is presented in Fig. 8. The flux remained constant until the operation time reached 1,300 min, and then it abruptly decreased. After an operation time of 1,800 min, the flux measured was approximately 2 kg m\(^{-2}\) h\(^{-1}\), which corresponds to an 89% reduction in membrane permeability. It is evident that the salts in the feed solution resulted in significant fouling due to scale formation and crystallization.

To recover the membrane permeability, physical and chemical cleaning were applied, as shown in Fig. 9. The physical cleaning was performed using distilled water for 10 s after the fouling test. The physical/chemical cleaning was performed using an acidic solution with a pH of 2 for 10 s, and then the membrane was flushed using distilled water for 10 s. The flux profiles before the fouling test and after the cleaning were compared to estimate the recovery of flux. Furthermore, the permeate quality was measured after the cleaning to confirm the integrity of the membrane. The physical cleaning alone indicated a cleaning efficiency of 84.2% of the initial flux. The physical/chemical cleaning demonstrated a better efficiency, which was as high as 95%. In both physical and chemical cleaning methods, the salt rejection was observed to be 99.9%, implying that the membrane was neither damaged nor wetted.

Figs. 10a and b show the SEM images of the membrane surfaces after the physical cleaning and physical with chemical cleaning, respectively. Compared with the SEM image of the membrane before cleaning (Fig. 10c), substantial amounts of foulants were removed in both cases. However,
the physical cleaning does not seem to completely remove foulants (Fig. 10a). On the other hand, the physical with chemical cleaning showed a better removal efficiency for the foulants (Fig. 10b). It is evident that the physical with chemical cleaning was more efficient than the physical cleaning in terms of flux recovery and foulant removal efficiency.

3.5. Cleaning by ultrasonic irradiation at 45 kHz

Fig. 11a presents the results of membrane cleaning using ultrasonic irradiation at 45 kHz and 30 W. The water flux and permeate conductivity after membrane cleaning are shown as a function of time. The water flux did not significantly change with time, and the recovery of flux was almost 90%. However, the permeate conductivity increased with time, indicating that the membrane was either damaged or wetted. As previously described, the membrane exposed to ultrasonic irradiation under these conditions exhibited a low LEP and a reduced CA. Accordingly, it is evident that the ultrasonic cleaning should not be applied under these conditions, and thus the ultrasonic frequency should be increased to reduce the damage. In Fig. 11b, the SEM image
of the membrane after the ultrasonic cleaning is shown, indicating that some foulants still remained. This implies that ultrasound under these conditions (45 kHz and 30 W) is not appropriate for the complete removal of the foulants from the membrane surface.

3.6. Cleaning by ultrasonic irradiation at 72 kHz

The results of ultrasonic cleaning at 72 kHz are illustrated in Fig. 12. Unlike the previous case, the permeate conductivity values were stable over time in these cases, suggesting that the membrane was neither damaged nor wetted. But the cleaning efficiency was found to be sensitive to the ultrasonic power. Flux recovery under 30 W conditions was 87.29%, which is 3.09% higher than physical cleaning, and the salt rejection was 99.99% (Fig. 12a). In 150 W condition, flux recovery was almost 100%, which is even better than the chemical cleaning efficiency, and the salt rejection was 99.99% (Fig. 12b). Under 300 W conditions, the flux became slightly higher than that of the pristine membrane, but there was no change in salt rejection (Fig. 12c). The mitigation of fouling due to membrane scaling was also found in previous study [33] but it was applied only during the MD operation. This may be attributed to the changes in the membrane properties by ultrasonic irradiation, which leads to increased water permeability. It is also possible that removing impurities from the pristine membrane using ultrasound does not change the membrane properties. Although the membrane was cleaned, it may still contain some impurities that would affect the water permeability. The application of ultrasound can remove both the foulants as well as these impurities, thereby improving the flux recovery. The improvement of water flux by ultrasonic irradiation was also reported in other membrane processes [27].

The SEM images after the ultrasonic cleaning at 72 kHz were confirmed to examine the effect of ultrasonic intensity on foulant removal. As expected, no foulants were observed at 300 W, as shown in Fig. 13a. Compared with this, the foulants were not completely removed at 150 W (Fig. 13b) and
These results clearly indicate that the ultrasonic irradiation under appropriate conditions can effectively remove foulants from the MD membranes caused by inorganic salts and scales. It is important to note that the ultrasonic irradiation does not need any cleaning agents, such as acids and chelating chemicals; thus, being an eco-friendly method for MD membrane cleaning.

4. Conclusions

In this study, an ultrasonic cleaning method was applied to MD membranes fouled by inorganic scales during the treatment of high-TDS feed waters. The following conclusions were obtained:

- The ultrasonic irradiation at low frequencies (28 and 45 kHz) resulted in either structural damage or wetting of the MD membranes when the intensities were set to 150 and 300 W. No apparent damage was observed at 28 and 45 kHz when the intensity was set to 30 W. However, the LEP and the CA significantly reduced, indicating that wetting had occurred.

- On the other hand, the ultrasonic irradiation at a higher frequency (72 kHz) exhibited neither membrane damage nor wetting when the intensity ranged from 30 to 300 W.

- Compared with the physical and physical/chemical cleaning of the fouled MD membranes, the ultrasonic cleaning at 72 kHz resulted in a better efficiency. As the intensity decreased, the flux recovery and foulant removal efficiency decreased as well. This suggests that the ultrasonic irradiation demonstrated its potential as an eco-friendly method of cleaning MD membranes without the use of cleaning chemicals.

Acknowledgement

This work was supported by the Korea Agency for Infrastructure Technology Advancement (KAIA) grant funded by the Ministry of Land, Infrastructure, and Transport (Grant 18IFIP-B116951-03).

References


J. Wang, X. Gao, Y. Xu, Q. Wang, Y. Zhang, X. Wang, C. Gao, Ultrasonic-assisted acid cleaning of nanofiltration membranes fouled by inorganic scales in arsenic-rich brackish water, Desalination, 375 (2016) 172–177.


L. Wang, Q. Wang, Y. Li, H. Lin, Ultrasound-assisted chemical cleaning of polyvinylidene fluoride membrane fouled by lactic acid fermentation broth, Desalination, 326 (2013) 103–108.


