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Performance restoration of membranes degraded by fouling and wetting in membrane distillation

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Membrane distillation (MD) is a promising technology for desalination due to its ability to produce high-purity water using low-grade or waste energy. However, despite its potential, MD still faces challenges such as membrane fouling and wetting, necessitating continued research and development. In this study, restoration protocols were developed and evaluated at different stages of $CaSO_4$ – induced fouling and wetting in a lab-scale direct contact MD system. During the early stage of fouling, flushing with deionized water restored membrane performance without noticeable difficulty. However, when fouling progressed to the point immediately before a significant decline in distillate flux, complete recovery of both distillate flux and cumulative volume was achieved only through cleaning using high concentration of citric acid. At the stage of severe fouling and complete pore wetting, even strong acid cleaning was unable to fully restore membrane performance. In addition, when the fouling layer was allowed to dry prior to cleaning, the effectiveness of citric acid cleaning was substantially reduced, even when the cleaning was applied before the onset of severe fouling. These findings emphasize the importance of timely chemical cleaning before advanced fouling or membrane drying occurs in order to maintain stable long-term performance in MD operations.

Water impact

Membrane distillation is a promising technology for sustainable water production, but its practical application is often constrained by fouling and membrane wetting. This study demonstrates that timely chemical cleaning can effectively mitigate these limitations and restore membrane performance. The findings contribute to the development of more realistic operation and maintenance strategies for membrane distillation.

1. Introduction

Membrane distillation (MD) has emerged as a promising technology for desalination, wastewater treatment, and solvent recovery due to its high separation efficiency and low energy consumption.[1] Recent research has emphasized the importance of effective fouling management to improve the sustainability of the overall process.[2] MD operates based on a vapor pressure difference generated by a temperature gradient across hydrophobic membranes. Under this driving force, only water vapor is transported through membranes from the hot feed side to the cold distillate side, while liquid water is effectively rejected. This mechanism enables MD to achieve highly efficient separation of water from non-volatile contaminants including salts.[3–5]

However, membrane fouling, primarily caused by salt scaling on the membrane surface, can significantly reduce water flux and overall system efficiency. Scaling not only obstructs membrane pores, decreasing permeability, but also alters the membrane surface properties, making it more susceptible to wetting.[6,7] Membrane wetting results in the loss of the membrane hydrophobicity that ensures selective vapor transport. Therefore, once wetting occurs, liquid water containing dissolved salts can pass through the membrane pores, thereby increasing distillate salinity and compromising water quality. Previous studies have reported that certain inorganic compounds, such as calcium and magnesium salts, significantly promoted membrane wetting.[8,9] Membrane wetting has been demonstrated to degrade MD performance, necessitating frequent membrane module replacements and consequently escalating operational costs.[9,10] Therefore, the development of effective

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restoration protocols that address both membrane fouling and wetting is essential to prolong membrane lifespan and to decrease costs in MD applications.

Numerous studies have been conducted to address membrane fouling or wetting, with emphasis on the efficiency of physical and chemical mitigation strategies. Physical cleaning methods, such as flushing with distillate water, have been demonstrated to effectively restore membrane flux, particularly in treating produced water containing oil and surfactants. This approach avoids the complexities associated with chemical cleaning agents.[9] The utilization of chemical cleaning agents, such as ethylenediaminetetraacetic acid (EDTA), sodium hypochlorite (NaOCl), and citric acid has been extensively studied for removing biofilms and inorganic scaling. EDTA and NaOCl have demonstrated comparable effectiveness in flux recovery without inducing pore wetting.[11] Peng *et al.* investigated the effectiveness of acid-based cleaning agents, such as citric acid, in mitigating scaling during membrane distillation, demonstrating effective flux recovery after inorganic scale removal.[12,13] Chang *et al.* emphasized cleaning methodologies that effectively restore membrane hydrophobicity by removing low-surface-tension compounds and adsorbed layers that induce wetting.[14] Similarly, Yao *et al.* explored the application of membranes with engineered surface properties, such as superhydrophobic and omniphobic surfaces, to enhance resistance to wetting and improve flux stability under harsh saline conditions.[15] Guillen-Burrieza *et al.* investigated cleaning strategies at the plant scale, demonstrating that effective cleaning during intermittent operation significantly reduced wetting but inactive periods could exacerbate wetting issues.[16] Lim *et al.* provided evidence that the performance of wetted membranes could be effectively recovered through high-concentration citric acid treatment combined with pump circulation, resulting in near-complete restoration of their original hydrophobicity.[17]

Despite these advancements, most previous studies have treated fouling and wetting as separate phenomena. This leaves a knowledge gap regarding their simultaneous restoration. Therefore, further research that considers the interaction between fouling and wetting is essential for sustaining MD performance. Chen *et al.* provided a detailed understanding of surfactant-induced progressive wetting, offering mechanistic clarity on wetting initiation and transition states; however, inorganic scaling effects were not considered.[18] Liu *et al.* advanced the understanding of calcium sulfate scaling dynamics using optical coherence tomography, demonstrating how crystalline layers evolve on MD membranes, but this study did not address wetting behavior.[19] Amin *et al.* investigated biofilm development and cleaning strategies, showing how organic fouling influences MD operation, but wetting was not the focus of their analysis.[11] Additional studies have explored inorganic scaling mechanisms. Specifically, the scaling behavior involving $CaCO_3$ and $CaSO_4$ has been characterized in seawater and brine systems, with a predominant focus on fouling rather than its association with wetting progression.[20] Although a recent study on cleaning strategies has yielded valuable insights into MD performance recovery after mineral scaling, this investigation has predominantly focused on scale removal rather than the comprehensive restoration of both fouling and wetting.[21] Comprehensive reviews of MD fouling highlight the distinct roles of inorganic fouling, organic fouling, biofouling, and wetting, implying that these mechanisms have generally been studied largely independently.[22] Collectively, these contributions establish a strong foundation for understanding individual fouling and wetting mechanisms in MD. Nevertheless, the interactions between these processes and their subsequent impact on membrane restoration remain insufficiently explored.

In this study, restoration protocols were systematically applied and evaluated at three distinct stages of membrane fouling and wetting in a lab-scale direct contact membrane distillation (DCMD) system using feed solutions containing $CaSO_4$. The stages were defined as follows: (I) nucleation of $CaSO_4$ crystals, (II) partial wetting immediately before total loss of water vapor transport, and (III) complete wetting and the total loss of water vapor transport. These stages were selected to investigate critical points of membrane performance deterioration associated with membrane fouling and wetting and to assess membrane restoration effectiveness through the application of restoration protocols using citric acid at the end of each stage. Two different concentrations of citric acid cleaning solutions were employed to evaluate their effectiveness in restoring membrane performance. In addition, the effectiveness of membrane restoration when fouling layers were allowed to dry prior to cleaning was investigated. To characterize membrane fouling and wetting behaviors, distillate flux and conductivity were continuously monitored during MD operations. Furthermore, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) was used to analyze the morphology and chemical composition of fouling deposits. Liquid entry pressure (LEP) analysis was also performed to quantitatively assess changes in membrane wettability following wetting and subsequent restoration.

2. Materials and methods

2.1 Chemicals and membrane

The feed solutions were prepared using calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, >98.0%, Samchun Chemicals, Seoul, Republic of Korea), sodium chloride (NaCl, >99.0%, Samchun Chemicals), sodium bicarbonate ($NaHCO_3$, >99.5%, Duksan Pure Chemicals, Ansan, Republic of Korea), and sodium dodecyl sulfate (SDS, $CH_3\ (CH_2)_{11}OSO_3Na$, 10% solution, Sigma-Aldrich, St. Louis, MO, USA). A 1N sodium hydroxide (NaOH) solution (Samchun Chemicals) was utilized for pH adjustment. Citric acid anhydrous ($C_6H_8O_7$, >99.5%, Samchun Chemicals) was used to prepare membrane cleaning solutions. MD experiments were carried out using flat-sheet membranes of polyvinylidene fluoride (PVDF), a hydrophobic material, with a nominal pore size of 0.22 μm (GVHP 14250 Durapore®, MilliporeSigma, Burlington, MA, USA).

2.2 Operation of a lab-scale MD system

The feed was prepared with 2000 ppm $CaSO_4$ as the principal foulant, while 50 000 ppm NaCl, 200 ppm $NaHCO_3$ (used as a buffer), and 5 ppm SDS were added as background components in deionized (DI) water. The initial pH was adjusted to 8 using a NaOH solution. $CaSO_4$ was selected to represent inorganic scaling, one of the most frequently reported foulants in desalination-related MD applications, and its rapid flux declining behavior facilitated clear identification of fouling stages. The same concentration of SDS was added into all feed solutions to intentionally accelerate membrane wetting by lowering surface tension, thereby enabling observation of coupled fouling and wetting behavior within practical experimental timescales, as naturally induced wetting in seawater progresses very slowly.[23,24] Although the fouling–wetting stages defined under $CaSO_4$-dominant conditions with SDS-assisted wetting are specific to this study, the proposed stage-based framework may be broadly applicable for interpreting progressive fouling and wetting behavior in other MD systems.

Although $CaSO_4$ was employed as the principal scaling species in this study, the presence of carbonate alkalinity (200 ppm $NaHCO_3$ at pH 8) also provides the potential for some $CaCO_3$ formation. Calcium carbonate has been widely reported as a common and early forming inorganic scale in thermal desalination and MD processes, largely due to its strong dependence on pH and temperature.[22] However, because sulfate was present at concentrations approximately six to seven times higher than bicarbonate on a molar basis, $CaCO_3$ precipitation was expected to exert a significantly lesser influence than $CaSO_4$ under the experimental conditions. Consequently, $CaSO_4$ remained the predominant fouling species in the examined MD system.

A lab-scale direct contact membrane distillation (DCMD) system, as illustrated in Fig. 1, was employed to conduct the MD experiments. The system was equipped with a membrane module with an effective membrane surface area of 12 cm^2. A feed reservoir was placed on a hot plate for temperature control, while a distillate reservoir containing cool DI water was positioned on an electronic balance to monitor the increase in distillate mass. The distillate temperature was controlled by a heat exchanger connected to a chiller. The temperatures of the feed and distillate streams entering the module were maintained at 60 °C and 20 °C, respectively, and monitored using temperature sensors. A gear pump (WT3000-1JA, Longer Precision Pump Co. Ltd., Bury St Edmunds, UK) was used to circulate the feed and distillate in a counter-current flow configuration, with volumetric flow rates set to 1.0 and 0.7 L min^{-1}, respectively. Distillate conductivity was measured continuously using a conductivity meter (BC3020, Trans Instruments, Singapore).

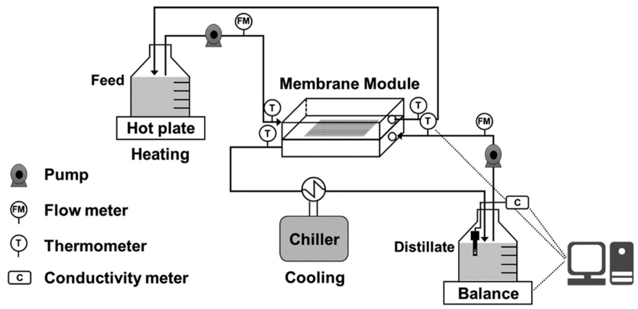

Fig. 1 Schematic diagram of the laboratory-scale MD system.

In this study, each membrane was subject to two filtration operations, the first designed to induce fouling and/or wetting and the second performed after the application of restoration protocols, to evaluate the extent of performance recovery. For the first filtration operation, the termination criteria for each stage were defined as follows: stage I was terminated when the volume concentration factor (VCF) increased by 10% relative to its initial value, and stage II was terminated immediately prior to the total loss of water vapor transport, as indicated by a noticeable decline in distillate flux and a simultaneous increase in conductivity. For stage III, experiments were terminated either upon the total loss of water vapor transport due to membrane fouling or when the distillate conductivity reached 500 μS cm^{-1} as a result of membrane wetting. For all the second filtration operations conducted after the application of restoration protocols, the same termination criteria as those used for stage III were applied to enable comparison of each distillate flux and conductivity following restoration at stages I, II, and III. The distillate flux, expressed in LMH (═L m^{-2} h^{-1}), was calculated by dividing the distillate volume – converted from the measured distillate mass – by the effective membrane surface area and the operation time.

2.3 Restoration of membrane performance

Following the first filtration operation that induced membrane fouling, the membrane was cleaned by circulating a cleaning solution through the module using a pump, as illustrated in Fig. S1. Citric acid was selected as the cleaning agent due to its well-established efficiency in removing inorganic scaling, particularly calcium-based fouling, without causing considerable damage to the membrane structure.[1] The circulation flow rate during the cleaning process was set to 0.8 L min^{-1}, corresponding to 0.47 m s^{-1}.

To evaluate the degree of membrane performance restoration at each stage of fouling and wetting, three different restoration protocols were systematically applied. Protocol A consisted of flushing with DI water for 5 min and served as a control. Protocols B and C employed citric acid solutions at concentrations of 200 and 2000 ppm (pH 3.6 and 2.9, respectively) for 1 h, followed by DI water flushing for 5 min. These concentrations were chosen to evaluate the effect of acid strength on the efficiency of fouling removal and the extent of membrane performance restoration. For all three protocols, the final step was post-drying the membrane at room temperature for 24 h to induce membrane dewetting for hydrophobicity restoration, corresponding to the recovery of MD vapor selectivity after cleaning through the removal of inorganic salt deposits from the membrane surface and internal structure. This step also ensured consistent conditions prior to the second filtration operation to evaluate performance restoration.

To evaluate the impact of pre-drying on membrane restoration efficiency, membranes operated up to stage II were allowed to dry for more than 2 d, after which protocols B and C were applied. It should be noted that this pre-drying step simulates unintended membrane drying before cleaning during practical MD operation and is different from the 24 h post-drying step used for dewetting after cleaning.

2.4 Analytical methods

The surface morphology and elemental composition of the fouling layers formed on the membrane surface were analyzed using a SEM–EDX (JSM-7001F, Jeol Ltd., Tokyo, Japan). The LEP of the membranes was measured using a custom-built device by gradually increasing nitrogen gas pressure until the first droplet of DI water penetrated the membrane, which was taken as an indication of membrane wetting after operation.[8]

To quantify the concentration of foulants on the membrane surface, the cleaning solution used in section 2.3, containing the dissolved foulants, was analyzed using ion chromatography (IC, ICS5000+, ThermoScientific, Waltham, MA, USA) and inductively coupled plasma spectroscopy (ICP, 5110, Agilent, Santa Clara, CA, USA).

3. Results and discussion

3.1 Membrane fouling and wetting by $CaSO_4$

The lab-scale DCMD system was operated using a feed solution containing 2000 ppm of $CaSO_4$. The results of the MD operation are presented in terms of the distillate flux and conductivity as functions of the cumulative distillate volume, as shown in Fig. 2. The distillate flux gradually decreased due to membrane fouling, while the conductivity remained almost constant until the cumulative distillate volume reached approximately 1.5 L. However, beyond this point, a sharp decrease in distillate flux and a steep increase in conductivity were observed, indicating severe membrane fouling and wetting, respectively. When the concentration of $CaSO_4$ in the feed solution exceeds its solubility limit, excess $CaSO_4$ precipitates as solid crystals on the membrane surface, which can obstruct vapor transport either by forming a scaling layer on the membrane surface or by blocking the membrane pores. $CaSO_4$ scaling has been shown to occur through both homogeneous and heterogeneous nucleation mechanisms.[25] These scaling phenomena ultimately lead to a substantial reduction in both distillate flux and salt rejection performance.[7,26]

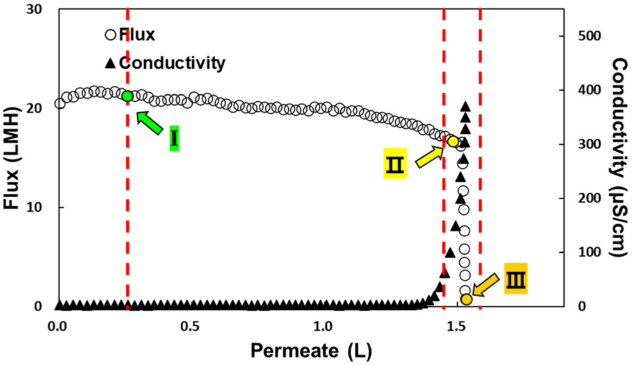

Fig. 2 Three stages of membrane fouling and wetting induced by $CaSO_4$; stage I, nucleation of $CaSO_4$ crystals; stage II, partial wetting immediately before total loss of water vapor transport; stage III, complete pore wetting and total loss of water vapor transport.

To quantitatively represent the extent to which the feed solution was concentrated during the MD process, the VCF was calculated. It is defined as the ratio of the initial feed volume to the remaining feed volume after distillate extraction and widely used as an indicator of the increasing risk of membrane fouling, as higher concentrations of solutes promote crystallization and scaling on membrane surfaces.[27,28] It was calculated using the following equation:

$$\mathrm{VCF} = \frac{\text{Initial feed volume}}{\text{Initial feed volume} - \text{Distillate volume}}$$

The cleaning effectiveness of three different protocols was compared at three stages of $CaSO_4$-induced membrane fouling as shown in Fig. 2. In the initial stage (stage I; VCF = 1.1), the onset of $CaSO_4$ crystal nucleation may occur. At this point, however, no notable change in distillate flux was observed, and the conductivity remained nearly constant (below 10 μS cm^{-1}), indicating that membrane wetting was negligible and overall membrane performance was well maintained.

As filtration progressed to stage II (partial wetting immediately before the total loss of water vapor transport; VCF = 3.9), the flux declined by approximately 20% relative to the initial flux. This finding suggests that vapor transport through membrane pores was significantly diminished, most likely due to substantial crystal growth within or on the membrane surface. Furthermore, a notable increase in distillate conductivity was observed at this stage, reaching approximately 100 μS cm^{-1}. This phenomenon indicates the onset of partial membrane wetting, as evidenced by the penetration of feed water into the membrane pores, resulting in a substantial deterioration in membrane performance. SEM images showed clear visual differences between stages I and II (Fig. S2). At stage I (Fig. S2(a)), only small and sparsely distributed $CaSO_4$ particles were observed, indicating an early nucleation stage. In stage II (Fig. S2(b)), the particles became noticeably larger and formed dense clusters, resulting in extensive coverage of the membrane surface and indicating clear progression of scaling. These morphological changes demonstrate that stage II corresponds to a more advanced fouling state than stage I, even prior to pronounced changes in distillate flux or conductivity.

At stage III (complete pore wetting and total loss of water vapor transport and; VCF = 4.3), vapor transport through the membrane ceased entirely. This phenomenon was evidenced by a reduction in flux of more than 96% compared to the initial value. In addition, a sharp and substantial increase in conductivity, reaching nearly 400 μS cm^{-1}, was observed. These findings suggest that the membrane was almost completely covered by a $CaSO_4$ scaling layer and that complete pore wetting had occurred, indicating severe membrane failure that required immediate and intensive cleaning or membrane replacement.[29–31] The reproducibility and consistency of the observed flux and conductivity trends were confirmed through a duplicate experiment, as shown in Fig. S3.

3.2 Efficiency of restoration protocols: flux and conductivity

After applying three different restoration protocols to the membranes for which (the first) MD operations had ceased at stages I–III, subsequent (the second) MD operations were conducted to assess their restoration effectiveness, and the results are presented in Fig. 3. The three protocols were as follows: (A) DI water flushing followed by dewetting through post-drying, (B) 200 ppm citric acid cleaning followed by dewetting through post-drying, and (C) 2000 ppm citric acid cleaning followed by dewetting through post-drying. These protocols were applied at each fouling and wetting stage depicted in Fig. 2. For comparison, Fig. S4 shows the first MD operations with pristine membranes up to each stage (stages I, II, and III), representing the baseline membrane performance prior to restoration. At stage I, the first MD operation exhibited negligible fouling (Fig. S4(a)), as indicated by the absence of any observable changes in distillate flux or conductivity. After applying the three restoration protocols at this stage (Fig. 3, left panel), the initial flux values were fully recovered to approximately 20 LMH, exhibiting a close match with that of the pristine membrane, irrespective of the utilized protocols. An increase in conductivity occurred at approximately 1.5 L of distillate volume, which is similar to the behavior observed with the pristine membrane. The final VCF values after restoration were comparable to that of the pristine membrane (VCF = 4.3), reaching 4.0 for protocol A, 4.1 for protocol B, and 4.2 for protocol C. These results indicate that simple DI water flushing followed by drying was sufficient to restore membrane performance at stage I, with no significant additional benefit observed from citric acid cleaning.

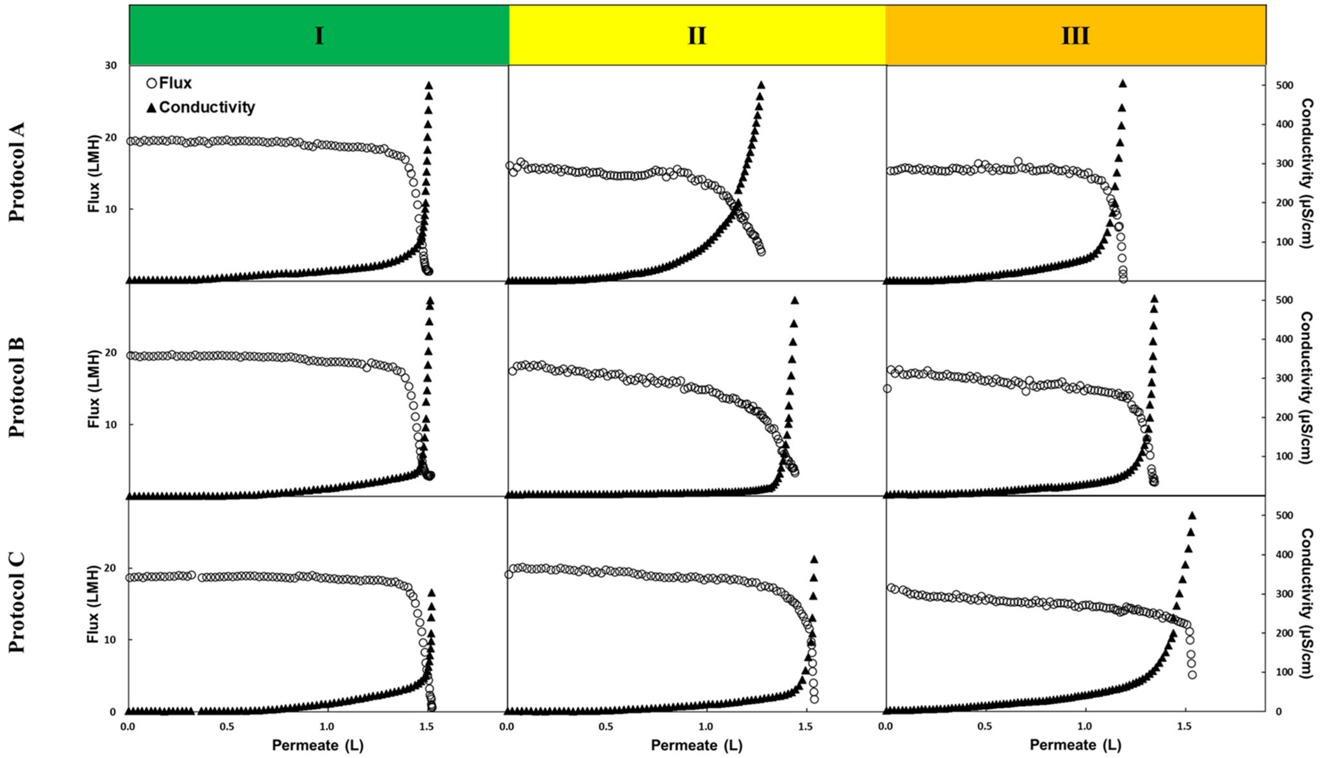

Fig. 3 Distillate flux and conductivity during the second MD operations after applying protocols A, B, and C to three different stages of fouling and wetting.

At stage II, the first MD operation exhibited clear signs of fouling and partial wetting (Fig. S4(b)), as evidenced by a noticeable decline in flux and an increase in conductivity compared to stage I. Following the application of the restoration protocols at this stage (Fig. 3, middle panel), the recovered initial flux values were approximately 16, 17, and 20 LMH for protocols A, B, and C, respectively. The corresponding distillate volumes at the end of the subsequent operations were approximately 1.3, 1.4, and 1.5 L for protocols A, B, and C, respectively. The final VCF values clearly reflected the relative effectiveness of each protocol; protocol A yielded a VCF of 2.7, protocol B attained a VCF of 3.5, and protocol C achieved a VCF of 4.3. In comparison with the pristine membrane performance (initial flux = 20 LMH, and distillate volume = 1.5 L), protocols A and B did not fully restore membrane performance. Only protocol C was successful in restoring both flux and distillate production to levels comparable to those of the pristine membrane. This result quantitatively demonstrates that a higher citric acid concentration is required for complete restoration at stage II.

At stage III, the MD operation exhibited severe membrane fouling and complete pore wetting (Fig. S4(c)), characterized by extremely low flux and a rapid increase in conductivity compared to earlier stages. At this stage, the implementation of the restoration protocols (Fig. 3, right panel), resulted in the partial recovery of the initial flux. The recovered values ranged from approximately 15 LMH for protocol A to around 17 LMH for protocols B and C. The final distillate volumes were approximately 1.2, 1.4, and 1.5 L for protocols A, B, and C, respectively. In comparison with the pristine membrane, none of the protocols fully restored the initial flux, although protocol C restored distillate volume to a level comparable to that of the pristine membrane. The final VCF values were significantly lower for protocols A and B (2.5 and 3.1, respectively), clearly indicating their limited restoration effectiveness. In contrast, protocol C achieved a VCF of 4.3, closely matching the pristine level despite incomplete flux recovery. Fig. S5 provides additional data on flux and conductivity as a function of VCF for all of the restoration protocols.

Fig. 4 summarizes the initial flux and cumulative distillate volume following the application of the restoration protocols A, B, and C based on the results shown in Fig. 3. At stage I, all three protocols successfully restored membrane performance to pristine levels, achieving an initial flux of approximately 20 LMH and a distillate volume of around 1.5 L. In contrast, at stage II, where fouling and partial wetting had progressed to the point immediately before the total loss of vapor transport, protocols A and B failed to fully restore performance. Only protocol C effectively restored both water flux and cumulative distillate volume to levels comparable to those of the pristine membrane. At stage III, none of the protocols were capable of fully restoring the initial flux. These findings clearly demonstrate that at the advanced fouling and complete wetting stage, even intensive cleaning with high-concentration citric acid is insufficient to fully restore the membrane flux, emphasizing the challenges associated with membrane restoration under such conditions. The rapid increase in conductivity observed during the second MD operations is attributed to residual salts remaining on the membrane surface as a result of incomplete cleaning. Even small amounts of residual scaling can further accelerate wetting by enabling heterogeneous salt nucleation within membrane pores, ultimately degrading membrane performance.[32–35] Therefore, the residual salts remaining after incomplete restoration may promote liquid penetration into membrane pores once MD operation resumes, leading to a pronounced increase in distillate conductivity.

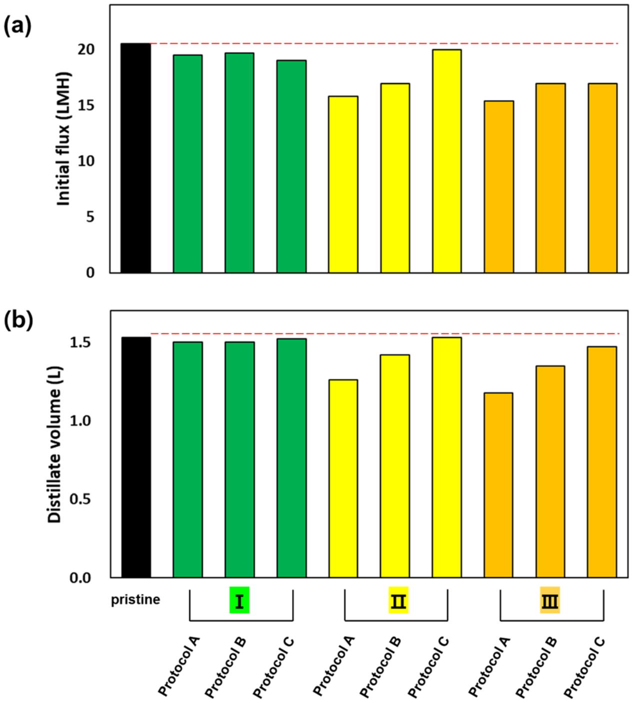

Fig. 4 Comparison of (a) initial flux and (b) distillate volume between the pristine membrane and membranes restored using protocols A, B and C at three different stages of fouling and wetting.

3.3 Efficiency of restoration protocols: LEP and SEM-EDX

A series of photographic images and LEP values of membranes following the application of the three restoration protocols at three fouling and wetting stages are presented in Fig. 5. The extent of scaling on the membrane surface progressively increased from stage I to stage III. At stage III, severe surface scaling was clearly visible, indicating that protocol A was unable to effectively remove the scale. In contrast, protocols B and C showed clearer and more effective removal of surface scaling.

The LEP of the membranes decreased from 160 kPa at stage I to 62 kPa at stage II, and further to 54 kPa at stage III, prior to restoration. After applying the restoration protocols,

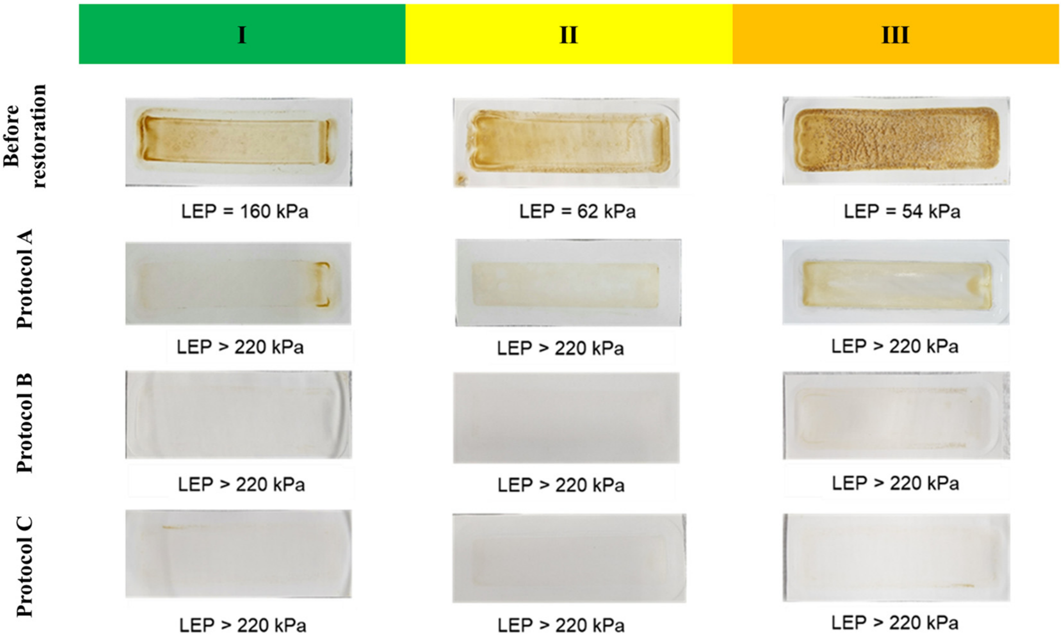

Fig. 5 Photographs of the membranes and LEP values for restoration protocols applied at three different stages of fouling and wetting.

the LEP values recovered to levels comparable to that of the pristine membrane, reaching 220 kPa. It should be noted that the LEP measurement device used in this study had an upper measurement limit of 220 kPa. Despite the apparent full recovery of LEP to this maximum measurable level, Fig. 4 and 5 demonstrate that membrane performance was not completely restored, suggesting that LEP alone does not entirely represent membrane wettability or fouling status. Membrane wetting is governed by complex physical and chemical mechanisms, whereas LEP primarily reflects the minimum pressure required for water penetration based on surface hydrophobicity and pore structure. Previous studies have also reported that LEP alone cannot fully describe membrane wetting behavior or functional performance, as wetting is governed by multiple factors beyond capillary entry pressure.[36]

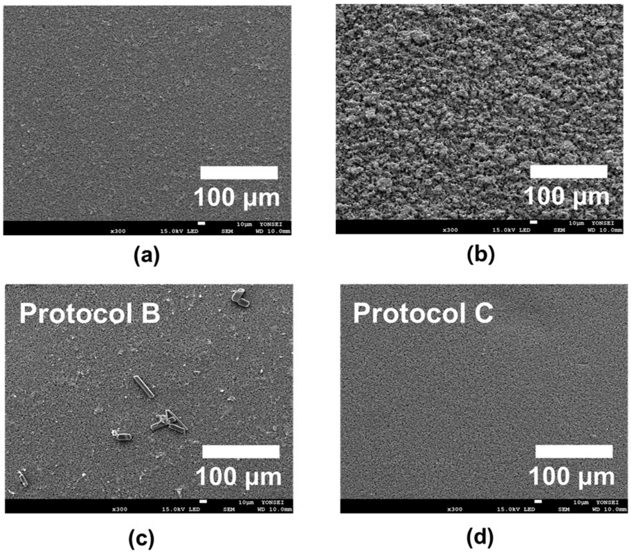

Fig. 6 SEM images of (a) the pristine membrane, (b) the fouled membrane without the application of any restoration protocol, and (c) and (d) membranes fouled and subsequently restored using protocols B and C, respectively. All fouled membrane samples were collected at stage III.

To further investigate the incomplete performance restoration observed in Fig. 3 and 4, SEM-EDX analyses were performed. Fig. 6 shows SEM images of (a) the pristine membrane, (b) the fouled membrane without restoration, and (c) and (d) membranes restored using protocols B and C, respectively. All fouled membrane samples were collected at stage III. The SEM images revealed the presence of significant residual foulants even after protocol B, with distinct crystal deposits remaining on the membrane surface (Fig. 6(c)). In contrast, protocol C effectively removed all observable surface contaminants (Fig. 6(d)). These observations correlate well with distillate flux and conductivity trends shown in Fig. 3, in which protocol C exhibited superior restoration performance.

The observed difference in effectiveness between protocols B and C is primarily attributed to the chemical interactions between citric acid and calcium-based fouling layers. Citric acid functions as a chelating agent for Ca^{2+}, thereby facilitating the dissolution of $CaSO_4$ scaling. At lower concentrations (200 ppm), its chelating capacity is insufficient to completely remove robust crystalline structures, resulting in residual scaling. This residual scaling subsequently accelerates membrane wetting and leads to increased distillate conductivity during operation (Fig. 3). Conversely, the higher concentration of citric acid (2000 ppm) significantly enhances this chelation process,

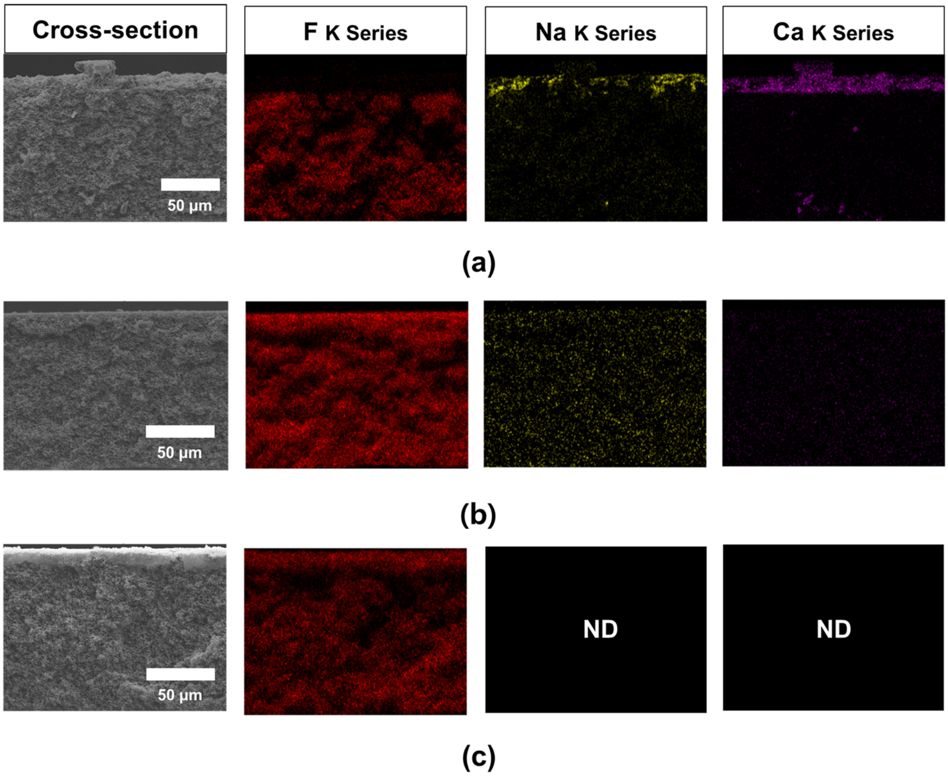

Fig. 7 SEM-EDX data of fouled membranes (a) without the application of any restoration protocol, (b) restored using protocol B, and (c) restored using protocol C. All fouled membrane samples were collected at stage III.

enabling more thorough dissolution and removal of scaling.[37,38] Recent studies on advanced chemical cleaning further support these findings, demonstrating that higher citric acid concentrations significantly enhance scaling removal efficiency through improved chemical interactions and deeper penetration into fouling layers.[25]

This explanation is further supported by SEM-EDX cross-sectional analyses depicted in Fig. 7. The results of protocol B indicated the presence of residual Na, Ca, and Cl within the membrane cross-section, suggesting that the internal cleaning was incomplete (Fig. 7(b)). In contrast, protocol C exhibited no detectable residual salts within the membrane cross-section, indicating thorough internal cleaning facilitated by effective penetration of highly concentrated citric acid into wetted membrane areas (Fig. 7(c)). Additionally, Fig. S6 (SI) illustrates that at stage III even minor residual scaling resulting from incomplete cleaning can substantially deteriorate membrane performance by promoting rapid membrane wetting and increasing distillate conductivity. This finding highlights the necessity for more intensive cleaning strategies under conditions of severe membrane fouling.

3.4 Effect of drying prior to restoration protocol

During practical operation, fouling layers may dry when an MD membrane module is removed from operation and left idle for a period of time prior to cleaning. Under such conditions, the drying of the fouling layer may adversely influence the efficiency of membrane cleaning. To evaluate the impact of drying prior to membrane restoration on the efficiency of the restoration protocols, performance evaluations were conducted after the operation of the system up to stage II, followed by a deliberate membrane-drying step and subsequent application of protocols B and C.

Fig. 8 presents the distillate flux and conductivity during MD operations after the application of a pre-drying step and subsequent implementation of protocol B or C. For protocol B with pre-drying, the initial flux and the distillate volume were approximately 16 LMH and 1.2 L, respectively (Fig. 8(a)). To facilitate a clear comparison with the results shown in Fig. 3, the initial flux and distillate volume of the membranes restored under protocols B and C, both with and without a pre-drying prior to cleaning, are summarized in Fig. 9. Without pre-drying, the initial flux and the distillate volume after the application of protocol B were approximately 17 LMH and 1.4 L, respectively. A comparison of the results obtained with and without pre-drying demonstrates that membrane drying prior to restoration has a detrimental effect on restoration performance. This effect was more pronounced for protocol C: the initial flux decreased substantially from approximately 20 LMH without pre-drying to 15 LMH with pre-drying. The distillate volume for protocol C accordingly decreased from 1.5 L without pre-drying to 1.2 L with pre-drying. Consequently, the final VCF values following the pre-drying step were notably lower (2.6 for

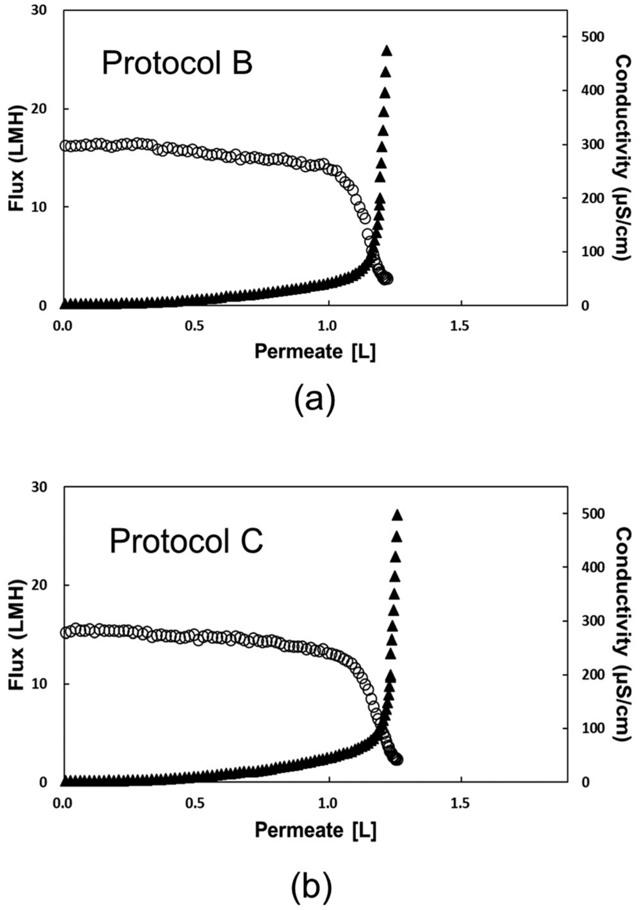

Fig. 8 Distillate flux and conductivity during the second MD operations after applying (a) protocol B and (b) protocol C to membranes fouled to stage II, with pre-drying.

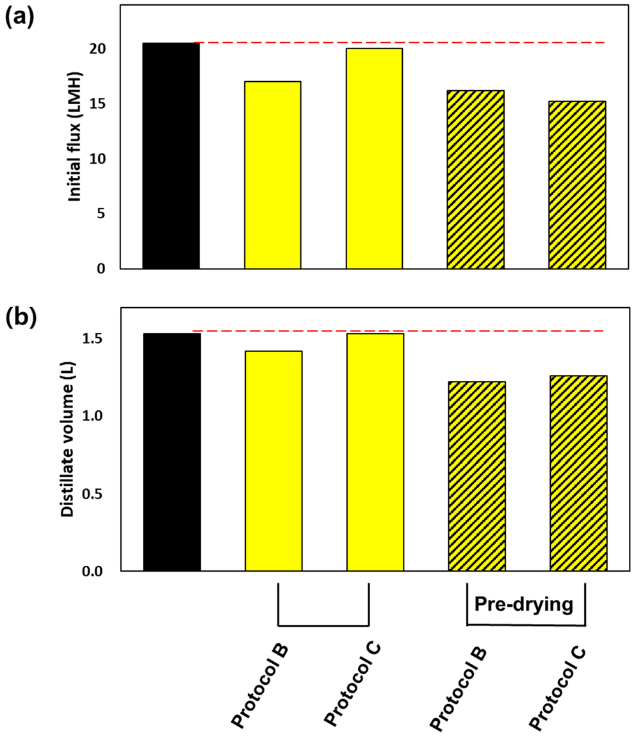

Fig. 9 Comparison of (a) initial flux and (b) distillate volume between the pristine membrane and membranes restored using protocols B and C, with and without the pre-drying step. All fouled membrane samples were collected at stage II.

protocol B and 2.7 for protocol C) than those obtained without pre-drying (3.5 for protocol B and 4.3 for protocol C). These findings indicate that membrane restoration efficiency is reduced when membrane drying occurs prior to the restoration procedure. Notably, without pre-drying, protocol C nearly restored membrane performance to that of the pristine membrane. In contrast, when the fouling layer was allowed to dry before restoration, even protocol C failed to fully restore the original membrane performance, as evidenced by the lower initial flux and distillate volume.

As depicted in Fig. 10, the SEM images of membranes operated up to stage II show membrane surfaces restored (a) without and (b) with pre-drying. The images indicate that pre-drying the membrane before restoration led to a greater extent of the fouling coverage on the membrane surface. Although high-concentration citric acid (protocol C) might remove more foulants than protocol B, drying before cleaning still reduced the overall removal efficiency and consequently limited the extent of performance restoration. These observations strongly suggest that drying enhances the adhesion of fouling layers, thereby reducing the effectiveness of subsequent restoration protocols. Table 1 summarizes the Na and Cl concentrations measured in the cleaning solutions for restoration protocols applied with and without a pre-drying step. The slightly lower ionic concentrations observed after pre-drying indicate that fewer salts were removed during cleaning following pre-drying. Consistent with these findings,

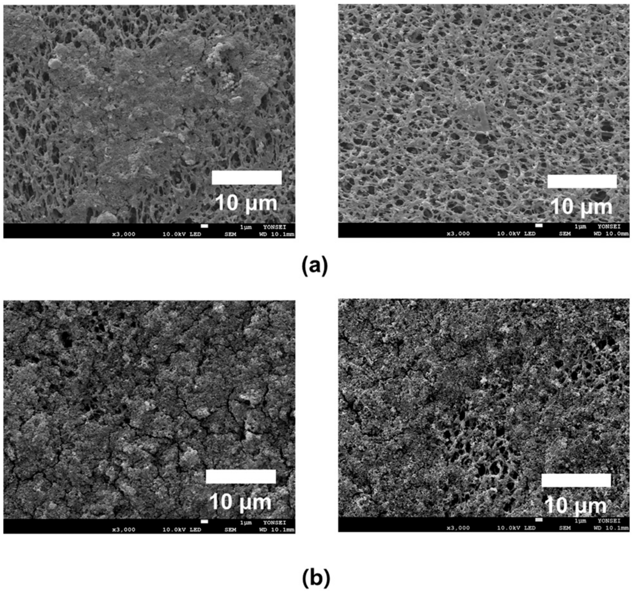

Fig. 10 SEM images of membranes restored using protocol B (left) and protocol C (right) (a) without and (b) with pre-drying. All fouled membrane samples were collected at stage II.

Table 1 Concentrations of Na^+ and Cl^- removed during protocols B and C, comparing restoration with and without a pre-drying step

	Restoration protocols	Concentration [mg cm^{-2}] Na	Cl
w/o pre-drying	B	0.29	0.51
	C	0.49	0.73
w/Pre-drying	B	0.27	0.47
	C	0.41	0.72

previous studies have reported that drying of salt deposits during intermittent MD operation can aggravate fouling and wetting by altering membrane surface properties and consolidating inorganic scales on the membrane surface.[10] In addition, $CaSO_4$ is known to undergo dehydration-induced phase and structural changes under dry conditions (*e.g.*, gypsum to bassanite/anhydrite), which may modify crystal morphology and compactness.[39] Such changes could potentially hinder the accessibility of chelating agents to reactive sites on the scale surface. Under such conditions, fouling layers dried on the membrane surface exhibit stronger adhesion and increased crystallization of foulants, significantly reducing cleaning effectiveness due to the diminished solubility and reactivity of the fouling components.[16,40,41]

These findings emphasize the importance of timely cleaning during MD operations. In particular, delaying cleaning after reaching stage II and allowing the fouling layers to dry significantly reduces the effectiveness of even intensive chemical cleaning with 2000 ppm citric acid, thereby preventing full restoration of membrane performance. Therefore, the immediate and proactive application of restoration protocols at intermediate fouling stages is crucial for maintaining optimal membrane performance.

In the present study, the influence of organic matter on membrane fouling and wetting was not investigated. However, in practical seawater systems, organic matter commonly coexists with inorganic scalants and can interact with mineral scales to form coupled organic–inorganic fouling layers. Such interactions may further modify fouling structure and adhesion properties, potentially reducing the effectiveness of restoration protocols compared to the $CaSO_4$-dominant system examined in this study.[42,43] A more detailed investigation of restoration strategies under coupled organic–inorganic fouling conditions will be addressed in future work.

4. Conclusion

This study evaluated the effectiveness of three membrane restoration protocols in recovering the performance of membranes fouled and wetted by $CaSO_4$ in a DCMD system. The results demonstrated that simple DI water flushing was effective during the early stage of fouling and wetting (stage I), but its effectiveness diminished substantially as fouling and wetting progressed. Under intermediate fouling and partial wetting conditions (stage II), only high-concentration citric acid cleaning (2000 ppm) restored membrane performance to levels comparable to that of a pristine membrane, whereas lower-concentration citric acid (200 ppm) exhibited limited recovery. At severe fouling and complete wetting conditions (stage III), even high-concentration citric acid failed to fully restore performance. From an operational perspective, although the use of high-concentration citric acid increases chemical consumption, effective restoration at fouling stage II can extend membrane service life and reduce the frequency of membrane replacement. This trade-off suggests that preventive chemical cleaning at appropriate fouling stages may be operationally favorable in long-term MD operation, despite the higher short-term chemical cost.

Furthermore, this study demonstrated that allowing the fouling layer to dry prior to restoration significantly reduced cleaning effectiveness. These findings underscore that timely intervention to prevent fouling-layer drying is crucial for maintaining the effectiveness of chemical cleaning and minimizing resistance to foulant removal.

Overall, the results provide practical insights into optimizing cleaning strategies for MD operations. In practical MD operation, cleaning decisions should be guided by operational indicators such as sudden increases in distillate conductivity or sharp changes in distillate flux decline trends over time. Timely and proactive restoration before such sudden increases in conductivity or severe decreases in flux plays a critical role in enhancing membrane longevity and operational efficiency, ultimately contributing to the long-term sustainability of membrane distillation processes.

Author contributions

Joowan Lim: methodology, data curation, investigation, visualization, and writing – original draft. Seung Mo Kang: data curation and investigation. Chanyoung Kim: data curation and formal analysis. Dowon Chae: methodology and validation. Hosung Lee: formal analysis and visualization. Sangho Lee: project administration and funding acquisition. June-Seok Choi: methodology and funding acquisition. Pyung-Kyu Park: supervision, conceptualization, resources, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

All experimental data supporting the findings of this study have been fully presented in the manuscript and its supplementary information (SI). Additional information can be provided from the authors upon reasonable request.

Supplementary information is available. See DOI: https://doi.org/10.1039/d6ew00053c.

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