

Application of Seeded Membrane Distillation Crystallization for Zero Liquid Discharge

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Zero liquid discharge (ZLD) is a crucial requirement in industrial operations concerned with water scarcity and environmental protection. This study investigates the feasibility of using membrane distillation combined with crystallization (MDC) as a potential solution for ZLD. High-saline NaCl solutions were used to evaluate the performance of a seeded MDC system, which demonstrated excellent recovery rates for both water (over 95 %) and salt (over 95.5 %). The presence of seeding crystals in the MDC system was found to inhibit membrane wetting. The MDC system achieved an average thermal efficiency of 61.5 %, showcasing its potential for long-term processes. These results indicate that introducing seed crystals to the membrane's feed side enhances the MDC system's viability as a promising solution for ZLD. Additionally, the MDC system offers the prospect of high water and salt recovery, making it a sustainable approach to wastewater treatment and water reclamation.

Keywords: Desalination, Membrane distillation crystallization, Wastewater, Zero liquid discharge

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1 Introduction

Water scarcity is an increasingly urgent global issue due to population growth and industrial development, which also leads to a drinking water shortage. With the world's population exceeding eight billion human beings, over one billion people face severe water shortages each year, while 2.3 billion experience such shortages at least once a month. Consequently, the production of drinking water has become very important. Insufficient tap water availability is particularly problematic in arid regions and certain parts of Europe [1–5]. Concerns over water scarcity gained significant attention in the 1980s [6]. Water scarcity is exacerbated by the discharge of untreated or poorly treated industrial wastewater, which contributes to the depletion of limited water resources; therefore, the use of tap water in industries, along with the resulting wastewater, presents a significant challenge [7]. The establishment of water recycling plants for industrial use has been initiated to address these issues, driven by future concerns. The European Union's chemical strategy for sustainability, which aims to create a toxic-free environment, emphasizes the need for further purification of municipal and industrial wastewater. Moreover, rising wastewater costs [7, 8] highlight the necessity for enhanced and integrated processes.

Desalination serves as a crucial source of drinking and industrial water in arid regions and coastal cities [5, 9]. However, desalination processes generate a significant

amount of rejected brine, which requires effective management methods [10]. One such method is zero liquid discharge (ZLD), a process that enables the recovery of large amounts of water from rejected brine, reducing environmental impact and promoting sustainability [7, 10, 11]. Early ZLD processes, developed in the 1970s for high-saline water in power generation, primarily relied on thermal-based technologies such as brine concentrators, crystallizers, spray dryers, and solar ponds [7, 12, 13]. However, thermal evaporation is often economically impractical, even when using [14–16] green energy sources like solar evaporation [17, 18] and wind-aided intensified evaporation. Evaporation ponds, while cost-effective, require large land areas and are associated with the risk of wastewater leakage into groundwater, posing severe environmental consequences [10, 13, 19]. Scaling on evaporator surfaces during the evaporation process is another expensive challenge to address,

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often requiring the use of expensive corrosion-resistant metals like stainless steel or alloys [10]. Consequently, membrane-based ZLD processes have emerged as an alternative approach to achieving ZLD [20–22].

In recent decades, the focus on achieving zero wastewater production has intensified, driven by concerns about rising wastewater costs. Various measures have been implemented, including stricter limits for chemicals and substances in wastewater. Environmental regulations and policies aim to prevent wastewater pollution and protect public health. Accomplishing the recovery and reuse of phosphorus from wastewater streams has been adopted [23]. ZLD technology is commonly used as a closed water circuit, minimizing water discharge into the environment [24, 25]. Given the high salt concentration and brine generated, ZLDs find application in membrane water desalination [12]. Membrane distillation (MD), an innovative membrane-based process capable of handling highly saline solutions, is particularly suitable for water production [26, 27].

Membrane distillation crystallization (MDC) comprises two distinct processes. The first process is MD, which operates on the principle of thermal driving force. It utilizes hydrophobic polymer membranes, such as polypropylene (PP), polyvinylidene fluoride (PVDF), or polytetrafluoroethylene (PTFE), to prevent wetting of the membrane pores and enable low-pressure and low-temperature operations [29]. However, membrane scaling [28–30] and fouling [31–33] remain significant challenges for membrane-based technologies [20]. MDC, as an advanced application of MD, offers several advantages, including the removal of solvents from saturated solutions and the production of crystals [34]. It allows for controlled nucleation and growth kinetics, faster crystallization rates, and shorter induction times [35]. It is worth noting that excessive concentrations in the brine can adversely affect the MD process, leading to membrane contamination and scaling [32]. Previous MDC processes involved a separate crystallization stage, requiring additional energy for evaporation or cooling of the solution. In contrast, membrane-based crystallization on the membrane itself has been explored as an alternative approach [36, 37], though scaling and overgrowth of the membrane surface remain concerns, leading to reduced permeate flux throughout the process. The permeate flux for the MDC process decreases with increasing NaCl concentration because of the decrease in the partial vapor pressure difference [38, 39]. The water recovery increases with the addition of crystallization to the MD process and is reported with a recovery rate of up to 90 % [36, 40, 41]. In addition, water recovery through MDC using seeding has also shown promising results, leading to high water recovery rates [42–44]. Concerning the thermal efficiency of air gap MD (AGMD), a higher efficiency is obtained by AGMD compared to DCMD since the membrane is not in contact with the cold water stream [45].

The second part of MDC involves the process of crystallization, which occurs when a substance in a solution reaches

a state of supersaturation [46, 47]. Controlled crystallization is crucial to effectively separate salts from the aqueous solution, and factors such as solubility and temperature fluctuations play a significant role in facilitating unobstructed crystallization [48]. Previous studies have explored the use of seed crystallization to prevent uncontrolled crystallization, demonstrating slower crystal growth rates compared to evaporation methods. Precipitation in the metastable range allows for better control over the crystallization process [35]. Uncontrolled crystallization in membrane distillation crystallization is undesirable as it can lead to membrane scaling, which impacts permeate flux, permeate quality, and overall membrane performance negatively [32].

This study aims to evaluate the potential of a seeded air gap membrane distillation crystallization process (AGMDC) and draw conclusions based on the results regarding wetting prevention. By employing seed crystallization, the pores of the membrane are suggested to be protected against wetting and scaling. The crystallization process is planned to occur within the membrane module, and the resulting crystals will be collected and removed from the process in the classifier section. The findings of this study contribute to a better understanding of using an AGMDC plant without the need for a commonly applied crystallizer and help to ensure the long-term stability of the process.

2 Materials and Methods

2.1 Feed Solution

The feed solution used in this study consisted of sodium chloride (NaCl, >99.5 %, Carl Roth, CAS No. 7647-14-5) due to its stable temperature solubility and its abundance in industrial wastewaters. NaCl solubility remains relatively constant with increasing temperature, with a solubility of 358 g L^{-1} at room temperature and 371 g L^{-1} at 60°C . To prevent undesirable nucleation on the membrane surface, seeding crystals were introduced, utilizing quartz sand (SiO_2 , white quartz, Honeywell Fluka, CAS No. 14808-60-7) with a grain size ranging between 0.21 and 0.3 mm. The seeding crystals were selected in quantities ranging from 0.05 to 0.5 wt %. The seeds must be of high quality (99.9 % purity) and uniform in size. For the seeding crystallization process, quartz sand within the range of 0.21 and 0.3 mm, comprising at least 85 % of the total quartz sand used, was employed. A 22.25 % NaCl saline solution containing 0.05 % quartz sand as seeding crystals was prepared using NaCl (>99.5 %, Carl Roth, CAS No. 7647-14-5) and quartz sand (SiO_2 , white quartz, Honeywell Fluka, CAS No. 14808-60-7).

2.2 Membrane Material

Tubular membrane Accurel hydrophobic polypropylene (PP) V8/2 HF membrane from 3M[®] is used in this study. The membrane has an effective contact area of 0.017 m², a nominal pore size radius of 0.2 μ m, a thickness of 1550 μ m, and a porosity of 73 %. The inner and outer diameters of the membrane are 5.5 mm and 8.6 mm, respectively. The chosen hydrophobic membrane has been proven to be an effective MD membrane.

2.3 Air Gap Membrane Distillation Crystallization Plant

A modular pilot air-gap membrane crystallization (AGMDC) plant was employed for conducting the experiments. The setup consisted of three main components: an air gap membrane module equipped with a PP tubular membrane (described in Sect. 2.2), a heat exchanger module with a PP-GR tube, and a classifier part. The performance of the membrane in the AGMDC setup was evaluated, as shown in Fig. 1. The experiment commenced with the utilization of a high-saline NaCl solution as the feed. The feed solution was heated using a tubular heat exchanger to maintain a constant temperature, achieved through a thermostat (Haake, NB 22). Subsequently, the feed was pumped into the tubular membrane from the top using a peristaltic pump (Ismatec ISM 1080, ecoline), with the feed flow

adjusted by controlling the rotational speed of the pump. The flow rate was measured using a magnetic flow meter (Kobold, MIK 5N15AL343).

Water was employed to cool the condensation plate of the air gap module, and the resulting condensed permeate was collected in a permeate vessel and weighed using a balance (Kern, DE60K2N). Resistance thermometers (Kobold, MWE PT100) were employed to measure the inlet and outlet temperatures of the membrane module, as well as the permeate temperature in the permeate vessel and the temperature of the heat exchanger. The conductivity of the concentrating loop (Kobold, LCI SG40MPF) and the permeate electrical conductivity (Kobold, ACS-Z2T1G) were measured using conductivity meters. The pH of the concentrating loop, determined by an inline pH meter, was measured using a gel-filled pH electrode (Kobold).

An initial salt feed solution was prepared and filled into the feed vessel, with the feed inlet temperature set to 60 °C. The mean temperature difference between the feed and permeate was maintained at 40 °C, to achieve a higher driving force. The feed flow rate (F) was selected within the range of 60–90 L h⁻¹ to prevent crystallization in the plant pipes. The permeate flux was calculated once a constant flux was achieved (at least 20 min). To investigate the effect of seeding crystals in the solution, the process was continuously run in a batch experiment. The crystal size was measured during the process with a camera (Allied Vision Alvium 1800 U-240) with a telecentric lens (Edmund Industrial Optics 34010).

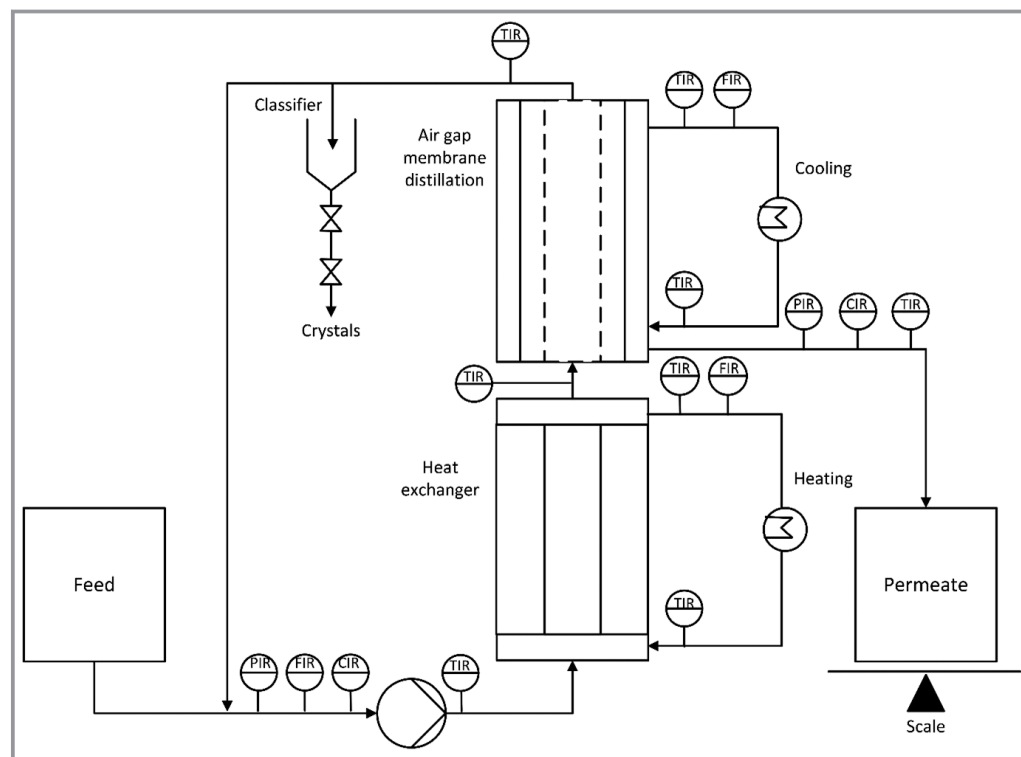


Figure 1. Schematic drawing of the pilot-scale AGMDC plant.

2.4 Functional Principle

The distillate flux is determined by calculating the permeate mass Δm (kg) per effective surface area of membrane A (m^2) and the collection time Δt (h).

$$J = \frac{\Delta m}{A \Delta t} \quad (1)$$

The production flux of solids is obtained by

$$\text{production flux of the solids} = \frac{m_{\text{total}}}{A t} \quad (2)$$

where m_{total} is the total salt recovery (kg) and t as the total operating time of the MDC (h).

The water recovery is calculated by

$$\text{water recovery} = \frac{m_p}{m_f} \quad (3)$$

where m_p is the mass of the permeate (kg) and m_f is the water mass of the feed solution (kg).

As the temperature of the evaporating water increases, the enthalpy of evaporation decreases. When the temperature range is 273–373 K, then the latent heat of evaporation of water $\Delta H_{v,w}$ is expressed as

$$\Delta H_{v,w} = 1.7535T + 2024.3 \quad (4)$$

The specific heat capacity (cp) of aqueous NaCl is $0.86 \text{ kJ kg}^{-1} \text{K}^{-1}$ and that of water is $4.18 \text{ kJ kg}^{-1} \text{K}^{-1}$. The specific heat capacity of mixtures (cp_{mixture}) based on

$$cp_{\text{mixture}} = \left(\frac{m_1}{m_{\text{mixture}}} \right) cp_1 + \left(\frac{m_2}{m_{\text{mixture}}} \right) cp_2 \quad (5)$$

and

$$\dot{m} = \nu \rho \quad (6)$$

where ρ is the density (kg L^{-1}) and ν is the flow rate of the feed (L h^{-1}). The heat flow of the plant and the heating area ($\dot{Q}$) results from

$$\dot{Q} = \dot{m} cp_{\text{mixture}} \Delta T \quad (7)$$

where ΔT is the temperature difference between the inlet and the outlet temperature of the membrane module or the heat exchanger (K).

The total heat flux of the feed solution and the infiltrate volume flux (Q) result from the addition of the two heat fluxes occurring in the hydrophobic membrane, namely the latent heat of vaporization (Q_v) and the heat conduction (Q_c) by the vapor in the membrane holes and through the membrane material. Water evaporates on the external surface of the membrane on the feed side, passes through the membrane pores, and condenses at the vapor-liquid interface on the permeate side, resulting in the following heat flux

$$Q_v = J \Delta H_{v,w} \quad (8)$$

By conduction, the second heat flux is due to the temperature variations between the two sides of the membranes and is given by

$$Q_c = h_m (T_f - T_p) \quad (9)$$

The temperature difference between the inlet and outlet is 0.7 K, while heat loss to the environment is minimized by insulating the plant pipes. The thermal efficiency results as

$$\eta = \frac{Q_v}{(Q_c + Q_v)} \quad (10)$$

2.5 Crystal Characterization Method

Crystals were examined using direct optical microscopy (Keyence VHX-7000), which offers exceptional depth of field for flexible crystal viewing. The optimal observation condition was determined by adjusting the brightness to ensure an accurate analysis of crystal size and growth behavior. Further detailed studies were conducted on the crystals.

3 Results and Discussions

3.1 Effect of the Seeding in a High-Saline Solution

A hydrophobic membrane that becomes completely wet exhibits behaviour similar to that of a hydrophilic membrane, resulting in increased permeate flux but significantly reduced salt rejection. However, membrane wetting hampers the effectiveness of desalination and other separation processes, as the saline solution can permeate through the membrane, leading to permeate contamination [49]. To mitigate scaling and scaling-induced wetting on the membrane surface, seed crystals are introduced into the feed solution, promoting crystallization in the metastable region and facilitating crystal growth on the seeds. An advantage of seeding crystallization is that it eliminates the need for an external crystallizer. The crystals settle as very small particles ($130\text{--}200 \mu\text{m}$) in the classifier part, where they are collected. The effect of the seeded solution is shown in the permeate flux diagram (Fig. 2), revealing only a negligible decrease of $0.38 \text{ kg m}^{-2} \text{L}^{-1}$ over the 1070-minute experiment duration. The permeate flux was $2.3 \text{ kg m}^{-2} \text{h}^{-1}$ for an initial NaCl concentration of 4.9 M and remained constant throughout the process, indicating stable operation. The flux is in the range reported by other work, as Balis et al. [38], whereas in their application, a decrease in permeate flux was observed. Moreover, the high quality of the permeate with low salt content affirmed the absence of complete pore wetting [50].

Initially, the feed conductivity increases until it reaches the solubility limit after 450 min. Crystallization starts before the conductivity decreases from 214 to 188 mS cm^{-1}

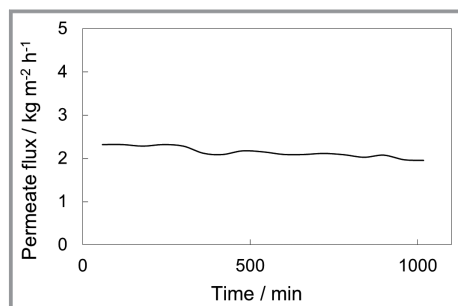


Figure 2. Permeate flux from 0 to 1070 min. Between 0 and 300 min the permeate flux is $2.32 \text{ kg m}^{-2} \text{ h}^{-1}$. At the end of the experiment at 1070 min the permeate flux decreased to $1.95 \text{ kg m}^{-2} \text{ h}^{-1}$.

and the conductivity decreases, which is also observed in batch experiments [51,52]. The decrease might result from an insufficient mixing resulting from a short blockage of the pumping circuit. By increasing the flow rate again to the setpoint, the solution is thoroughly mixed again and stabilizes at a conductivity of 214 mS cm^{-1} , representing the solubility limit. NaCl continues to crystallize continuously between 500 and 1070 min (Fig. 3). Additionally, the crystallization in the process is observed with the installed camera. The average conductivity of the permeate is $0.8 \mu\text{S cm}^{-1}$.

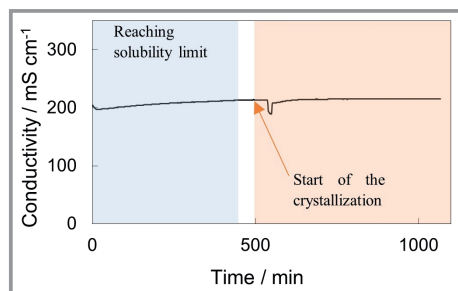


Figure 3. Conductivity is increasing from 196 to 214 mS cm^{-1} in 450 min (blue). From 450 to 500 min the conductivity is constant at 214 mS cm^{-1} and there is a drop to 188 mS cm^{-1} after the crystallization starts (orange) and then it increases to 214 mS cm^{-1} again.

The classifier module was utilized to recover solid salt, resulting in a salt recovery of 44 %. It is worth noting that, in a continuous process, a salt recovery of 95.5 % is achievable. In the present study, the solid production rate (Eq. (2)) is measured at $0.39 \text{ kg m}^{-2} \text{ h}^{-1}$. In contrast, Balis et al. [38] reported a higher solid production rate of $0.598 \text{ kg m}^{-2} \text{ h}^{-1}$. The solids production serves as an indicator of the amount of salt that can be recovered per unit of membrane area per hour in MDC. Since salt recovery plays a crucial role in achieving nearly 100 % water recovery, it serves as a key parameter to evaluate the effectiveness of the process.

3.2 Water Recovery

The water recovery from the NaCl experiment reached 61 % (Fig. 4) and showed a linear trend over time. After an initial equilibrium period of 20 min, the water recovery started to take effect. It is important to note that the water recovery system can be operated continuously, allowing for a potential water recovery of 95 %, which is similar to the findings of Ji et al. [41]. By implementing a continuous process, water recovery could approach the desired level of nearly 100 %.

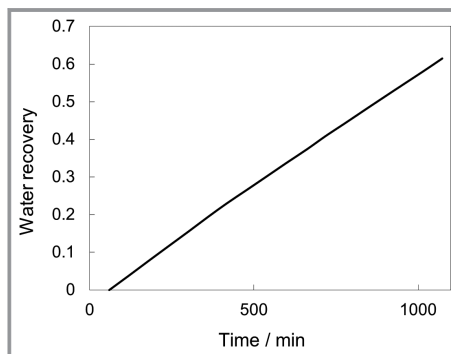


Figure 4. Water recovery of a NaCl solution with an initial concentration of 4.9 M. The water recovery increases linearly until the experiment ends after 1070 min.

3.3 Thermal Efficiency of the Experiment

Thermal efficiency, as defined by the ratio of heat contributing to evaporation to the total heat transferred from the feed to the permeate (Eq. (10)), remains relatively stable between 60 and 63 %, which is similar to the work of Alobaidani et al. [45]. Interestingly, despite the increase in feed solution concentration from 285 to 370 g L^{-1} , there was no notable impact on thermal efficiency (Fig. 5). However, it is worth noting that enhancing thermal efficiency can be accomplished by elevating the temperature of the feed solution.

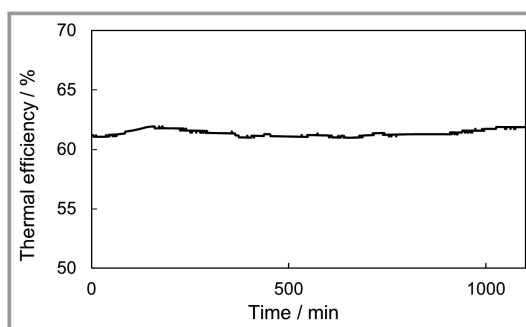


Figure 5. Thermal efficiency is stable over the whole experiment. The thermal efficiency is between 60 and 63 %.

3.4 Salt Characterization

The addition of SiO_2 to the system resulted in the precipitation of NaCl on the seeding crystals instead of the membrane surface, even at a salinity of 29 %. The crystal size in the process is, on average, 250 μm when the crystals sediment in the classifier part. Once crystallization and settling occurred in the classifier part, the crystals were collected, filtered, and subsequently dried. Throughout the drying process, it was observed that the crystals continued to grow and also formed clusters. The average crystal size increased by 300 % after the drying process compared to the crystal size during the process (Fig. 6). A bimodal distribution is observed with maxima at 700 μm and 1000 μm . Under microscopic investigation, the NaCl crystals displayed their characteristic square shape. An online measurement technique will be installed to monitor crystal growth continuously. The obtained particle size after drying instead gives a first indication of further application of the recovered salts.

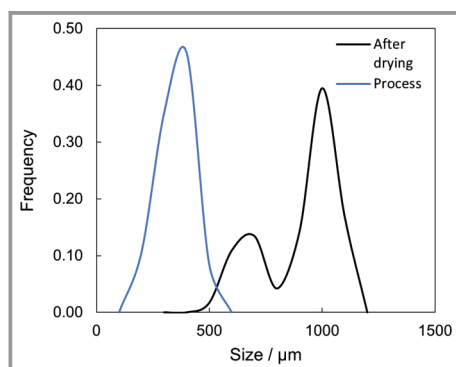


Figure 6. Crystal size distribution of the crystal size during the process (blue) and after drying (black). The crystal size is between 150–350 μm in the process and grows further to 550–700 μm or forms cluster, on average, 900–1100 μm after drying.

4 Conclusion

Zero liquid discharge (ZLD) processes have been developed to recover water from brine waste, minimize environmental impact, and achieve sustainability. Traditional thermal-based ZLD technologies, such as brine concentrators and crystallizers, have limitations in terms of cost, land requirements, and potential environmental risks. As a result, membrane-based ZLD processes, including membrane distillation (MD), have gained attention as an alternative approach. MD is a thermally driven separation process that uses a hydrophobic membrane to separate water vapor from the brine solution. Air gap membrane distillation (AGMD) is a specific type of MD that involves an air gap between the membrane and the condensing surface. AGMD offers advantages such as low pressure and temperature requirements, making it cost-effective and suitable for large-scale implementation. To prevent scaling and fouling, which are

common challenges in membrane-based technologies, seeding crystallization using quartz sand has been employed.

This study focused on evaluating the potential of air gap membrane distillation crystallization (AGMDC) for the recovery of pure water and solid salts from a high-saline NaCl solution. A modular pilot AGMDC plant was utilized, incorporating a polypropylene (PP) tubular membrane and a heat exchanger module. The experimental conditions, including feed solution composition, membrane material, seeding crystallization, and operation parameters, were carefully controlled.

The results showed that AGMDC with seeding crystals effectively prevented uncontrolled crystallization and scaling on the membrane surface, enabling the recovery of both pure water and solid salts. The chosen membrane material, 3M[®] Accurel hydrophobic PP V8/2 HF, demonstrated satisfactory performance in the AGMDC setup. By optimizing the operating parameters, such as feed flow rate and temperature difference, a constant flux of permeate was achieved. The recovery of solid salt was achieved through the utilization of the classifier module, resulting in a salt recovery rate of 44 %. However, in a continuous process, a significantly higher salt recovery rate of 95.5 % is attainable. The water recovery system showed promising results, with a water recovery rate of 61 % in the NaCl experiment. Implementing a continuous process would bring water recovery closer to the desired level of nearly 100 %. Thermal efficiency, a crucial factor in the process, remained stable between 60 % and 63 %. The solid production rate serves as a key parameter to evaluate the effectiveness of the process, with the current study achieving a value of 0.39 $\text{kg m}^{-2}\text{h}^{-1}$. The presented seeding crystallization approach offers the advantage of eliminating the need for an external crystallizer. Finally, this study highlights the feasibility of AGMDC as a promising technology for ZLD and the potential for scaling up the process for industrial applications.

Symbols used

A	$[\text{m}^2]$	Membrane area
c_p	$[\text{kJ kg}^{-1}\text{K}^{-1}]$	Specific heat capacity
$H_{v,w}$	$[\text{kJ kg}^{-1}]$	Enthalpy of water vapor
$H_{f,g}$	$[\text{kJ kg}^{-1}]$	Enthalpy of evaporation
h_m	$[\text{W m}^{-2}\text{K}^{-1}]$	Heat transfer coefficient of membrane
J	$[\text{kg m}^{-2}\text{h}^{-1}]$	Permeate flux
m	$[\text{kg}]$	Mass
m_f	$[\text{kg}]$	Feed mass
m_p	$[\text{kg}]$	Permeate mass
m_{total}	$[\text{kg}]$	Total salt mass
$\dot{m}$	$[\text{kg s}^{-1}]$	Mass flow rate
T	$[\text{K}]$	Temperature
T_f	$[\text{K}]$	Temperature of the feed
$T_{f,in}$	$[\text{K}]$	Feed inlet temperature
$T_{f,out}$	$[\text{K}]$	Feed outlet temperature

T_p	[K]	Temperature of the permeate
t	[s]	Time
Q	[W]	Heat flux
Q_c	[W]	Conduction heat transfer
Q_v	[W]	Latent heat transfer

Greek symbols

η	[%]	Thermal efficiency
ρ	[kg m ⁻³]	Density
ν	[L s ⁻¹]	Volume flow

Abbreviations

MD	Membrane distillation
MDC	Membrane distillation crystallization
AGMD	Air gap membrane distillation
DCMD	Direct contact membrane distillation
PP	Polypropylene
ZLD	Zero liquid discharge

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Application of Seeded Membrane Distillation Crystallization for Zero Liquid Discharge

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Research Article: This study shows the feasibility of treating high saline solutions by a combination of membrane distillation and seed crystallization. The addition of seed crystals minimizes membrane wetting and scaling. This method achieves a high recovery of water and results in a possible solution for (near)-zero liquid discharge. ■

