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Engineering Advances

Membrane-assisted crystallization

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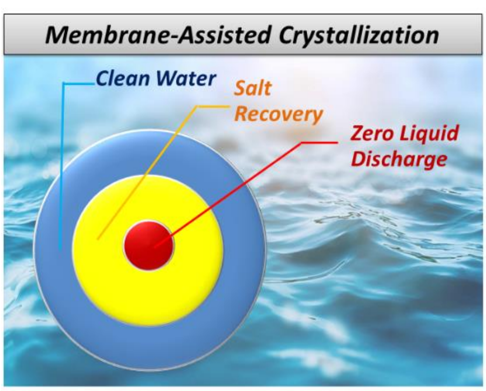
ABSTRACT

Membrane systems are of significant importance in the processes of mineral recovery and water reclamation from wastewater, particularly in response to the growing need for fresh and reusable water resources. Membrane crystallization (MCr) is a new technique that has arisen in response to the demand for the production and retrieval of superior crystals from saltwater and wastewater. This process allows for the manipulation of polymorphic morphology by adjusting the operational parameters. Furthermore, the utilization of membrane crystallization in conjunction with membrane distillation or pressure-driven membrane techniques like nanofiltration and reverse osmosis has demonstrated the potential for attaining substantial desalination efficiencies. Nevertheless, there are still lingering issues within the realm of film crystallization technology. The main factors encompassed in this category are temperature polarization, contamination, and wetting. This study elucidates a novel technological advancement and showcases its diverse range of applications.

KEYWORDS: Membrane-assisted crystallization; MCr; Salt recovery; Zero liquid discharge; Seawater.

GRAPHICAL ABSTRACT



HIGHLIGHTS

- MCr is a new technique that produces and recovers high-quality crystals from saltwater and wastewater.
- MCr can adjust crystals form according on operational circumstances.
- MCr can recover clean water and critical metals such as Li, Mg, Ba, and Sr.
- MCr control is crucial for optimal crystal output and quality.
- Cost-effective, energy-efficient, and green technologies, scaled and globally adopted, can address battery material.

1. Introduction

Water is widely recognized as a crucial resource in several aspects of human existence, including both the sustenance of living organisms and the fulfillment of industrial and agricultural requirements. The anticipated rise in population, along with the expansion of industrial and agricultural sectors, is expected to result in a surge in water requirements in the coming years. This surge has the potential to exert significant pressure on the sustenance of both human populations and ecological systems. According to a recent study, a substantial proportion of the global population, above 4 billion individuals, now experiences water stress, indicating a noteworthy magnitude in relation to the whole populace. The global dilemma of water resource scarcity is a significant issue, as highlighted by Mekonnen and Hoekstra (2016).

With the oceans comprising over 97% of Earth's water, they represent the most plentiful reservoir of natural water. Consequently, the focus lies on the judicious utilization and recycling of water, as well as the potential for extracting freshwater from seawater (Ali et al., 2018). The resolution of this

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issue necessitates a substantial augmentation of the desalination procedure. Consequently, there is an increasing need and significance attributed to these processes. The membrane process assumes a significant role in addressing these issues as an environmentally sustainable approach capable of resolving them. Indeed, there exists a range of technologies that are founded on membrane processes, including reverse osmosis (RO) and the more recent but less prevalent membrane distillation (MD). These technologies have been introduced into the market. These techniques are capable of producing freshwater from saltwater, with the key distinction being that MD operates at a much lower pressure compared to RO, which necessitates surpassing the osmotic pressure threshold (Cappizano et al., 2021). Consequently, the residual effluent resulting from the aforementioned process has a tendency to accumulate all of the salts that were previously present and that remain after the desalination process. Waste recovery and reuse have been identified as potentially effective strategies for mitigating waste generation in diverse industrial operations. The provided illustration, depicted in Figure 1, serves as an exemplification of an RO desalination procedure. In this particular procedure, the waste undergoes further processing by membrane crystallization, resulting in the production of a greater quantity of drinkable water alongside the formation of salt crystals typically present in saltwater. Membrane-assisted crystallization (MCr) has emerged as a compelling prospect for this particular objective. This process facilitates the retrieval of salt from the residue of reverse osmosis, while also generating freshwater. The methodology employed in this procedure relies on the process of solvent evaporation from a feed solution that is in direct contact with a hydrophobic membrane. The process of solvent evaporation results in the concentration of the feed solution to a state of supersaturation, leading to the formation of highly organized crystals. The operational mechanism of MCr is fundamentally analogous to that of the broader MD process, relying on the application of a partial pressure gradient across a microporous hydrophobic membrane. In contrast to conventional desalination methods, MCr has a reduced operational temperature, enabling the utilization of alternative energy sources like as solar, wind, and geothermal (Ko et al., 2018). Moreover, it has the potential to achieve complete elimination of all non-volatile constituents in theory. The latter benefit is utilized in MCr to achieve solution saturation and then induce crystallization. Table 1 presents a comprehensive overview of the primary benefits and drawbacks associated with MCr.

Table 1
The primary advantages and challenges of MCr.

Advantages	Challenges
Narrower distribution in crystal size	Concentration Polarization
Accelerated kinetics in macromolecular crystallization	Fouling phenomena
Orientation of molecules induced by laminar flow	
Greater control of supersaturation with consequent greater control of the crystallization process	

2. Membrane-assisted Crystallization process

Membrane crystallization (MCr) possesses the capability to facilitate the retrieval of purified water and important salts, such as lithium, sodium, magnesium, barium, and strontium, among others. The motivation for the utilization of MCr stems from the requirement to generate, isolate, and refine components found in seawater and wastewater, manifesting as solid crystals, inside diverse industrial, technical, and scientific study domains. A wide range of commonly used items are manufactured in the form of crystalline powders, including several categories such as cosmetics, hygiene goods, personal care items, medicines, fine chemicals, pigments, and numerous food additives. The use of crystalline solids enhances the stability, user-friendliness, and functionality of these goods. Additional applications encompass the fabrication of devices such as organic semiconductors and photonic crystals, as well as the progress of medical science through the systematic exploration of novel pharmaceuticals derived from crystal structures (Curcio and Drioli, 2005).

Furthermore, the utilization of crystalline materials in heterogeneous catalysis is prevalent as it allows for the attainment of optimal surface-to-volume ratios and enhanced catalytic efficiencies by means of regulated discharge of active chemicals (Margolin and Navia, 2001; Falkner et al., 2005). The selection of a certain polymorphic form can significantly impact the observed effects of crystalline characteristics. The shape of crystals is the fundamental determinant for crystalline powders. Within the pharmaceutical sector, several polymorphs of a given compound are regarded as separate entities, each with distinct physical, chemical, and biological characteristics. Consequently, each polymorph is considered an own patentable pharmaceutical product. In order to determine the atomic-level structure of proteins using X-ray diffraction analysis, it is necessary to have large crystals with diameters of at least 100 mm in two dimensions, which possess a well-organized crystal lattice (McPherson & Gavira, 2014). Additional applications of MCr are being explored in the field of wastewater treatment for the purpose of obtaining silver with high purity (Tang et al., 2010), sodium sulphate (Li et al., 2014), CO2 recovery (Ye et al., 2013; Ruiz Salmon et al., 2017), as well as for the synthesis of BaSO4 and CaCO3 particles (Jia et al., 2003), recovery of antibiotics (Li et al., 2004), and polystyrene microparticles (Drioli et al., 2014).

Process control plays a crucial role in maximizing crystal output and ensuring high quality in the field of MCr. The adjustment of the evaporation rate of the solvent and the occurrence rate of supersaturation may be achieved by considering the chemical-physical characteristics of the membrane and the process parameters, such as temperature, concentration, and flow rate. Consequently, the overall outcome is the regulation of both the initiation and expansion speed of crystalline structures. Therefore, in comparison to traditional techniques of crystallization, the utilization of MCr enables the production of very precise crystal morphologies and structures. In addition, it should be noted that the surface composition of voided membranes has the ability to capture dissolved molecules. This capture process leads to the creation of localized areas with higher concentrations of these molecules, resulting in supersaturation and subsequent nucleation. These circumstances are crucial for the development of crystals, as they promote homogeneity and nucleation, which would otherwise be insufficient (Curcio et al., 2003).

The membranes that are utilized in this method can be fabricated from inorganic materials, polymeric materials, or a hybrid or composite structure that combines the properties of both types of materials. It is possible to employ both hollow fiber and flat membrane in this application. According to Curcio et al. (2005), the membrane that is employed must have a hydrophobicity level that is high enough to prevent liquids from passing through the porous structure.

3. MCr applications

The MCr technology is accessible in the four primary MD modes, namely direct contact, vacuum, sweep gas, and air gap. The direct contact membrane distillation process (DCMCr) utilizes the flow of cold liquid permeate. According to Baghbanzadeh et al. (2016), the transport over the membrane is facilitated by the vapor pressure differential, which is generated by the temperature difference across the membrane. The process of vacuum membrane crystallization (VMCr) involves the application of a vacuum or low pressure to the permeate side, while an external condenser is connected to collect the permeate and condense water vapor (Ko et al., 2018; Kiefer et al., 2018; Ma et al., 2018). In the Swept Gas Membrane Crystallization (SGMCr) process, a gas, such as air or nitrogen, is employed on the permeate side of the membrane instead of the vacuum utilized in Vacuum Membrane Crystallization (VMCr). This gas flow facilitates the transportation of vaporized molecules out of the membrane module, where they subsequently condense (Bernardo et al., 2009; Xie et al., 2009; Gasconsviladomat et al., 2006). In the context of membrane crystallization, the technique known as air-gap membrane crystallization (AGMCr) involves the introduction of an air gap between the membrane and the cold condensing surface located within the membrane module. According to Khayet and Cojocaru (2012) and Meindersma et al.

(2006), the presence of an air gap results in an elevated barrier to conductive heat transfer, hence reducing heat loss by conduction across the membrane.

Indeed, as elucidated in subsequent sections, the phenomenon of heat dissipation emerges as a paramount concern within the realm of membrane distillation. Di Profio et al. (2009) offered an advancement to the MCr procedure, which involved the utilization of an antisolvent to stimulate the crystallization process. This novel methodology operates inside two potential configurations. The initial process may be characterized as the separation of solvent and antisolvent, while the subsequent step can be described as the addition of antisolvent. In both instances, the migration of solvent/antisolvent and the crystallization of the film take place in the gas phase. The utilization of porous membranes enables enhanced regulation of solution composition in the course of the process by means of selective and accurate administration of anti-solvents, hence enhancing the ultimate characteristics of the crystals. The primary focus of early research was directed on the process of protein crystallization (Falkner et al., 2005). In their study, Brito et al. (2014) employed the method of microwave radiation with MCr for the purpose of facilitating the crystallization process of medicinal substances. The researchers reached the conclusion that MCr has the potential to generate crystals that exhibit similar quality and cost as crystals now available on the market. The utilization of MCr for the retrieval of salts has garnered significant interest in recent studies (Diprofio et al., 2005; Cui et al., 2014; Drioli et al., 2006). The literature has also examined real saltwater as well as various compositions of synthetic seawater (Diprofio et al., 2005; Edwie and Chung, 2013). In several studies, a combination of CaCO3 and HA has been utilized to examine the fouling phenomena (Greenlee et al., 2009; Susanto, 2011).

The research focus at MCr (Quist-Jensen et al., 2016) has shifted towards the recovery of LiCl due to the surge in demand for electronic gadgets, particularly those equipped with lithium batteries, in recent years. The utilization of MCr in vacuum setups, reaching industrial-scale production, is facilitated by the extraction of Li from salt lakes, seas, and other brines. Curcio et al. (2010) also examined additional inorganic source materials, including Na2SO4, KNO3, and MgSO4. The feed solution containing a mixture of Na2SO4 and NaCl was subjected to testing in an MCr reactor equipped with a polyvinylidene fluoride (PVDF) membrane. Subsequently, both types of crystals were successfully recovered. Table 2 provides a summary of several uses of MCr.

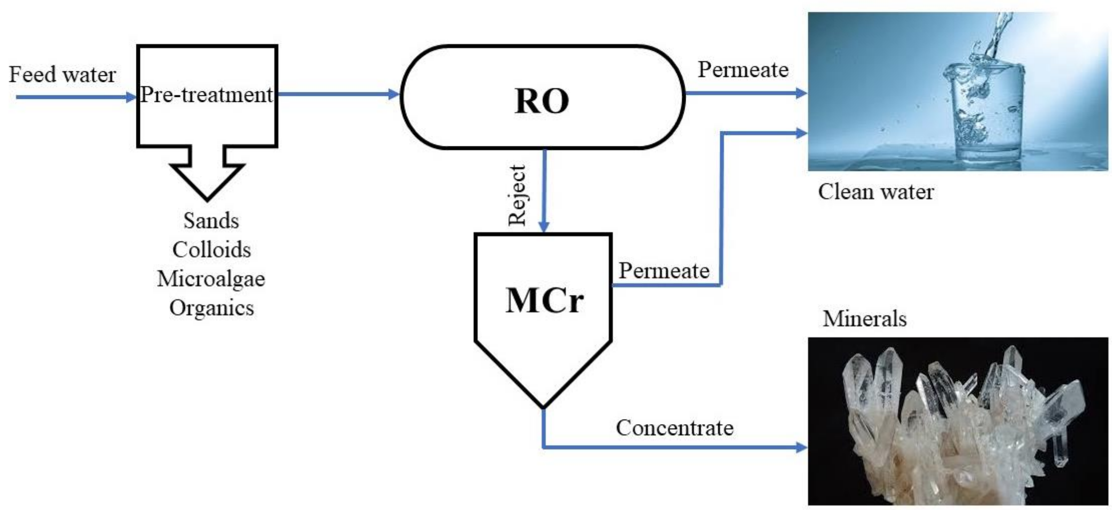

Fig. 1. Possible reuse of process waste from desalination through the use of membrane crystallizers.

Table 2
Application of MCr for mineral recovery.

Feed solution	Configuration	Membrane	Mineral recovery	Flux (kg/m^{2}h)	Productivity (kg/m^3)	Reference
Seawater RO brine (artificial)	----	PP (hollow fiber)	NaCl	0.972	17	(Ji et al., 2010)
Seawater RO brine (natural)	----	PP (hollow fiber)	NaCl	1.116	17	(Tun et al., 2005)
4.5 M NaCl	DCMCr	PVDF (flat sheet)	NaCl	16	----	(Tun et al., 2005)
2 M Na_2SO_4	DCMCr	PVDF (flat sheet)	Na_2SO_4	13	----	(Tun et al., 2005)
NF-pretreated wastewater	DCMCr	PP (hollow fiber)	Na_2SO_4	1.6	----	(Curcio et al., 2010)
Seawater	DCMCr	PVDF (hollow fiber)	Epsomite	1.4	----	(Quist-Jensen et al., 2016)
NF seawater retentate	----	PP (hollow fiber)	NaCl	0.45	35.5	(Drioli et al., 2004)
NF seawater retentate	----	PP (hollow fiber)	$MgSO_4 \cdot 7H_2O$	0.45	8.4	(Drioli et al., 2004)
NF seawater retentate	----	PP (hollow fiber)	Epsomite	0.45	----	(Drioli et al., 2004)
5.5 M NaCl 13 M LiCl	DCMCr	Ceramic composite membrane (hollow fiber)	NaCl and LiCl	17; 3.2	----	(Ko et al., 2018

4. MCr configurations

Typically, the process of crystallization is initiated by augmenting the concentration of the solution undergoing crystallization. According to Di Profio et al. (2010), MCr may be categorized into many forms based on the underlying principle governing the process:

1. Membrane distillation and osmotic distillation are processes that involve the diffusion of solvent molecules in the vapor phase through a chemically induced potential gradient.

2. MCr operates on the basis of applied pressure.

3. Solid, non-porous hollow fibers are utilized as heat exchangers to induce supersaturation through cooling.

4. The process involves the utilization of a membrane to facilitate the passage of the crystallizing liquid (also known as antisolvent) through its pores under the influence of a pressure gradient.

5. A method of MCr is employed to introduce the antisolvent into the crystallizing solution. This is achieved by utilizing a membrane, following the operational principles described in point 1, in both the solvent/antisolvent demixing and antisolvent addition configurations mentioned earlier.

Table 3 provides a concise overview of the primary benefits and drawbacks associated with the aforementioned setups, excluding MCr, as this information is previously included in Table 1.

Table 3
Main advantages and disadvantages for each MCr configurations.

Technology	Advantages	Disadvantages	Ref.
Membrane distillation / processes based on osmotic distillation	Lower operating temperatures with respect to conventional distillation columns Reduced influence of concentration polarization with respect to pressure-driven membrane processes Theoretical 100% rejection to non-volatile solutes	Temperature polarization phenomena Heat losses by conduction through the polymeric membrane Lower transmembrane fluxes with respect to Pressure-driven membrane processes	(Eykens et al., 2017)
Solid (non-porous) hollow fibers used as heat exchangers	High heat transfer coefficient Low costs, easy manufacturing, anti-fouling and anti-corrosion properties, Low energy consumption in production	Low polymer heat conductivity The lack of extensive experience and testing data with plastic heat exchangers Limited temperature operation below about 200 °C,	(Zarkadas et al., 2004; Raudensky et al., 2017)
Antisolvent (or crystallizing solution)	Change in solvent composition may favour one crystalline structure in those cases where the solute may crystallize in two or more crystalline phases (what is called polymorphism)	Highly dependent on mixing High local supersaturation at antisolvent induction zones Crystallizes very quickly (instantaneously) in batches with no possibility to control the speed. So grinding and other steps are required to get good size distribution.	(Nowee et al., 2008; Cheragoui et al., 2023)
MCr using an antisolvent	Lower energy consumption in supersaturation control, small particle size for the targeted products, Suitable for heat-sensitive materials The membranes allow you to control the mass transfer of the antisolvent and the mixing is better	Limited by the time-consuming steps of solvent selection and solvate formation Single component crystallization potential Needs special equipment to keep the mixture in a high grinding frequency The target products often contain impurities	(Di Profio et al., 2009; Cheragoui et al., 2023)

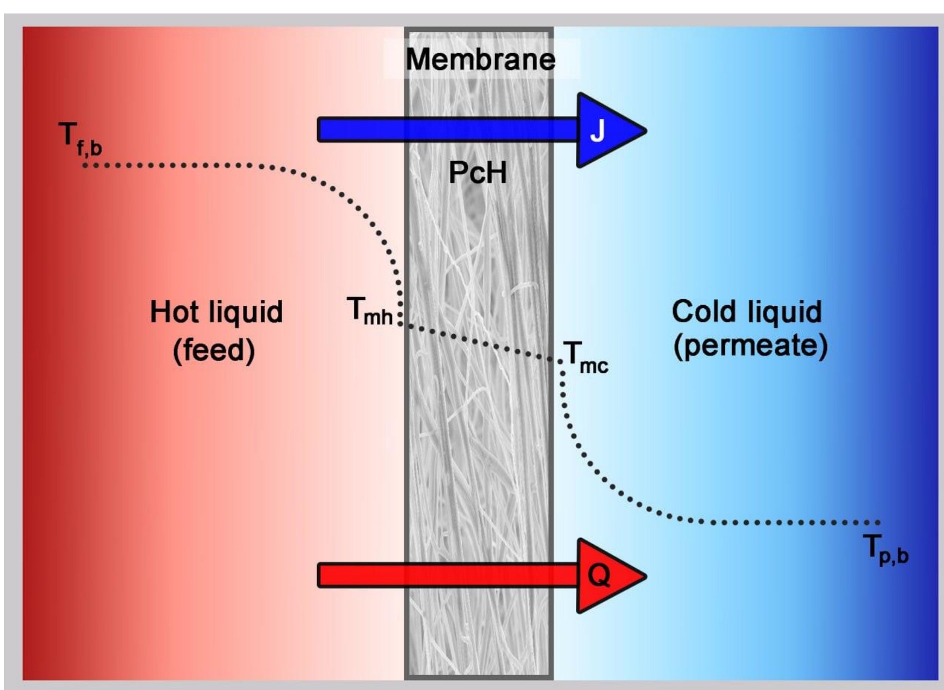

Fig. 2. Simplified process at the basis of Membrane Crystallization ($T_{f,b}$, is the bulk temperature, T_{mh} is the temperature on the surface of the membrane in the feed channel, PcH stands for membrane material, T_{mc}, is the temperature on the membrane surface in the permeate channel, $T_{p,b}$, is the bulk temperature in the permeate channel, J refers to the permeate flux, and Q refers to the heat flux).

Regardless of the specific configurations mentioned, all of them result in nucleation and crystal formation in the feed solution. This is due to the phenomenon of supersaturation, which occurs as a result of the continual withdrawal of solvent from the feed solution. According to Macedonio and Drioli (2019), in-depth investigations of the MCr process can employ the principles and methodologies established in the field of membrane distillation to elucidate intricate connections and construct comprehensive frameworks for analyzing heat and mass transfer phenomena occurring across the membrane. Typically, the phenomenon of heat and mass transfer across membranes is observed exclusively in cases when the whole system is not in a state of thermodynamic equilibrium. The process of mass transport may be categorized into three consecutive stages: mass transfer occurring inside the boundary layer on the feed side, mass transport across the pores of the membrane, and mass transport within the boundary layer on the permeate side. The latter option is not taken into consideration due to the fact that the mole fraction of the species presents in the permeate is about 1, since it just consists of distilled water.

Figure 2 illustrates a simplified depiction of the process involved in film crystallization utilizing a porous film accompanied by a boundary layer. Within the context of the boundary layer, the membrane is conceptualized as a slender film that facilitates the process of mass transfer, as per the principles of membrane theory. Conversely, the thin layer is employed to elucidate the mechanism of mass transfer occurring across the membrane, with the dusty gas model (DGM) serving as a suitable representation of the membrane. In the context of direct contact membrane crystallization, the Dusty Gas model, as discussed by Macedonio and Drioli (2019), primarily focuses on the Knudsen-molecular diffusion transition model while disregarding other factors. The model has the potential to undergo additional simplification in the context of certain unique circumstances. The Knudsen diffusion model is applicable in scenarios where the predominant mechanism of mass transfer is the result of molecular collisions with pore walls. Conversely, in cases when intermolecular collisions significantly contribute to mass transport across membranes, the utilization of molecular diffusion models seems to be beneficial. Nevertheless, in the event that there is a high occurrence of both molecule-pore wall collisions and molecule-molecule collisions, it is advisable to employ the Knudsen molecular diffusion transition model. In both scenarios, the rate of transmembrane flow is directly proportional to the porosity of the membrane, denoted as ε, and inversely proportional to the thickness of the membrane, denoted as δ. Hence, the film's structural characteristics have a significant impact on the process of crystallization, including the pace of solvent evaporation as well as the initiation and expansion of crystal formation. Indeed, the phenomenon of crystallization may be conceptualized as the migration of a certain quantity of solute molecules amongst the collisions of solvent molecules, resulting in the amalgamation of particular molecules to generate clusters. As stated by Wagner (1939), the essential crystal size is contingent upon the level of supersaturation. There is an inverse relationship between supersaturation and size, whereby an increase in supersaturation leads to a decrease in size, often ranging from a few tens of molecules. Hence, the manipulation of film chemical-physical characteristics and process parameters such as temperature and concentration enable the regulation of flow rate, degree of supersaturation, supersaturation rate, nucleation, and growth.

5. Conclusion and future perspective

The utilization of membrane crystallization exhibits promising prospects as a viable method for attaining a zero-waste outcome in desalination facilities. The Zero Liquid Drainage (ZLD) concept is an engineering methodology that prioritizes the complete retrieval of water resources while minimizing the generation of residual liquid waste (Katsoyiannis et al., 2015). The water recovery range described in the literature varies from 80% to 95%, but the salt recovery range ranges from 37% (Ali et al., 2015) to 100% (Quist-Jensen et al., 2016; Ghaffour et al., 2019). In addition to surpassing the restrictions of thermal systems, MCr exhibits the ability to transcend the limitations associated with traditional membrane systems, such as reverse osmosis (RO). Contrary to other processes, concentration polarization has minimal impact on the driving power of the process, hence enabling the attainment of elevated yields even under conditions of high concentrations (Macedonio et al., 2013). Concentration polarization occurs as a result of the establishment of a boundary layer on the surface of the film. The approach for mitigating concentration polarization bears resemblance to addressing temperature polarization, wherein enhancing the flow rate serves to augment the mixing phenomenon and eliminate the boundary layer.

According to Ahmed et al. (2020), hybrid desalination systems have been identified as having several benefits, including increased plant capacity, the ability to produce high-quality water, operational flexibility, and reduced energy specific use. Curcio et al. (2010) have stated that the integration of NF-MCr has demonstrated a salt rejection rate of 99.6%, hence indicating a significant potential for attaining near-zero liquid discharge (ZLD). Ahmed et al. (year) asserts that the integration of energy systems in hybrid and multi-hybrid desalination technologies is now in its nascent and underexplored phase. There have been multiple reports on the utilization of renewable energy sources for desalination, as documented by Alkaisi et al. (2017) and Ahmed et al. (2019). However, the number of studies specifically examining the energy demands of renewable energy resources for desalination and their comparison to conventional energy resources is limited, as noted by Shemer and Semiat (2017). One of the primary technical obstacles encountered in procedures such as MD and MCr is to the mitigation of fouling and wetting phenomena on the membrane surface. Given the current state of MCr's development, further investigation is required regarding performance measures, optimization of operational parameters, examination of scaling processes, and calculation of energy consumption (Kim et al., 2018). In order to fully evaluate the potential of large-scale MCr, it is imperative to conduct more research focusing on power efficiency and commercial viability, notwithstanding the encouraging findings revealed thus far. The efficacy of MCr has been thoroughly examined through rigorous experimentation conducted in laboratory settings. The integration of pilot studies on an industrial platform, in conjunction with novel laboratory investigations, presents a potential trajectory for the advancement of this technology in the future.

On the other hand, it is important to give special consideration to the fouling and wetting of the membrane. Membrane fouling may be categorized into many types, including organic fouling, inorganic fouling (such as silt), biological fouling, and colloidal fouling. In some situations, the feed solution may contain mixtures of pollutants, which might result in the occurrence of more intricate membrane fouling scenarios. Several anti-contamination approaches have been documented in order to address these issues, which encompass mechanical pre-treatment alternatives such microfiltration (MF) and nanofiltration (NF). Additional pre-treatment procedures encompass antiscalants, temperature conditioning, and membrane cleansing. Furthermore, there has been a comprehensive assessment of the efficacy of chemical cleaning in the restoration of MCr function. The utilization of commercially accessible membranes has been employed in the MCr procedure. However, future investigations will prioritize the development and alteration of diverse fouling-resistant membranes. Nevertheless, it is important to acknowledge and confront the various obstacles that arise in the research and industrial implementation of film crystallization, including:

- The development of membranes that are appropriate for the function of MCr involves the utilization of novel materials and the integration of characteristics such as extended lifespan, elevated hydrophobicity, enduring stability, and properties that are well-suited for this particular technology. These properties include dimensions, pore coefficient, thickness, thermal conductivity, surface roughness, and others.
- In order to enhance process efficiency and reliability, it is imperative to enhance membrane performance and address fouling issues.
- The process of technology transfer to the industry involves the practical implementation and experimentation of technological advancements on a large-scale industrial level, as well as the assessment of its advantages and disadvantages in comparison to traditional methods.
- Process optimization: Subsequent investigations may focus on the enhancement of operational parameters and crystallization conditions in the context of MD. This encompasses investigations into the impacts

of temperature, pressure, solution concentration, and flow rate on the formation of crystals, the efficiency of separation, and the overall performance of the process.

- The field of crystal engineering offers promising opportunities for investigating the regulation and modification of crystal characteristics, such as form, size, and morphology, through the utilization of MD processes. The comprehension and regulation of crystal formation can yield enhanced product quality, heightened separation efficiency, and favorable crystal characteristics tailored to specific applications.
- Energy Efficiency: Investigation into energy conservation techniques and the incorporation of renewable energy resources into the crystallization process of MD have the potential to enhance its sustainability. This can be achieved through the implementation of advanced heat recovery systems, optimized energy consumption practices, and exploration of hybrid approaches to mitigate energy requirements.
- The scalability and practical deployment of MCr technologies pose issues that might be addressed in future research endeavors. Various factors are taken into consideration, including process design, system integration, economic feasibility, and technological viability at a wider scale. The aforementioned solutions now pose significant obstacles, however, acquiring proficiency in addressing these challenges has the potential to propel the industrial utilization of MCr and facilitate the realization of effective separation and crystallization techniques.

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