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Membrane crystallization via membrane distillation

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ABSTRACT

Crystallization is a solid-liquid separation technique in which solid crystals are formed from a liquid solution. It has been usually employed in separation and purification of industrial streams using traditional devices as crystallizers or evaporators. Nowadays, membrane technology appears as the alternative technology that could replace the conventional crystallizers because of its advantages related to its adaptability and the low energy consumption in comparison with the conventional technology.

In this review, membrane crystallization via membrane distillation is addressed. The membrane performance, operating conditions, technical obstacles and the novelties of the technology are presented, including the applications and the future perspectives.

1. Introduction

The continuous improvement of processes and products in the industry is an essential requirement to ensure a sustainable future and further contribution to human progress. Three main aspects play a key role in that improvement: the environment, the society and the economy. Thus, it is of utmost relevance to develop new technological solutions that give response to current challenges that we are already facing. One of them is the climate change, caused by the increase of the global atmospheric concentration of carbon dioxide, from a pre-industrial value of about 280 ppm to 379 ppm in 2005 [1] and 400 ppm in 2016 [2]. Other challenges are the loss of biodiversity, the replacement of finite sources of energy, the search for cure of numerous and new diseases or the restoration and decontamination of ecosystems. Thus, increasing process efficiency while minimizing waste production and keeping the quality of the final product are requirements that have to be fulfilled by any new technological approach that is presented.

Process updating in the industry may suppose the survival and the success of an enterprise. Crystallization is an example of the technological evolution of a unit from the conventional operation to the high-efficiency process. Crystallization is a widely used unit operation for the separation and/or purification of crystalline solid products. This process has been industrially applied since the early nineteenth century, as in the case of the sugar industry [3–6], pharma and fine chemicals, bulk and commodity production [7] or microelectronics [8]. Currently, research is also focused on using this technology to recover valuable compounds from waste streams, such as the removal and recovery of phosphorous from swine wastewater [9], phenol recovery from dilute aqueous solutions [10] or the valorization of alkaline phosphate concentrates [11]. However, the main drawback of conventional crystallization, from an economic and environmental perspective, is the large amount of energy needed. This operation has been traditionally carried out using evaporators or crystallizers [12–15] where solute precipitation is produced thanks to heating or cooling, respectively. Although the progress on this field makes crystallization less energy-consuming than the past decades, it is still far to be a sustainable technology, knowing that a small increase in the temperature applied or in the residence time produces an important increment in the energy consumption [16].

During the seventies and more intensively during the eighties, research on crystallization increased dramatically in order to improve the design and operation of large scale systems, mainly to decrease the energy consumption. However, there is still a lack of knowledge about the crystallization kinetics, the influence of additives and the modelling and prediction of how polymorphs crystallize. Advances in fundamental knowledge on the crystallization process would help in the development of sensors that allow getting a better control of crystallization processes (nucleation, crystal modification and sizes, supersaturation, liquid inclusion in the crystals, impurities) [17]. Therefore, improving the efficiency of crystallization techniques requires paying attention to these aspects while developing novel and more energy-efficient processes. In this context, membrane crystallization appears as an innovative idea to incorporate membrane technology in crystallization processes to take advantage of its intrinsic benefits (some of them still under research because of potentiality of its innovation), such as a well-controlled nucleation and growth kinetics, fast crystallization rates,

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membrane surface promoting heterogeneous nucleation or good control of supersaturation [18]. In addition, membrane crystallization may be performed via a membrane distillation process when a temperature and/or concentration gradient is used as driving force in high concentrated solutions that are close to the supersaturation.

In this paper, membrane distillation is reviewed as crystallization technology in addition to its consideration as concentration technology. The potential of membrane crystallization from an intensification and integration point of view is addressed, with special attention to present and future applications, i.e. green economy and added-value production. This review also presents an overview of membrane distillation-crystallization processes and its main technical limitations (polarization, wetting, scaling, fouling) and economic and environmental implications (operating and investment costs, material and energy reuse) in order to show the current status of the technology and to address further research on this field.

2. Technical approach

Membrane distillation is usually applied for concentrating but not crystallizing. For this reason, knowing both the essential principles of membrane performance and the current challenges of the technology becomes essential. Therefore, membrane characteristics, system configurations and operating conditions are addressed in this section from a technical point of view.

2.1. Process description

Membrane distillation is typically used for treating solutions that need to be concentrated for further applications. In membrane distillation water crosses from the feed side to the permeate side through a (hydrophobic) membrane due to the difference in temperature and/or partial pressures across the membrane. Heating is applied in the feed solution to increase the vapor pressure of water at the feed side, leading to an increase of the driving force. The permeate is collected at the other side of the membrane, which may contain an aqueous solution (direct contact membrane distillation −DCMD- or osmotic membrane distillation −OMD), air/gas (air gap membrane distillation −AGMD- or sweeping gas membrane distillation −SGMD) or vacuum (vacuum membrane distillation −VMD-) [19–21]. If the concentration step continues up to very high concentrations, saturation may be reached and crystal precipitation of the solute would occur, leading to a membrane crystallization process.

Membrane contactors are the common device in which membrane distillation-crystallization is performed. In the membrane contactor, a non-dispersive contact is produced thanks to the membrane, which acts as a separation barrier (without providing selectivity) between two phases. This contact takes place inside the pores of the membrane [19]. Here, mass transfer is due to the driving force generated by a difference of chemical potential between both sides of the membrane. Thus, transport of the solvent (normally water) occurs from the feed side to the permeate side. However, the membrane does introduce a new resistance to mass and heat transfer (see Fig. 1). Conventional crystallization involves two resistances to mass and heat transfer, one in the feed side (liquid solution) and one in the receiving side (solid crystalline phase); whereas using membrane contactors implies a third resistance coming from the membrane itself, which is a physical barrier [21]. Resistances in membrane distillation can be theoretically calculated following the resistance-in-series model (widely studied in e.g. [19,22–24]). This model describes the phenomenon as the sum of the three different resistances, given by the transfer coefficients: mass and heat transfer coefficients in the feed boundary layer (k_f and h_f, respectively); mass and heat transfer coefficients in the permeate boundary layer (k_p and h_p, respectively), and mass and heat transfer coefficients in the membrane (k_m and h_m, respectively). Mass transfer takes place following three consecutive steps: i) diffusion of water from the bulk feed to the membrane wall, ii) vaporization and diffusion through the pores of the membrane, and iii) condensation in the membrane-liquid interface of the permeate side and diffusion into the bulk of the permeate. Two main aspects have a large influence in the importance of this extra resistance: the kind of membrane and the kind of configuration.

Regarding the kind and morphology of membranes, the main characteristics that affects the crystallization performance are: i) liquid entry pressure (LEP), which depends on the membrane hydrophobicity and the maximum pore size, is the pressure applied that should not exceed the limit pressure above which the liquid penetrates the hydrophobic membrane; if this happens, a decrease in the permeate flux occurs as well as an undesirable permeation of salts; ii) membrane thickness, inversely proportional to the permeate flux; iii) membrane porosity (the void volume fraction of the membrane) and tortuosity (the deviation of the pore structure from the cylindrical shape), having a direct effect on the liquid entry pressure; if LEP increases, permeation decreases; iv) mean pore size and pore size distribution and v) thermal conductivity (hot losses are minimized using a high porosity and/or thicker membrane) [25].

On the other hand, the membrane configuration also determines the crystallization since the water removal from the feed to the permeate is due to different sources of driving force and therefore, main parameters, such as the transmembrane flux, also vary. Fig. 2 shows the most developed membrane distillation configurations:

A.) Direct Contact Membrane Distillation (DCMD): A feed and colder aqueous solutions are maintained in direct contact thanks to the membrane, which should be hydrophobic in order to avoid that the aqueous feed penetrates the membrane pores. Thus, the transmembrane temperature difference induces the evaporation of the feed volatile molecules that cross the membrane to the permeate side and condense inside the module.

B.) Osmotic membrane distillation (OMD): The approach is similar to the DCMD. In this case, an osmotic agent (NaCl, $MgCl_2$, etc.) is used in the permeate side instead of the cold aqueous stream. Thus, the concentrations of the solutions involved are the contributors to create de partial pressure difference.

C.) Air Gap Membrane Distillation (AGMD): In AGMD the osmotic solution is substituted by a coolant. Here, molecules from the feed solution volatilize and cross both the membrane and the air gap up to the condensing over the cold surface (refrigerated by a coolant). In this case, feed can be used as the only material source if it is employed as the coolant by means of exchangers. There is also a variant, called Liquid Gap Membrane distillation (LGMD), where molecules condense between the membrane and the cooling plate but this technology has not been practically studied.

D.) Sweeping Gas Membrane Distillation (SGMD): It is characterized by the use of a cold inert or sweep gas in the permeate side to drag the molecules that have crossed the membrane. An extra condenser is often employed to change the permeate phase.

E.) Vacuum Membrane Distillation (VMD): It takes place when a vacuum pump system is connected to the permeate side (a condenser is usually included). The applied vacuum must be lower than the saturation pressure of volatile molecules in the feed solution to obtain the required driving force [20,21,25–29].

Crystallization by solvent removal involves an increase of concentration up to the saturation, leading to the precipitation of the solute and the crystals growth. Temperature plays an important role in both traditional equipment and membrane distillation. Conventional evaporators use a wide range of high temperatures to volatilize the water content of solutions, usually higher temperatures than those applied in most of membrane distillation processes, typically lower than 50° [19]. Regarding conventional crystallizers, very low temperatures are required to decrease the solubility of the solute in order to reach crystal

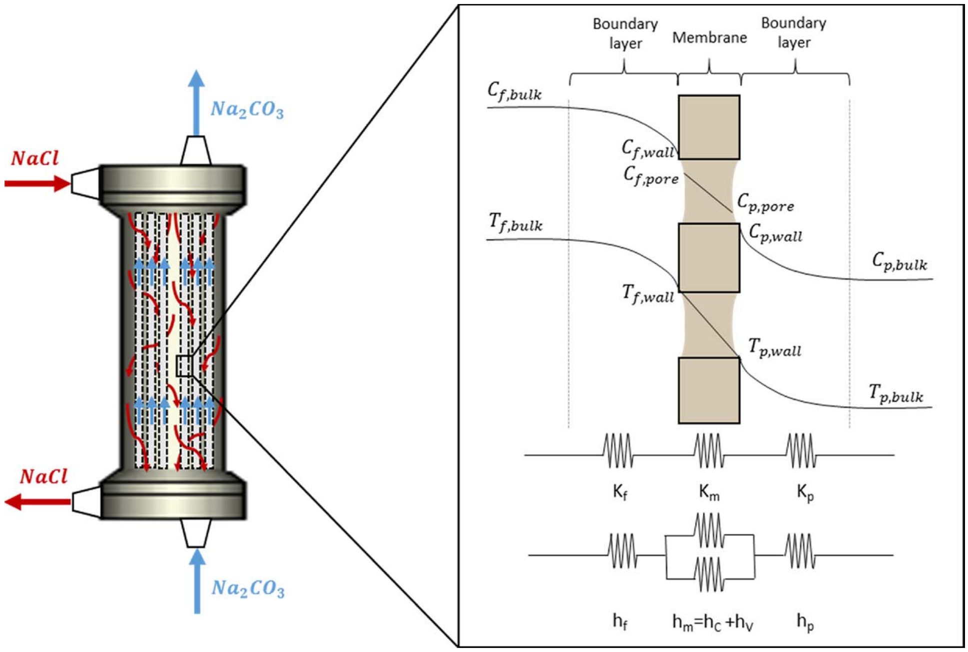

Fig. 1. Mass and heat resistances in a hollow fiber membrane contactor.

precipitation. However, membrane crystallization via membrane distillation can be adapted to different scenarios regarding the energy availability or the desired product, and residual heat can be used as a source of energy. For instance, Ruiz Salmón et al. [30] studied the crystallization of decahydrated sodium carbonate by means of osmotic membrane distillation at room temperature: no heating of the feed or cooling of the supersaturated permeate was carried out, a point that makes the difference with conventional crystallization processes. Nevertheless, if the feed temperature were higher than 32 °C and 35 °C, heptahydrated sodium carbonate and monohydrated sodium carbonate would be obtained, respectively. That and other studies [31,32] demonstrated the feasibility of salt crystallization using osmotic membrane distillation at room temperature and, therefore, involving a cost reduction since the feed stream does not have to be heated. Nevertheless, increasing temperature would play in favor of higher water flux through the membrane, with the possibility of using residual heat. But temperature is not the only operating condition to control the performance of membrane distillation. The use of vacuum, osmotic solution, pressure, circulation velocity and stirring rate has been also widely studied [25,26]. The optimization of the operating conditions will lead to an efficient process fulfill production requirements.

A point that deserves to be emphasized is how the performance in the membrane contactor determines the final cost. Therefore, choosing the optimal working conditions becomes essential and from an economic point of view, investment costs (i.e. membrane area) and operating costs (i.e. raw material, energy) can make a process feasible or not. In this respect, two parameters characterize the membrane contactor operation: the transmembrane flux and the mass transfer coefficient. The goal is to obtain the highest values of both parameters. In that case, it means that the highest performance of both the membrane contactor and the whole set-up occurs.

Regarding the main technical and economic issues, three scenarios could be marked. First, the higher the driving forces for water evaporation, the higher the water removal at the membrane surface. If the flux increases in the same ratio as the driving force a proportional performance takes place because there are not extra resistances (apart from the unavoidable intrinsic resistance in the membrane). This normally leads to an overall mass transfer coefficient mostly constant. Nevertheless, the performance of the membrane contactor may be affected by external factors, such as the osmotic agent or the operating conditions (temperature, flowrates, etc.) applied. Second, new resistances coming from polarization, wetting or scaling can produce a decrease in the mass transfer. In this case, the operating and investment costs are clearly not the optimum since material and energy are

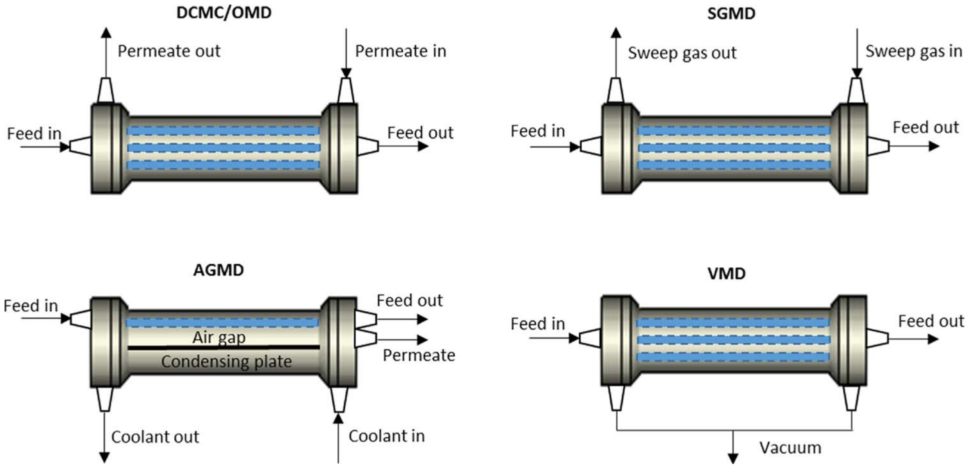

Fig. 2. Membrane distillation configurations: Direct contact membrane distillation (DCMC), osmotic membrane distillation (OMD), sweep gas membrane distillation (SGMD), air gas membrane distillation (AGMD) and vacuum membrane distillation (VMD).

underutilized and larger membrane area is necessary. Third, an appropriate combination of the variables (e.g. high feed temperature, high flowrates) may lead to an interesting synergy obtaining large water removal with less investment. This could happen, as previously mentioned, if the residual energy from a warm stream is used to generate the driving force between solutions at both sides of the membrane but also if high salty solutions (e.g. brines) are used as osmotic agent. Therefore, an economic evaluation is as important as the technical research for further scale-up and successful implementation in industry. Not surprisingly, the membrane crystallization is being studied to be applied in multiple fields.

2.2. Crystallization

Crystal formation is due to the simultaneous and competitive nucleation and growth that takes place in supersaturated solutions. Traditional crystallizers, namely batch stirred tanks, presents some drawbacks, such as the hydrodynamic and kinetics changes with the scale-up (and therefore a difficult supersaturation control) [19] or the batch character of the tank, avoiding the continuous process [33].

Crystallization using membrane distillation is characterized by laminar conditions what minimize the shear stress, promoting the formation of good structured crystalline forms. Besides, the membrane provides an excellent support for heterogeneous nucleation (nuclei grow at a surface), easier than the homogeneous nucleation (nuclei grow in the bulk solution). This happens because the energy barrier (Gibbs free energy) for heterogeneous nucleation is lower than the one for homogenous nucleation [19]. In this regard, the membrane selection plays an important role. Thus, a high surface area, porosity and roughness favor the nucleation because particles can deposit easily and “be trapped” [19,33], reducing the induction time, i.e. period between the moment in which supersaturation conditions are reached and the first crystal appears.

Results from Edwie and Chung [34] showed that the higher the temperature, the lower the average crystal size due to a higher rate of water evaporation, leading to a higher supersaturation of the retentate solution entering the crystallizer. Thus, growth rates of NaCl crystallization in the order of $10^{-8}\,\mathrm{m\,s^{-1}}$ are comparable with results reported by Ji *et al.* [35], where the growth rate of NaCl from real seawater RO brines varied within $0.8–2.5 \times 10^{-8}\,\mathrm{m\,s^{-1}}$. Meanwhile, Drioli et al. [36] studied an integrated membrane system combining nanofiltration with a precipitator and a membrane crystallizer. In this case, they confirmed that secondary nucleation, rather than primary one, is the dominant mechanism.

Furthermore, crystal nucleation and growing are often facilitated by adding seeds into crystallizers during the process. Creusen et al. [28] developed a process based on a combination of membrane distillation and osmotic distillation steps with integrated internal crystallization. A comparison between experiments with and without seeds showed that $CaCO_3$ crystallization on the seeds is preferred above crystallization on the membrane but membrane pores blockage could happen during the experiments. Besides the use of seeds in crystallizers, others authors investigated the inclusion of crystal inhibitors in order to avoid the crystallization on the membrane surface. Using a nanofiltration set-up, Bargeman et al. [37] have successfully controlled sodium sulphate supersaturation far outside the normal metastable region, by applying a primary nucleation inhibitor. Direct contact membrane distillation study from Curcio et al. [38] concluded that humic acid, even at low concentration, retarded the nucleation and growth of vaterite crystals at low supersaturation. On the other hand, $CaCO_3$ deposition on the membrane surface contributed to decrease the system performance (with minor magnitude than scaling issue). According to other studies, the presence of humic acid in brines produces a layer along the membrane and then crystal deposition on the surface occurs [39,40].

Production of protein hen egg white lysozyme crystals has been recently studied using membrane crystallization set ups [41–44]. Lysozyme forms part of many drugs to prevent infections and is also used in food industry as additive to destroy bacteria in dairy and meat products. Curcio et al. [41–43] employed polypropylene membranes to obtain protein crystals from supersaturated solutions. The main parameters studied were the nucleation and growth rates by varying concentration and flowrate of the stripping solution. Lysozyme crystals activity was measured in order to verify that recirculation flow did not cause denaturation of the protein solution. As result, no substantial variations were observed at increasing flowrates, and therefore, protein solution was not denatured by forced convection. Later, the influence of the morphological parameters of microporous PVDF membranes on the heterogeneous nucleation rate of lysozyme crystals was investigated. Authors concluded that a further knowledge of the relationship between physicochemical and structural membrane properties to the kinetics of nucleation would achieve a more logical design of a crystallization process.

Meanwhile, Zhang et al. [44], studied the influence of various membrane crystallization conditions including protein and precipitant concentration, the flow velocity of crystallization and stripping solutions, the pH and also ion strength of crystallization solutions. Lysozyme crystals were obtained in experiments carried out through microporous PVDF hollow fiber membranes. It was concluded that membrane crystallization is more rapid and with slower initial protein concentration than the traditional crystallization methods. Moreover, controlling the solvent evaporation rate can be made by varying the concentration and the flow velocity of stripping solutions.

The morphology of the crystals takes relevance since it may determine their future use or application. In the work performed by Di Profio et al. [45] the crystallization of paracetamol (a widely used antipyretic and analgesic found in over-the-counter drugs) was evaluated. The morphology of the paracetamol crystals obtained varied depending on the values of rate of solvent evaporation: a needle morphology, and either an elongated prismatic morphology. It was concluded that inducing polymorph selection and crystal habit modification during a crystallization process by using membrane-based techniques is possible.

Membrane technology also allows controlling the quality and size of crystals. Laminar regime of the mother liquor (against the high recirculation rates of a forced circulation crystallizer) and low shear stress (against the abrasion and attrition of crystal as produced in mechanical parts of a draft-Tube-Baffled) makes membrane crystallization competitive with conventional techniques [19]. Crystal control is mostly evaluated using the crystal size distribution (CSD), which defines the relative amount of crystals present according to size; the narrower distribution, the best crystal control. Thus, a narrow distribution is often characterized by a low coefficient of variation (CV). In this context, literature values of CV for membrane crystallization rounded 15–30% [34] or 30–38% [36], lower than CV values about 50% for traditional crystallizers [19].

In conclusion, the research on membrane crystallization using membrane contactors leaves no doubt about the feasibility to obtain crystals. Furthermore, the study of the simple configurations aforementioned opens the door to the development of more complex processes (i.e. combination of different devices to obtain synergy effects), making much more interesting and reliable this technology.

2.3. Applications of the membrane crystallization via membrane distillation

The large range of applications offered by the membranes and the future perspectives shown in the literature presents this technology as a promising and competitive alternative to conventional crystallizers for chemical production. The main applications are being developed for desalination of seawater and brines [35,46–48], wastewater treatment for the recovery of high-purity silver [49] or sodium sulphate [31], CO_2 capture [30,32,50], nanotechnology, such as the synthesis of $BaSO_4$ and $CaCO_3$ particles [51], or the recovery of antibiotics [52] or polyestirene microparticles [53].

Table 1
Main studies on recovery of salts from brines and saline waters. (*) Data obtained directly from the literature (explicit data or approximations by means of the figures).

Reference	Application	Membrane Process	Membrane type		Feed	Crystal product	J*	K*
			Material	Pore size (μm)				
[36]	Removal and crystallization of Na_2SO_4 from mother liquor saturated in NaCl and Na_2SO_4	NF	–	–	Mother liquor of NaCl and Na_2SO_4	Na_2SO_4	2.5–16.6 [Kg/(m^2 h)]	–
[77]	Water desalination	CMDC	PVDF	0.0082	NaCl solution	NaCl	20.63–66.56 [L/(m^2 d)]	–
[56]	Brine processing	DCMD	PVDF	0.164	NaCl solution	NaCl	–	–
[27]	Desalination of seawater, treatment of RO-brines	MDC	PTFE	0.07–0.1	Solution of $CaCO_3$ or NaCl	$CaCO_3$ and NaCl	6–16 [L/(m^2 h)]	–
		ODC		0.05	Solution of NaCl	NaCl	1–4 [L/(m^2 h)]	–
[37]	Seawater desalination	DCMD	PP	0.2	Synthetic seawater solution with NaCl, Na_2SO_4, $MgCl_2$, KBr, KCl, $CaCl_2{\cdot}2H_2O$, $NaHCO_3$, Na_2CO_3 and humic acid	$CaCO_3$	1.14–2.05 [L/(m^2 h)]	–
[35]	Seawater desalination	NF+ precipitator	–	0.45	Solution with NaCl, $CaCl_2$, $MgCl_2$ and $MgSO_4$	$CaCO_3$	–	–
		MCr	PP	0.2		NaCl, $MgSO_4{\cdot}7H_2O$	0.25–0.45 [Kg/(m^2 h)]	–
[45]	Seawater desalination	MF–NF–RO + MD or MCr	PP	0.2	Solution of Na_2SO_4, NaCl, $MgCl_2$, $CaCl_2$, $MgSO_4$ and $NaHCO_3$,	NaCl, $MgSO_4{\cdot}7H_2O$, $CaCO_3$		–
[46]	Water and salt recovery	MDC	DL-PVDF-PAN	max. 0.260	Solution of NaCl	NaCl	4–35 [Kg/(m^2 h)]	–
			DL-PVDF	max. 0.264				–
			SL-PVDF	max. 0.228				–
[33]	Treatment of saturated brine	SMDC	PVDF	max. 0.228	Solution of NaCl	NaCl	2–9 [Kg/(m^2 h)]	–
[103]	Treatment of salts	DCMD	PVDF-HFP	0.069–0.071	Solution of NaCl	NaCl	$0.15 \times 10^{-3} - 2.25 \times 10^{-3}$ [Kg/(m^2 s)]	–
[57]	Brine concentration	DCMD	PVDF	max. 0.16	Solution of NaCl or brine	NaCl, $CaSO_4$	2–6 [Kg/(m^2 h)]	–
[50]	Demineralization of tap water	MD	PP	0.22	Tap water	$CaCO_3$	410–740 [L/(m^2 d)]	–
[104]	Brackish water desalination	RO+ precipitator	–	–	Solution of $CaCl_2{\cdot}2H_2O$, $NaHCO_3$, $MgCl_2{\cdot}6H_2O$, $MgSO_4{\cdot}7H_2O$, NaCl	$CaCO_3$	–	–
[58]	Desalination process	DCMD	PP with/without fluorosilicone coating	0.2–0.6	Na_2SO_4, $CaCO_3$ and $CaCO_3$–$CaSO_4$ solutions	CaCO3 or CaSO4	5.1–14.3 [Kg/(m^2 h)]	–
[34]	Treatment of brines from seawater	RO+ MDC	PP	–	Raw seawater from Tyrrenian Sea beside the coastal city of Amantea (Calabria) and Synthetic RO concentrate (NaCl, $CaCl_2{\cdot}2H_2O$, $MgCl_2$, $NaHCO_3$, Na_2CO_3, Na_2SO_4 and KCl)	NaCl	$2.7 \times 10^{-4} - 4.5 \times 10^{-4}$ [Kg/(m^2 s)]	–
[62]	Effect of microwave irradiation on vacuum membrane distillation	VMD, MWVMD	PVDF	0.25	Solution of NaCl	NaCl	8–24 [Kg/(m^2 h)]	–
[79]	Desalination of high concentration salty water	MD	PVDF	0.2	Salt solution of $CaCO_3$ or NaCl	$CaCO_3$ and NaCl	24–26 [Kg/(m^2 h)]	–
		MWMD					28–30 [Kg/(m^2 h)]	–
[52]	Water desalination	RO	PA	–	Solution of $CaCl_2$, $NaHCO_3$, and in some cases NaCl	$CaCO_3$	7.6–14.6 [L/(m^2 h)]	–
[80]	Process highly concentrated aqueous solutions to recover water	DCMD	PVDF	0.22	Salt solutions of Na_2SO_4 and NaCl	Na_2SO_4 and NaCl	5–20 [Kg/(m^2 h)]	$3.8 \times 10^{-7} - 5.8 \times 10^{-7}$ [Kg/(m^2Pa s)]
[78]	Study the influence of magnetic pretreatment on NF performance.	NF	PA	3.64×10^{-4}	Solution composed of $CaCl_2$ and $NaHCO_3$	$CaCO_3$	62.87–64.49 [L/(m^2 h)]	–
			PPAA	3.68×10^{-4}			66.18–73.08 [L/(m^2 h)]	–
[66]	Seawater desalination	RO + MCr	PP	–	Standard seawater	NaCl	0.0035-0.006 [Kg/(m^2 min)]	–
[72]	Treatment of brines	MDC	PP	0.2	Solutions of $MgSO_4$ and NaCl	$MgSO_4$ and NaCl	100–300 [g/(m^2 h)]	–

(*continued on next page*)

Table 1 (*continued*)

Reference	Application	Membrane Process	Membrane type		Feed	Crystal product	J*	K*
			Material	Pore size (μm)				
[38]	Desalination	DCMD	PVDF PVDF-FTCS PVDF-PDTS	0.22–0.45	NaCl, $CaCl_2$ and humic acid	NaCl	1–14 [Kg/(m^2 h)]	$2.06 \times 10^{-7} - 6.79 \times 10^{-7}$ [Kg/(m^2Pa s)]
			PTFE	0.45				–
[39]	Desalination	DCMD	PP, PTFE	0.22–0.45	NaCl, $CaCl_2$ and humic acid	NaCl	4.43–4.49 [Kg/(m^2 h)]	0.436×10^{-7}
		VMD	PP, PTFE	0.22–0.45			7.62–8.06 [Kg/(m^2 h)]	-1.234×10^{-7} [Kg/(m^2Pa s)]
[48]	Seawater desalination	RO + VMD	PTFE	0.22	Synthetic concentrated solution, RO brine from a plant installed in the Mediterranean Sea	$CaCO_3$ and $CaSO_4$	1–160 [L/(m^2 h)]	–
[108]	Recovery of valuable salts from effluents and the processing of brine from desalination operations	DCMD	PVDF	0.22	Solution of Na_2SO_4 or NaCl	Na_2SO_4 and NaCl	5–20 [L/(m^2 h)]	$3.8 \times 10^{-7} - 5.8 \times 10^{-7}$ [Kg/(m^2Pa s)]
[49]	Treating highly saline and concentrated feed solutions	DCMD	PTFE	0.2	Solution of $CaSO_4{\cdot}2H_2O$	$CaSO_4{\cdot}2H_2O$	18–44.6 [L/(m^2 h)]	–
[51]	Treatment of aqueous solutions containing sparingly soluble salts	DCMD	PTFE	0.22	Solution of NaCl, $CaSO_4$, Na_2SiO_3, $CaCO_3$, KHCO3, and $CaCl_2$	$CaCO_3$ and $CaSO_4$	10–30 [L/(m^2 h)]	–

Membrane process: Nanofiltration (NF), continuous membrane distillation crystallization (CMDC), direct contact membrane distillation (DCMD), membrane distillation-crystallization (MDC), osmotic distillation-crystallization (ODC), membrane crystallizer (MCr), microfiltration (MF), reverse osmosis (RO), simultaneous membrane distillationcrystallization (SMDC), membrane distillation (MD), vacuum membrane distillation (VMD), Microwave vacuum membrane distillation (MWVMD), microwave membrane disitllation (MWMD). Material: polyvinylidene fluoride (PVDF), Polytetrafluoroethylene (PTFE), polypropylene (PP), dual-layer PVDF/polyacrylonitrile (DL-PVDF-PAN), dual-layer PVDF (DL-PVDF), single-layer polyvinylidene fluoride (SL-PVDF), Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), polyamide (PA), polypiperazineamide (PPAA), PVDF with 1H,1H,2H,2H-perfluorododecyltrichlorosilane (PVDF-FTCS), PVFF with of1H,1H,2H,2H-perfluorodecyltriethoxysilane (PVDF-PDTS).

Table 2
Main studies on recovery of high value added products. (*) Data obtained directly from the literature (explicit data or approximations by means of the figures).

Reference	Application	Membrane Process	Membrane type		Feed	Crystal product	J*	K*
			Material	Pore size (μm)				
[70]	Recovery of fumaric acid	MCr	PP	0.2	Fumaric acid and L-malic acid	Fumaric acid	0.60–0.65 [kg/(m^2 h)]	–
[41] [42]	Production of protein Hen egg white lysozyme (HEWL) crystals	MCr	PP	0.2	HEWL in NaAC and NaCl solutions	HEWL	24–90 [mL/(m^2 h)]	–
[40]	Production of protein Hen egg white lysozyme (HEWL) crystals	MCr	PVDF-Kynarflex PVDF-Kynar	0.056-0.22 0.034-0.19	HEWL in NaAC and NaCl solutions	HEWL	2×10^{-1}- 2×10^{-2} [μL/(cm^2 h)]	–
[109]	Production of protein Hen egg white lysozyme (HEWL) crystals	MCr	PP	0.2	HEWL in NaAC and NaCl solutions	HEWL	–	–
[81,82]	Preparation of Enzyme Crystals	MCr	PP	0.2	Lyophilized bovine pancreas (BPT) and porcine pancreas (PPT) trypsins	Trypsins	–	–
[44]	Production of Paracetamol	MCr	PP	–	Solution of Paracetamol	Paracetamol	–	–
[67]	Antisolvent crystallization	MCr	PP	0.03	Solution of L-asparagine monohydrate	L-asparagine	–	–
[43]	Production of protein Hen egg white lysozyme (HEWL) crystals	MCr	PVDF	0.04	HEWL in NaAC and NaCl solutions	HEWL	0.1–4.5 [μL/(mm^2 h)]	–
[87,88]	Separation of a high-value pharmaceutical compound from waste ethanol	NF	PES and NMP-PES	–	G-1 in ethanol solution (impurities: Carbon disulfide, bromine, pyridine, etc.)	G-1	0–180 [L/(m^2 h)]	–
[89]	Recovery of the active pharmaceutical compound G-1	MCr	PP	0.04	G-1 and Vitrofural solutions	G-1	1.2-2.5 [mL/(m^2 min)]	1.36×10^{-12} [m/(Pa s)]
[110]	Preparing of concentrated solution of the curative salts	DCMD	PP	0.2	Zabłocka Thermal Brine	Mixture of salt crystals, wetted by a residual of solution containing the majority of iodine	50–1000 [L/(m^2 d)]	–
[83,84]	Production of fine solids such as catalysts, pigments, and pharmaceuticals.	Precipitation with membranes	PES PP	0.2 0.03	K_2SO_4 and $BaCl_2$ solutions	BaSO4	0.235 [m^3/(m^2 h)] –	– –
[68]	Production of crystals from sulphate and adipic water systems	MaC-RO	–	–	$(NH_4)_2SO_4$ water system and adipic acid	$(NH_4)_2SO_4$ and adipic acid	0.57-14 [kg/(m^2 h)]	–
[69]	Chiral purification of glutamic acid enantiomers	MCr	–	–	DL-glutamic acid monohydrate	D-glutamic acid and L-glutamic acid	–	–
[111]	Antibiotic wastewater treatment and recovery of antibiotics	RO-UF		3, 10, 30 and 50 KDa (UF)	Oxytetracycline (OTC) waste liquor	OTC	10–20 [L/(m^2 h)]	–

Membrane process: membrane assisted crystallization using reverse osmosis (MaC-RO), ultrafiltration (UF). Material: Polyethersulfone (PES), PES with N-methyl-pyrrolidone (NMP-PES).

Three main fields of applications are addressed in this section: recovery of brines and salty waters, production of high-value added compounds and treatment of wastewater. These are currently the most important fields and complementary discussions can be also found in literature [18,25,26]. Nevertheless, the integration of membrane devices with conventional and new technologies opens up a world of possibilities for more and/or new operating conditions and applications (see Section 3).

2.3.1. Treatment of brines and salty water

Since the optimal is both water production and brine recovery, crystallization of brines has been developed recently and several alternatives have been already proposed [28,34,54,55]. Results of main salt recovery applications are shown in Table 1. High fluxes over 25 L/m^{2}h were obtained by researchers [56–59] and different ranges of operating conditions have been applied: feed temperature between 60 °C and 80 °C [54], linear velocity of the feed flow varied from 0.3 to 1.4 m s^{-1} [60] or the study of impurities –$CaCl_2$, $KHCO_3$, $CaCO_3$, Na_2SiO_3- in a $CaSO_4$ solution [61]. Unfortunately, only few works show the mass transfer coefficient, which is the main parameter to do an exhaustive comparison between different researches. Besides, theoretical models [48,62,63] or economic [28,64] and energetic evaluation [64,65] are not presented in the majority of the works and further studies should be done to know the possibilities of reaching the industrial scale from laboratory results.

The recovery of water and NaCl from brines is a key issue in the recent research since desalination has been studied for a long time focused on both traditional and membrane-based technology (i.e. membrane distillation, membrane crystallization, nanofiltration, reverse osmosis). "Creusen et al. [28] reported the relationship between the water recovery and the concentration factor of different salts in brines membrane treatment. The integration of membrane distillation and osmotic distillation could allow both objectives, but the strongly dependence of the transmembrane flux (water recovery) and the crystal production on the amount of each salt and its solubility, requires a commitment. For instance, first steps of membrane distillation obtained 90% of water removal but only 4% of crystals ($CaCO_3$ and $CaSO_4$ were the first salts to precipitate). Meanwhile, final osmotic distillation steps produced only 10% of water but the largest crystal production (being the NaCl the 77% of the total). Thus, the compromise between both goals would determine the energy consumption and overall costs (membrane area required, operating costs).

Chen et al. [55] proposed a zero salty water discharge by means of continuous membrane distillation crystallization (CMDC) that combines direct contact membrane distillation with crystallization. It was observed that a decrease in water and NaCl production occurs when the permeate flowrate decreases and the permeate temperature increases, under the studied conditions. The increase in the temperature and the flowrate of the feed showed a maximum because of a complex interaction between the membrane distillation unit and the crystallizer. According to the authors, high feed flowrates decline the residence time in the crystallizer avoiding salt crystallization and therefore, reducing the NaCl production. This in turn increases the concentration in the effluent stream, which is recycled, decreasing the water production flux. High temperatures caused an increment in the cooling load of the crystallizer and thereby crystal production flux reduces. As previously said, water flux also declines.

Simultaneous integration of membrane distillation with a cooling crystallizer (named simultaneous membrane distillation crystallization system) was proposed by Edwie and Chung [34], where the highest yield of NaCl is 34 kg m^{-3} after 200 min working at 70 °C.

2.3.2. Production of high-value added compounds

Investigation and innovation related to pharmaceutical development, production and distribution becomes imperative to improve universal access to health care and feeding and therefore, life quality. Drugs and high-value added products are traditionally obtained in batch reactors where crystallization often is present in separation and purification stages in order to obtain solid products. Recent studies focused on pharmaceutical production with membrane technology and some recovery applications are also reviewed in this work. Proteins [41–44,66,67], organic acids [68–70] or inorganic salts [71–74] are few examples. A collection of the principal conditions and results of high-value products applications is shown in Table 2.

Recovery applications in active pharmaceutical compounds are also present in the recent literature. Brito et al. [75–77] studied the recovery of 1-(5-bromo-fur-2-il)-2-bromo-2-nitroethane (named G-1) from waste aqueous solutions using membrane crystallization. They studied different parameters as concentration or flow rates in order to optimize transmembrane fluxes. They included a brief economic evaluation and showed the mass transfer coefficient obtained, two important issues that are often missed. Crystals obtained have the same morphology as the commercial G-1, thereby confirming that the recovery by membrane crystallization can be considered as a novel technique with high potential to recover pharmaceutical compounds from waste streams.

2.3.3. Treatment of wastewater

Membrane crystallization via membrane distillation emerges as a powerful technology to replace or complement the current technology, in many cases, technically obsolete or not appropriate enough for the new application fields. For this reason, environmental approach becomes essential since industries are forced to increasingly satisfy restricted requirements. Both greenhouse gases and pollutant disposals requires intensive treatments and membrane crystallization may be a way to valorize the waste streams.

New water plants use membrane technology (i.e. reverse osmosis) instead of conventional technology [78,79]. Nevertheless, desalination processes are mostly focused on achieving water and not in the disposal of brines from the process. It is a fundamental problem because the first practice usually is the discharge into the environment, a non-ecological habit [28].

Ions and salts, such as sulphates [31,80–82] and carbonates [83], are components that must be eliminated from the wastewater before the discharge into the environment. In Table 3, few examples are shown. Curcio et al. [80] studied the removal of sodium sulphate from aqueous wastes by means of membrane technology. It was employed a hybrid nanofiltration–membrane crystallization system to treat wastewater originated by the production process of base raw materials (Ni-H) for special rechargeable batteries. One of the main conclusions obtained was the demonstration that an integrated system exclusively composed by membrane technology can be implemented: a nanofiltration step to concentrate the solution and a posterior crystallization in a membrane module connected with a final crystallizer. Reasonably amount of crystals and good product quality were reached. Furthermore, clean water due to the recycling of treated water is also obtained. Meanwhile, a similar system is proposed by Li et al. [31] to recover Na_2SO_4. In this case, the approach is based on the use of reverse osmosis as a preconcentration stage.

The removal of some others components from industrial wastewater by membrane technology has been already researched such as pharmaceuticals, previously mentioned, organic pollutants or even precious metals [49]. Organic effluents are often treated by biological methods but it can be impeded if a high concentration of salts is present. Thus, Gryta [84] proposed the application of membrane distillation for the concentration of spent solution from heparin production as a previous step.

CO_2 capture by means of membrane processes is achieving exponential relevance in the last years. However, although CO_2 capture is a global issue, there is not yet a simple solution that can be applied in a global scale. The most extended capture method is absorption using amines (e.g. monoethylamine or MEA) but some drawbacks are present: large amounts of solvent due to the losses during the process [85], high

Table 3
Main studies on recovery wastewater. (*) Data obtained directly from the literature (explicit data or approximations by means of the figures).

Reference	Application	Membrane Process	Membrane type		Feed	Crystal product	J*	K*
			Material	Pore size (μm)				
[92]	Removal of sodium sulphate from aqueous wastes originated by the production process of base raw materials (Ni–H) for special rechargeable batteries	NF-MCr	PA	–	Solution of Na_2SO_4	Na_2SO_4	0.108–17.3 [L/(m^2 h)]	–
			PP	0.2			0.57–1.6 [kg/(m^2 h)]	–
[112]	Recovery of solid Microparticles from aqueous solutions	VMD	PP	0.2	Aqueous solution containing 10 wt% of polystyrene microparticles	Dry polystyrene	1–15 [kg/(m^2 h)]	–
[93,94]	Treatment of wastewater from ion-exchanger regeneration	DCMD	PP	0.22	Wastewater with ions: Ca, Mg, Na, K, Si, Cl^-, $SO_4{}^{-2}$	$CaSO_4$ and silicon compounds	104–532 [dm^3/(m^2 d)]	–
[30]	Recovery of Na_2SO_4 from aqueous solutions	RO-MCr	PA	–	Na_2SO_4 solution	Na_2SO_4	0.133 [L/(m^2 s)]	–
			PP	0.04			0.2–2 [mL/(m^2 min)]	$5.57 \times 10^{-11} - 1.25 \times 10^{-10}$[m/(Pa s)]
[95]	Remove ions from aqueous streams	MaC	–	–	Solution of $CaCO_3$	$CaCO_3$	–	–
[29]	Recovery of Na_2CO_3 from aqueous streams in CO_2 capture	MCr	PP	0.04	Na_2CO_3 solution	Na_2CO_3	0.25–2.25 [mL/(m^2 min)]	$6.53 \times 10^{-11} - 4.34 \times 10^{-10}$[m/(Pa s)]
[31]	Recovery of Na_2CO_3 from aqueous streams in CO_2 capture	MCr	PP	0.04	Na_2CO_3 solution	Na_2CO_3	0–1.6 [mL/(m^2 min)]	$(4.88 \pm 0.39) \times 10^{-11}$ [m/(Pa s)]
[101]	Recovery of Na_2CO_3 from aqueous solution in CO_2 capture	MaC	PP	0.04	Na_2CO_3 solution	Na_2CO_3	0.04–0.10 [L/(m^2 h)]	$8.00 \times 10^{-11} - 9.00 \times 10^{-11}$ [m/(Pa s)]
[113]	Recovery of Na_2CO_3 from aqueous solution in CO_2 capture	MCr	PA	–	Na_2CO_3 solution	Na_2CO_3	0–0.4 [L/(m^2 h)]	–

energy requirements to regenerate the solvent [86] critical operating limitations (e.g. emulsions, foaming) [87] and the high toxicity of the amines. Alternative technologies are thus a key issue in the development of processes for CO_2 capture [50]. The research on membrane technology focused on CO_2 capture started around 1990 and since then, great advances have been obtained: higher mass transfer coefficients, new materials for membrane synthesis, integration of membrane-based technology, etc. [88]. Consequently, an interesting approach has been recently proposed: the reuse of CO_2 as carbonates to be used as raw material, such as the Na_2CO_3 produced after the reaction with NaOH and that can be crystallized with membrane crystallization [30,32,89]. To do this, a membrane contactor is used. Here, the only role of the membrane is to increase the surface available for the mass transfer exchange between both phases by the action of a driving force [90] and thus, the principal parameter to evaluate the process is the overall mass transfer coefficient. Results confirmed that obtaining Na_2CO_3 crystals with commercial purity is technically possible and it can be concluded that the use of a membrane integrated system to valorize CO_2 provides a new alternative to the conventional absorption method using amines. Besides, most of works focused in this topic collects the mass transfer coefficients which characterizes the system and allows a better knowledge for further improvements and challenges.

Fig. 3 collects the main approaches to be taken into account in membrane crystallization regarding the flow of the material from an environmental point of view. A substantial reduction of the solid waste coming from the solute rejection could be found by performing crystallization. Although the physical barrier of the membrane contactors would be enough to achieve this purpose, the integration of other membranes, such as the ones with selectivity to certain compounds, would open a bigger chance for new applications and higher yields. Consequently, a more specific crystal production would be carried out.

In this stage, both solute and solvent have the opportunity to be incorporated in other processes as raw material or auxiliary services. Many examples can be addressed: permeate can be recirculated in the same process to improve the yield, setting the operating conditions or even cleaning the system; crystals may be involved in ceramic applications or as additives in food industry; and treated water can be reused depending on the quality of it. The lowest-quality water is used as utility for refrigeration and as much as the purity and conditions becomes better, it can be applied for irrigation purposes or even human consumption.

Although the energy used in membrane crystallization is already much lower than the traditional process (e.g. membrane distillation versus common distillation/azeotropic distillation) [19], a step forward can be done by focusing on two perspectives: 1) the use of feed solutions already warm because the heating has been irretrievably carried out for previous steps in the process and, 2) heat exchange between streams. These two ways lead to undoubted economic savings and environmental improvement of the process [65].

Unfortunately, researches about membrane distillation and membrane crystallization have historically focused in mass transfer more than in energy transfer and therefore, few studies analyze the energetic (and/or exergetic) implications. Consequently, more efforts should be done in this stage in order to clarify the environmental issues.

3. Further development of membrane distillation

Economic viability implies the need to integrate the crystallization as a purification and/or separation stage in existing (or new) processes and to make a comparative analysis between current technologies and membranes as alternative. Therefore, membrane intensification and integration as well as the multiple applications in chemical and environmental industry are addressed. But, in order to go a step further, it is necessary first to analyze the possible difficulties, in terms of process performance, that may appear.

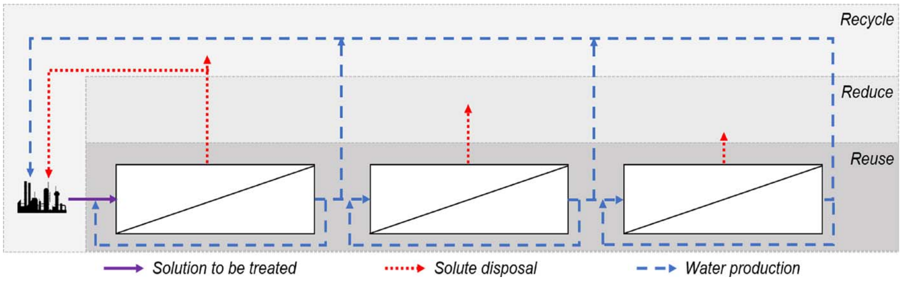

Fig. 3. Environmental approaches in a membrane system.

3.1. Technical obstacles

Besides the mass transfer resistance offered by the membrane, a decrease of efficiency may appear due to concentration or temperature polarization, membrane wetting, scaling and fouling. Those phenomena will lead to a reduction of the transmembrane flux or even the block and damage of the membrane in the case of scaling and fouling.

Membrane wetting in contactors is produced when liquid enters into the pores, preventing that the mass transfer takes place in gas phase. Thus, an extra resistance appears, decreasing the flux [23]. In consequence, membrane is not working efficiently and therefore, supersaturation level is reached in a longer time.

Wetting is caused due to the affinity between the liquid and the membrane material. If there is a good affinity between them, liquid droplets will have a tendency to form in the pore. Here, liquid entry pressure (LEP) commonly determines the presence or absent of wetting. If the operating pressure is above the LEP, wetting will occur. Therefore, the prevention of wetting comes from having the highest LEP possible and not exceeds it. This factor is influenced by the contact angle (θ) between the liquid (solvent) and the solid (membrane), the size of the pore and the surface tension. The more the liquid will have a strong affinity with the solid membrane, lower the surface tension between them will be and then the contact angle too, which will favor droplets formation and wetting [25]. Contact angle is also directly related with the type of nucleation of crystals. Thus, if the solutions wets the membrane completely ($\theta = 180^\circ$), the energetic barrier to heterogeneous nucleation is the highest; whereas 90° is the limit between hydrophobic and hydrophilic character [19]. Consequently, the choice of hydrophobic/hydrophilic character of the membrane and the kind of solution used are key parameters.

Besides, some other properties coming from the kind of membrane material, such as the thermal conductivity and the thickness, have important effects in mass and heat transfer. For instance, polymer materials have a poor thermal conductivity which usually is 100–1000 times lower than metals ($0.11\ \mathrm{W\,m^{-1}\,K^{-1}}$ for PP vs $401\ \mathrm{W\,m^{-1}\,K^{-1}}$ for copper). Although this weak point is partially compensated with the high surface area and the cheap cost, it is needed to develop composites including metals and/or ceramic particles into the polymers [33]. Regarding the thickness of the membrane, an opposite behavior is found: the thinner the membrane, the higher the permeability but with lower heat efficiency because heat loss by conduction occurs through the membrane matrix. The optimum thickness has been estimated within the range of 30–60 μm [26].

Polarization is the concentration or temperature gradient that appears between the bulk fluid and the membrane [27,46] in both sides of the membrane due to the lack of turbulence that allows mixing. If this effect becomes stronger, scaling may be produced because of crystal deposition on the membrane surface [25,26,54] or spontaneous wetting of the membrane may appear causing an increment of the overall resistance to mass transfer [23]. Polarization is a phenomenon mainly related to fluid dynamics. The only way to reduce it is to generate enough mixing and turbulence in the flow to decrease the thickness of the boundary layer. To do that two options exist: 1) increasing the flow rates [31,32] but this increment cannot produce an operating pressure above the LEP to prevent wetting or 2) including spacers promoting turbulence [91].

Scaling, characterized by the accumulation of inorganic salts in the membrane surface, is highly significant and if the issue continues over time severe dangers could be produced to the membrane until make it unusable. This problematic, linked to fouling (the deposits are mainly composed by organic material and microorganisms −biofouling) has been deeply taken into account by the researchers [39,56,57,60–62,92–97]. However, the effect of fouling and scaling may differ because of the multiple and diverse membrane systems. Scaling in membrane distillation is highly known and occurs as follows: first, the membrane surface is lightly covered by deposition and adsorption of scaling. At this moment, flux does not suffer a huge decrease because open pores are still available but if deposition increases, pores can be partially or total blocked. Besides, some pores can also be wetted due to the hydrophilic character of most fouling scaling. Consequently, the difference in water vapor pressure across the membrane is significantly reduced and, therefore, lower water vapor flux is obtained [94,95,97]. Membrane wetting and fouling were studied by Ge et al. [96] using hollow-fiber PVDF membranes to concentrate reverse osmosis brine in a direct contact membrane distillation process. It was found that when temperature feed was increased, membrane fouling and wetting also did and, therefore, flux and salt rejection decreased; when low feed temperature was used, the induction time for $CaSO_4$ crystallization may increase. Besides, when the feed flowrate was enhanced, flux became higher. But if the flowrate is too high, wetting may appear. Consequently, both temperature and flowrates control required special attention for having an efficient process. Alternative proposals have been also studied. As an example, Chen et al. [95] proposed the introduction of gas bubbling into membrane distillation process (NaCl solution as feed). It could significantly reduce the scaling resistance, due to the high shear stress induced by gas bubbles and the removal of tiny deposited crystals from the membrane surface. Nevertheless, the incorporation of supplementary membrane cleaning techniques is still necessary for effectively restoring the membrane performance as the scaling layer matures.

Many researchers focused their studies in membrane material properties, including modifications in their systems and devices leading to find new and better conditions. Thus, some of them developed new membranes by incorporating additives. Edwie and Chung [54] compared three different membranes to determine the influence of the layers involved (one or two) and the hydrophobic/hydrophilic character. Compared to dual-layer membranes, once the water purity and the permeability was observed, they concluded that the single-layer PVDF membrane resisted the wetting better than the other two membranes. He et al. [97] included a fluorosilicone coating on the porous polypropylene hollow fiber membranes and it was demonstrated to be helpful to eliminate membrane scaling during direct contact membrane distillation. Meng et al. [39], after developing hybrid membranes from PVDF ones, concluded that the overall flux for the PVDF-PDTS membrane (PVDF membranes coated with TiO_2 and fluoro-silane compounds) was lower compared to virgin and PVDF-FTCS membranes. This is due to its lower global heat and mass transfer coefficients. Higher crystal yields were achieved with virgin membranes due to more

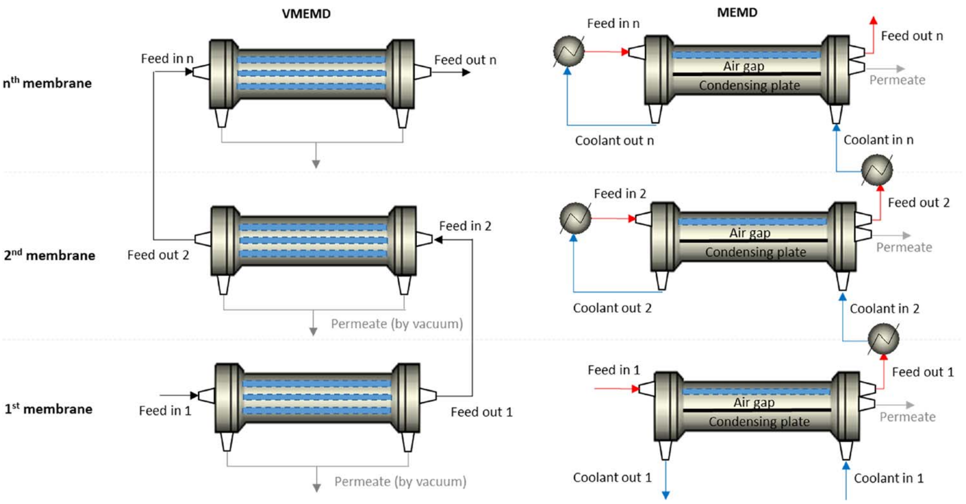

Fig. 4. Integrated processes in membrane distillation: multi-stage and multi-effect membrane distillation (MEMD) and vacuum multi-effect membrane distillation (VMEMD).

intimate interaction between the feed solution and the membrane surface.

It can be concluded that there is not a general solution for the eventual technical obstacles. Some recommendations are collected in function of a concrete application, defined by specific operating conditions and a kind of membrane contactor. This is due to the fact that the improvement in one variable may play against of another one.

3.2. Intensification and integration in membrane processes

In the chemical industry, two strategies are commonly used to develop new and more efficient processes: intensification and integration. Process intensification seeks to develop safer processes with very high efficiencies of equipment, reduce sizes thereof and operating costs, generate the least amount of waste and get the larger quantities of products with the least amount of raw material. On the other hand, the approach of the process integration is focused on the process design that emphasizes the unity of the process, and considers the interactions between different operating units from the beginning, rather than optimize separately [98].

With this philosophy, some researchers have developed hybrid processes incorporating reactors or microwave systems. In a study by Phattaranawik et al. [64] membrane distillation in a submerged membrane bioreactor (MDBR) has been experimented for wastewater reuse in order to produce high quality permeate in a single-step. Water was removed from the bioreactor by a thermally driven process across the hydrophobic membrane and the temperature of the bioreactor was adjusted in the range 40–60 °C, determined by the activity of thermophilic bacteria, to provide high water vapor pressure.

Microwave vacuum membrane distillation (MWVMD) was preliminarily investigated [99]. The results showed that microwave irradiation could effectively induce uniform heating in the radial direction of the membrane module, and significantly improve the mass transfer process of vacuum membrane distillation.

In addition, since membrane distillation can be operated at low temperature, renewable energy or waste heat (heat integration using Pinch analysis) can be used in order to increase the sustainability of the process [100]. Solar collectors can be used to provide the heat (solar thermal) or electrical energy (solar photovoltaic) requirements to operate a membrane distillation system [101,102] and pumps can be powered by wind generator [27].

As previously stated, this kind of technology allows large operational pliancy (i.e. gas and liquid flow rates can be independently controlled). Besides, since it is modular equipment, a linear scale-up is allowed and several membrane contactors can be connected. Thus, contactors are assembled in series and/or parallel configuration leading to a desired purity and/or amount of crystals. Pressure drop acquires special relevance due to the fact that a pressure limitation exists (the LEP afore mentioned). For this reason, an optimum, normally a combination of both series and parallel mode, must be found. Nevertheless, velocity decreases when more and more contactors are adding; the more (and bigger) devices the more membrane area, and therefore, investment cost [19]. Despite this, modular configuration of membrane contactors is advantageous against other technologies that cannot adjust easily its equipment to production requirements, having sometimes underutilized equipment or even incapacity to fast answer market demanding. Furthermore, membranes are clearly part of intensification technologies; comparing with conventional equipment such as mechanically agitated columns, membranes offer a surface area per volume between 3 and 40 times bigger [22]. All these questions are present in practical applications already investigated.

For example, in the review elaborated by Wang and Chung [29], multi-stage and multi-effect membrane distillation (MEMD) and vacuum multi-effect membrane distillation (VMEMD) configurations are considered. Multi-effect membrane distillation uses the feed as coolant as well by means of exchangers placed between correlatives membrane contactors. In vacuum multi-effect membrane distillation, feed crosses consecutive membranes while water is removed from each stage. Both configurations are shown in Fig. 4.

The operational management of membrane contactors also allows the development of whole membrane integrated systems including microfiltration, reverse osmosis or even crystallizers or precipitators [65,103]. Thus, possibilities of crystallization increase since the capacity of the system to remove water also does. Due to the fact that industrial crystallization applications are extremely extended and the availability of membrane devices and its multiple choice combinations, membrane technology is becoming an essential area in expansion and an interesting alternative to traditional equipment.

Zarkadas & Shirkar [104] demonstrated how process intensification can be implemented using membrane crystallization instead of conventional systems. In their study,L-asparagine monohydrate, used in leucemia treatments, was obtained using porous hollow fiber antisolvent crystallization and compared with traditional equipment: mixed-suspension mixed-product removal (MSMPR) crystallizers, batch stirred crystallizers and tubular precipitators. Authors concluded that runs with crystallization in the shell side could be considered successful instead of the lumen side ones, where the operation was characterized by a decrease of the permeation rate of the antisolvent and consequently the supersaturation generated with time. Besides, better crystallization control and comparable nucleation rates were obtained regarding the traditional systems employed to produce L-asparagine. Furthermore, hollow fiber device offers a large area per volume in a very small scale and promotes homogeneous concentration conditions without using large amount of energy.

Crystallization of organic acids can be done using hybrid process replacing rude devices where the control or the operating parameters is not always easy. Adipic acid crystallization was reported by Lakerveld et al. [68] and one of the main conclusions obtained was that the energy consumption of the integration of membrane crystallization with reverse osmosis is an order of magnitude lower compared to conventional evaporative crystallization in systems with moderate to low solubility (in terms of molar concentration). Therefore, both systems can be considered as complementary as optimal solubility characteristics for both processes are not overlapping. The energy efficiency of membrane technology integration is corroborated by Macedonio et al. [65]. They showed that besides producing salts of good quality and fresh water, the membrane crystallizer unit increased the plant recovery until 92.8%, higher than that of an reverse osmosis unit alone (about 40%) and much higher than that of a conventional multi-stage flash distillation (about 10%). Furthermore, regarding the energy consumption for several technologies, differences are quite large: 1.1 and 3.5 $\mathrm{KW\,kg^{-1}\,h^{-1}}$ in VMD and DCMD units, respectively [105]; 1–10.24 $\mathrm{KW\,kg^{-1}\,h^{-1}}$ in reverse osmosis (for different water qualities), 16–125 $\mathrm{KW\,kg^{-1}\,h^{-1}}$ in multi-stage flash distillation; 32–122.5 $\mathrm{KW\,kg^{-1}\,h^{-1}}$ in multi-effect distillation (MED) [106,107].

Meanwhile, Svang-Ariyaskul et al. [69] obtained glutamic acid crystals in a purification process using a hollow fiber membrane module. The major advance in the work is a demonstration of a novel hybrid process in which pure crystalline enantiomers are produced at high yield from a racemic mixture (D and L glutamic acid). Fumaric acid, from recovery proposal of Curcio et al. [70], is used both in the pharmaceutical industry and the food production. Authors used the membrane crystallization in order to recover the unreacted fumaric acid present in the outlet stream coming from a membrane bioreactor for the synthesis of L-malic acid.

Finally, a hybrid process may be necessary to achieve the required treatment specifications and/or to overcome possible limitations of self-stand membrane contactors. One example is scaling prevention. Anisi et al., 2017 [106] reported that achieving a certain level of supersaturation in the solution by using sweeping gas membrane distillation before adding seeds in the membrane-assisted crystallizer allowed crystal growing far from the membrane surface. Besides this, a temperature difference between the crystallizer (30 °C) and the buffer vessel buffer (50 °C) was applied. This produces a solubility difference in the solute, keeping the solution undersaturated throughout the experiment and avoiding crystal deposition on the membrane. A similar approach was employed by Lakerveld et al., 2010 [68], where a buffer vessel was used as intermediate between the crystallizer and the reverse osmosis membrane. In this case, two ways were followed to prevent the scaling. On one hand, authors kept a temperature difference between the crystallizer and the buffer vessel. On the other hand, a crystal free solution was circulated at high flow rate through the membranes to remove solvent and minimize concentration polarization and prevent crystal deposition. In addition to scaling prevention by playing with operating conditions, Wang and Chung [29] concluded that investigation in membrane material could improve the resistance to fouling/scaling for both organic and inorganic matter.

4. Conclusions

Membrane crystallization using membrane distillation has been briefly evaluated in order to give an overview about technical considerations and to show the eventual perspectives of the technology.

Membrane crystallization reveals important advantages against the traditional crystallization due to the easy scale-up and good crystallization control. Operating conditions such as temperature and feed flowrate requires special attention because the optimization of those parameters and the minimization of technical obstacles (polarization, wetting, etc.) imply the compromise between the best efficiency in terms of transmembrane flux and the best efficiency in terms of membrane contactor performance. The higher the temperature and flowrate, the higher the flux but also the possibility for wetting appearance. On the contrary, when temperature and flowrates are low, the energy consumption decreases but the fluxes also do and polarization and scaling may occur. Besides, although membrane incorporates an extra resistance to mass transfer, it also gives a surface which favors the heterogeneous nucleation. But, solute deposition on the surface may produce scaling and fouling.

It can be concluded that there is not a unique solution for all operating problems. For instance, a general approach for wetting prevention is that the liquid entry pressure cannot be exceeded and, therefore, membrane materials with low water-membrane surface affinity are required (high hydrophobicity). But, in the case of scaling or fouling, it depends more on the specific application and system. Inhibitors, gas bubbling, seeds on the crystallizer, new coatings on membranes or enhancing the turbulences on the fluid (high flowrates, spacers, etc.) are reported in literature as improvements.

This review reveals that membrane technology is mainly extended in desalination applications and last steps of common processes (i.e. purification). However, recent research is addressing the application of this technology for recovery of waste streams is technically viable and its incorporation as a fundamental technology is possible into the green economy (e.g. CO_2 capture). Besides, membrane technology is usually focused on water production but solid recovery (solutes) is often neglected as a non-relevant issue. Few works reported the double objective of water production and solute recovery and this should be noted by researchers in order to reach a truly sustainable process or industry.

In terms of key membrane concepts, it must be highlighted that some important parameters, such as the mass transfer coefficient, are missing in the majority of the studies. The presence of this kind of parameters in all the works would allow develop a more complex overview incorporating an exhaustive comparison between the principal factors affecting them: operating conditions and membrane characteristics.

In addition, the large variety of membrane distillation systems and the potential of intensification and integration becomes this technology as alternative to conventional crystallization. This is due to the facility to use waste raw (e.g. brines in osmotic distillation) and energy (e.g. heat streams in direct contact membrane distillation, cool streams in air gas membrane distillation) coming from other processes to be used as driving force.

Finally, the technical viability of this technology is not enough if the objective is to achieve the industrial scale. Despite the fact that some works include an economic and energy study, most of them ignore it and therefore, steps must be taken in this field. Thus, future researches including these aspects are needed to achieve a system with real implementation in the industry.

Operating conditions have been largely studied in membrane crystallization for decades and few real novelties may be found regarding the current performance. For this reason, two approaches should be followed, leading to finally reach the industry scale: on the one hand, research should focus on the intensification and integration of membrane technology with other systems; on the other hand, material science should receive the attention in next years in order to overcome and/or minimize the current technical obstacles.

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