



Review Paper

Progress of Membrane Engineering for Water Treatment

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- Membrane processes for water recovery
- Membrane distillation and crystallization in desalination
- Membrane condenser for water and chemical recovery from atmosphere

Abstract

Together with the supply of energy and the environmental protection, fresh water is one of the three keys elements for the sustainable development of every society. Where the availability of water cannot be carried out by using conventional sources, unavoidable appears the resort of the major water source: the sea. Today, RO is one of the most used membrane processes for the production of fresh water from seawater and brackish water, reclamation of wastewater and the treatment of various industrial wastewaters. Further improvements can be achieved via the integration of reverse osmosis with other membrane operations, such as membrane distillation and membrane crystallization. The integrated system can lead to important benefits in terms of product quality, compactness of the system, environmental impact and energy consumption. In this work, first a brief introduction to RO process and recent developments will be given. Then, the status and development of membrane distillation and membrane crystallization will be illustrated. Finally, membrane condenser (i.e., another innovative membrane process for water recovery and reuse based on the use of porous hydrophobic membranes) will be described.

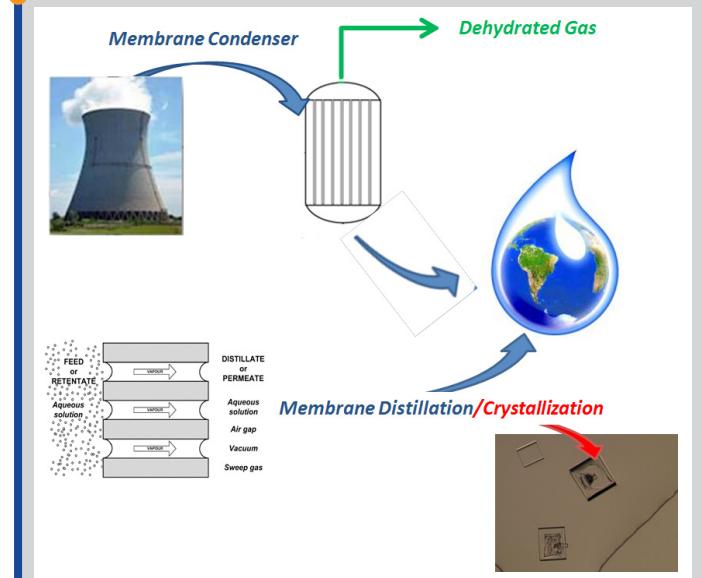
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Graphical abstract



1. Introduction

Membrane engineering has already provided interesting solutions to some of the major problems of our modern industrialized society. Membrane techniques are essential to a wide range of applications including the production of potable water, energy generation, tissue repair, pharmaceutical production, food packaging and the separations needed for the manufacture of chemicals, electronics and a range of other products. However, water treatment is the sector that accounts for the majority membrane application. Actually, growing global demand for WATER makes membrane filtration the prominent technology in desalination and wastewater treatment: the global cumulative contracted capacity, dominated by Reverse Osmosis (SWRO), reached 104.7 million m³/day in 2018 [1], and membrane desalination technologies account for more than 90% of all desalination plants [2]. Despite the enormous success of membrane desalination technology, improvements are still required in terms of desalinated water cost, higher productivity (that means higher water recovery factors), better water quality and enhanced eco-sustainability of the desalination process.

In this work, first a brief introduction to RO process and recent developments will be given. Then, some of the main innovative membrane processes for water recovery and reuse from alternative water sources (such as the brine streams of the desalination plants, the plume of the cooling towers, etc.), based on the use of porous hydrophobic membranes, will be described. In particular, the status and development of membrane distillation (MD), membrane crystallization (MCr) and membrane condenser (MCo) will be illustrated. The aim is to illustrate the main characteristics and development of the membrane operations that are either more widespread (i.e., RO) or highly innovative (i.e., MD, MCr, MCo) in the important sector of water production.

Membrane Distillation (MD) is a thermally-driven technology for removing volatile components for solutions and therefore useful for desalting highly saline waters. The driving force is the difference of vapour pressure existing between the two membrane surfaces. It forces only volatile molecules to pass through a porous hydrophobic membrane [3–5]. Membrane assisted crystallization (MCr) is an extension of MD where the continuous evaporation of volatile components from the feed (with a high concentration of solute) generates a supersaturation of the solute. This phenomenon, with a simultaneous separation and purification of chemical species from the solution, allows the solute to precipitate in an orderly way, forming well-defined crystals [6–8]. Furthermore, the surface structure of the membrane promotes heterogeneous nucleation because it may trap solute molecules in its cavities, thus leading to a localized supersaturation, which encourages nucleation and crystals formation at supersaturation conditions [4,9,10]. The crystallization has been applied in food, pharmaceutical, chemical and environmental divisions [3,4].

Subsequently, the new and innovative membrane condenser will be introduced. It allows the recovery of clean water from waste gaseous humidified streams and/or it can be used for pre-treating gas streams that have to be fed to another membrane unit for CO₂ separation [11–14].

2. Membrane-based desalination systems

2.1. Reverse osmosis

Reverse osmosis (RO) is the most commonly used technology for the recovery and production of fresh water from seawater, brackish water and wastewater. Over the last few decades, this technology became successful because it has the highest water recovery factor, the lowest energy consumption and the lowest water cost with respect to any other conventional distillation process [15].

RO uses semipermeable membranes with excellent separation performance and good chemical stability [16]. The water to be treated is pushed into the membrane module by a pump, which exerts a pressure higher than the osmotic pressure of the feed water so as to allow pure water to pass through the membrane, while the remaining part comes out with a high salt concentration, due to the retention of all the components that did not cross the membrane. The separation takes place thanks to diffusion and dissolution mechanisms, which intervene in varying degrees and allow action up to ionic level. The performance of the membrane depends on the membrane structure, membrane material as well as on temperature and concentration of feed. As a matter of fact, feed osmotic pressure increases with the growing of the last two feed parameters as indicated by the following Van't Hoff's law (valid for dilute solution):

$$\Pi_s = -\frac{n_s}{V} R T i \quad (1)$$

where Π_s is the osmotic pressure, n_s is the total amount of moles of solutes in solution, R the ideal gas constant, V the volume of solvent and i Van't Hoff's coefficient.

Current state-of-the-art SWRO plants consume between 3 and 4 kWh/m³ and emit between 1.4 and 3.6 kg CO₂ per cubic meter of produced water [17–20], depending strongly on the fuel used to produce the electricity. The thermal desalination technologies, less efficient, generally emit between 8 and 20 kg CO₂/m³, with the exception of stand-alone MED at 3.4 kg CO₂/m³. As small as these numbers may appear through a global lens, they can be large in regional grids and ecosystems. In term of costs, energy consumption is one of the main cost components in RO desalination [21–24] even if concentration polarization and membrane fouling are Achilles' heel of this membrane process. Concentration polarization is the result of the selective transport of some species through the membrane. Retained species accumulate in front of the membrane and might cause the creation of a concentration gradient between the solution at the membrane surface and the bulk. This leads to a back transport of the material accumulated at the membrane surface by diffusion. The direct consequence of concentration polarization is the reduction of both water flux and rejection. Membrane fouling is due to the dissolved, colloidal or biologic matter that can accumulate at the membrane surface, building a continuous layer that reduces or inhibits mass transfer across the membrane. For efficient RO desalination, an adequate pre-treatment, supplying high quality feedwater is essential. Notable examples of very productive and large seawater reverse osmosis (SWRO) desalination plants are the ones in the Middle East (such as the Sorek SWRO desalination plant), United States (such as the Carlsbad Desalination SWRO Plant in San Diego County), Oman (such as the Al Ghubrah plant or the Barka IWPP expansion –both SWRO), United Arab Emirates (for example the Al Fujairah IWPP expansion).

The further improving of SWRO desalination processes require high-permeability and/or antifouling membranes. Recently, the application of nanotechnology and biotechnology to membrane fabrication has heralded a new generation of RO membranes, whose water permeabilities potentially surpass conventional polymeric membranes by several orders-of-magnitude. Examples can be found in the carbon nanotube- (CNT) and other carbon-based membranes (like graphene and graphene oxide), as well as in inorganic membrane, mixed matrix membranes and biomimetic membranes. These are emerging as developed membranes with superior permeability, durability and selectivity in particular for water purification.

2.2. Membrane distillation

A membrane process with high potentialities in seawater desalination is membrane distillation (MD). Whilst RO is a pressure driven membrane process, driving force in MD is the partial pressure difference between the two sides of a microporous hydrophobic membrane which generates a mass transport of volatile components through the membrane pores. MD has been applied for desalination [25–27] and for the treatment of aqueous solutions with different concentration of non-volatile components, such as wastewater treatment, groundwater and drinking water purification, production of chemicals, concentration of fruit juices, removal of water from blood and protein solutions in biomedical industries, removal of dyes in textile industries, removal of boron and arsenic from aqueous solutions, etc. Theoretically, MD can reject 100% of the non-volatile components from the feed solution. In fact, the volatile components, at high temperature, spread from bulk to the boundary layer of the feed, vaporize at the liquid / vapor interface, and pass through the pores of the hydrophobic membrane. At permeate side, the water vapor molecules condense at the vapor/liquid interface. Depending on the type of condensation used, we can distinguish different MD configurations: *Direct contact* (DCMD) where a current of cold distilled water is in direct contact with the permeate membrane side [5,25,28–30]; *vacuum membrane distillation* (VMD) where the vapour phase is vacuumed from the liquid through the membrane, and condensed, if needed, in a separate device [31–33]; *Sweep Gas Membrane Distillation* (SGMD) where an inert gas, in general air or nitrogen, sweeps through the permeate side carrying the evaporated molecules outside the membrane module for condensation [4,34,35]; *Air Gap Membrane Distillation* (AGMD) where an air gap is interposed between the membrane and a cold condensation surface thus substantially reducing the conductive heat loss through the membrane [36,37].

The main advantages of MD, compared with the traditional RO, are the lower operating pressure, the theoretical ability to achieve 100% salt rejection, the reduced influence of concentration polarization phenomenon. The latter offers the possibility to apply MD to high temperature and/or high concentrated solutions with which RO cannot operate due to the osmotic

phenomena.

Since last decade or so, a “research boom” has been observed in various aspects of MD. Recently, some companies have been involved in commercialization efforts for MD. Example can be found either in the MD distillation plant delivered by Aquaver to the small island of Gulhi, the Maldives [30] or in the MD pilot systems developed by AQUASTILL [172].

Until now, the fundamental barrier in widespread application of MD is the unavailability of appropriate membranes for MD applications, with proper thickness, porosity, mean pore size, pore distribution and geometry as well as with good thermal stability, excellent chemical resistance to feed solutions and stable hydrophobic character over time. Due to the broad spectrum of membrane features required for an appropriate MD membrane, several materials have been tried, both polymeric and ceramic, as well as graphene-based membranes [38], thermally rearranged polymers [39], two dimensional (2D) membranes (with for example zeolites, mixed-organic frameworks, bismuth chalcogenides [40], etc.). The current main challenges for the commercial scale implementation of these membranes include limited available techniques for exfoliating the high aspect ratio and intact nanoporous monolayers from bulk crystals, drilling of the pores with required characteristics (uniform, high-density, large-area, subnanosized) in membrane matrix and scaling up of these atomic scale membranes into real scale separation devices [41].

Another important characteristic of MD membrane material is its thermal conductivity that has to be as low as possible in order to prevent heat loss through the membrane.

Traditionally, the commercial membranes widely used in MD are polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinylidene (PVDF), eventually with special coatings to improve MD performance [42].

Table 1 reports various data from literature of trans-membrane flux as achieved in different MD configurations, utilizing various membrane materials and different feed compositions. As it can be observed, the values changes largely: from 0.6 LMH for ceramic tubular membranes in DCMD to 20LMH for ceramic hollow fibers in VMD [4]. At the beginning, for practical reasons, membranes were fabricated in flat sheet configurations. The flat membranes can be assembled in spiral-type membrane modules that are ideal for minimizing footprint because this design tries to maximize surface area in a minimum amount of space. On the other hand, however, this type of structure, given its shape, cannot be used for any type of material, such as ceramic membranes that are not prone to be moulded [43–55].

Conventionally, MD has been considered for desalination purposes as an alternative to RO or to overcome limited recovery of RO and other thermal desalination techniques [61]. However, due to the separation principle different from the traditional pressure driven membrane processes and to

lesser fouling tendency, a lot of other interesting applications of MD have been explored, such as for processing of temperature sensitive products (pharmaceutical compounds, juices, dairy products, natural aromatic compounds, etc.), for the treatment of nuclear water, produced water [62,63] and wastewater [64]. Similarly, the potential of MD for removal of heavy metals, such as boron, from drinking water has been established at lab scale [65].

2.3. Membrane crystallization

The evaporative mass transfer of volatile solvents through microporous hydrophobic membranes under a partial pressure driving force is utilized not only in MD but also in membrane assisted crystallization (MCR) technology. The aim of MCR is to concentrate feed solutions above their saturation limit, thus attaining a supersaturated environment where crystals may nucleate and grow [30]. In a MCR, the membrane allows the precise control of the removal of solvent from the crystallizing solution. Moreover, membrane morphological and physicochemical properties (such as pore size, porosity, roughness, thickness, hydrophobicity) can be used to control the crystallization kinetics. These aspects are mutually related: the intensity of transmembrane flux affects the level and the rate of supersaturation generation and, consequently, the heterogeneous nucleation rate. Therefore, depending on the chemical–physical properties of the membrane and on the process parameters (temperature, concentration, flowrate, etc.), the solvent evaporation rate, and hence supersaturation degree and supersaturation rate, might be regulated very precisely. The effect would be the control of the nucleation and growth rate by choosing a broad set of available kinetic trajectories in the thermodynamic phase diagram, that are not readily achievable in conventional crystallization methods, and which would lead to the production of specific crystalline morphologies and structures.

The crucial requirement of a MCR is to avoid crystals deposition or accumulation on the membrane surface and inside the membrane module. On an engineering point of view, this aspect is controlled through a proper choice of operative conditions (in particular of the temperature and the flow rate of feed solution).

From a process design point of view, the membrane can be applied for a membrane assisted operation (i.e. on a mixture recirculating loop), or directly for in situ crystallization purposes. The first case can be seen as a typical hybrid process approach and it is shown in Figure 1a). The membrane module is here used to generate the supersaturation, or simply to concentrate the solid phase, but the nucleation and the crystal growth take place in the crystallizer (e.g. [66,67]). In the second case (Figure 1b), the crystallization takes place directly in the membrane module where the supersaturation is generated [68–70].

Table 1
Membrane distillation performances in literature.

Membrane material and/or code	Membrane configuration	MD operation mode	Feed	Feed flow rate [L/h]	Perm flow rate [ml/min]	Temperature feed [°C]	Temperature perm [°C]	Flux [L/(m ² *h)]	Ref.
PVDF	flat sheet	DC	1% NaCl	27	7.5	81.6	19,8	13.17	[43]
PVDF-H	hollow fiber	DC	1% NaCl	27	7.5	85,4	16,6	14.21	[43]
CM-L	Tubular	DC	Pure water	18	60	50	17,5	0.6	[4]
CM-L	Tubular	Vacuum	1 M NaCl	18	n.a.	47,5	n.a.	1.3	[4]
CM-S	Hollow fiber	Vacuum	1 M NaCl	8.4	n.a.	50	n.a.	20	[4]
AD60/PVDF	hollow fiber	Vacuum	35 g/L NaCl	120	n.a.	70	n.a.	10	[56]
PDMS-PVDF	flat sheet	Vacuum	20 g/L NaCl	0.6	n.a.	50	n.a.	15.4	[57]
PP Accurel S6/2 MD020CP2N	Hollow fiber	DC	Distilled water	11.5-26.3	23.4	80	20	8.56-6.36	[58]
PE	Hollow fiber	DC	35g/L NaCl	75	200	60.5		0.24	[59]
PE	Hollow fiber	Vacuum	35g/L NaCl	75	n.a.	60.5		1.11	[59]
PFS/anodics	Flat sheet	DC	0.1M NaCl	7.2	8.4	53	18	4.8	[60]

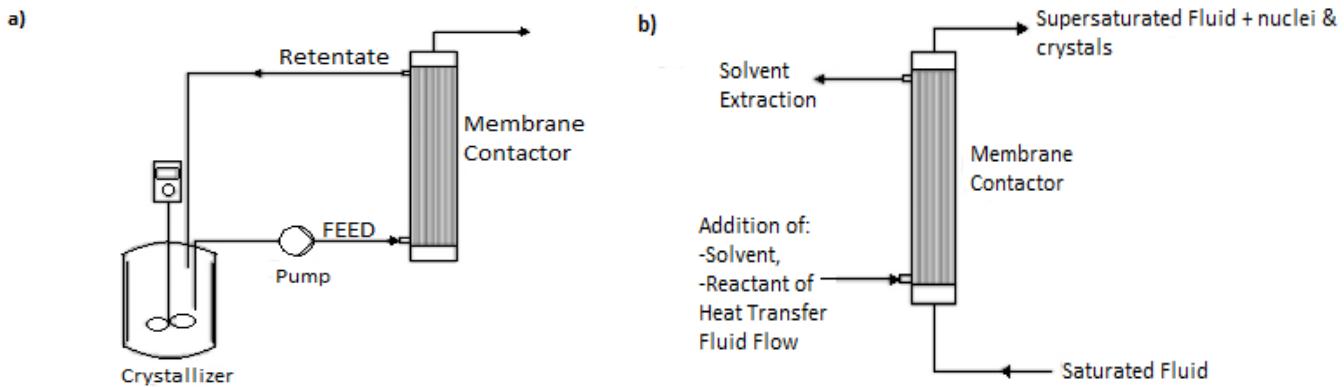


Fig. 1. Schematic representation of the two process designs: a) Hybrid membrane crystallization process. b) The crystallization takes place directly in the membrane module.

In a recent development of the process, Di Profio et al. [71] proposed a new design of the MCr process in which crystallization is induced by using antisolvent. This new approach operates in two configurations: first, solvent/antisolvent demixing and second, antisolvent addition. In both cases, solvent/antisolvent migration occurs in the vapor phase, according to the general concept of membrane crystallization and, unlike the above-mentioned configuration, not by forcing it in liquid phase through the membrane. The selective and precise dosing of the antisolvent, controlled by the porous membrane, allows a finer control of the solution composition during the process and at the nucleation point, with consequent improvement of the final crystal characteristics.

For what concerns MCr applications, a state-of-the-art summary is proposed in Table 2 whereas in Table 3 various experimental data (from literature) are reported. Membrane assisted and in-situ crystallizers studies are listed respectively in Table 2 (a) and (b). Each membrane process, membrane material and structure, but also system type are detailed for the different studies reported. Studies are focused on the crystallization or precipitation of a few model compounds (such as lysozyme, NaCl, carbonates, etc.) using mainly a limited number of membrane materials (polypropylene PP, polyvinylidene fluoride PVDF, polyamide, etc.). Table 3 reports various experimental data from literature, as achieved in different MCr experiments.

Table 2

List of publications on membrane processes applied for crystallization/precipitation operations. (Updated from [72]).

Membrane process	Membrane material	Membrane structure	System type	References
(a) Hybrid membrane crystallization process				
Membrane contactor	PP	Porous	CaSO ₄ , NaCl, MgSO ₄ · 7H ₂ O, LiCl, Na ₂ SO ₄	[73], [9], [74], [75], [76], [3], [77]
Membrane distillation	PVDF	Porous	Na ₂ SO ₄ , NaCl	[67], [78], [79], [80]
Membrane distillation	Hybrid PVDF	Porous	NaCl	[81], [40]
Microfiltration	Ceraver ZrO ₂ , PP	Porous	Ions, NaCl, MgSO ₄ · 7H ₂ O	[82], [83]
Nanofiltration	PS on PE Polyamide, PP	Composite, Porous	Na ₂ SO ₄ , NaCl, MgSO ₄ · 7H ₂ O	[83], [84]
Reverse osmosis	Polyamide, PP	Composite, Porous	(NH ₄) ₂ SO ₄ , NaCl, MgSO ₄ · 7H ₂ O	[83], [85]
Ultrafiltration	Polysulfone	Porous	Glutamic Acid	[86]
(b) In-situ crystallizers				
Heat exchanger	Nitrocellulose, PP, PP-g-MA	Dense	(NH ₄) ₂ SO ₄ , HCl, NaCl, KNO ₃	[87], [88], [89], [90], [91], [92]
Membrane contactor	PP, PTFE, PVDF, PDMS	Porous, Dense	Trypsin, Na ₂ CO ₃ , NH ₄ HCO ₃ , CaCO ₃ , NaCl, MgSO ₄ · 7H ₂ O	[73], [93], [94], [95]
Membrane distillation	PVDF, PP	Porous	NaCl, Taurine, CaCO ₃	[96], [66][97],
Membrane crystallizer	PP, PVDF, Cellulose Acetate, PES, EtOH	Porous, Liquid	Lysozyme, Fumaric acid; Paraffins, L-Asparagine, Paracetamol, L-Glutamic acid, Glycine, BaSO ₄ , Ions, Na ₂ CO ₃ , NaF	[70], [98], [68], [69], [99], [100], [101], [71], [102], [103], [104], [105], [106], [107], [108], [109]
Nanofiltration	PAA, PSS, PAH, PES, PA(6,6), SiO ₂	Dense	CaSO ₄	[110]
Pervaporation	PEBA 2533	Dense	Phenols	[111]
Reverse osmosis	PAA, PSS, PAH, PES, PA(6,6), SiO ₂ , Polyamide, Cellulose Acetate	Dense, Composite, Porous	Ca(COO) ₂ , CaCO ₃ , Lysozyme, CaSO ₄ , Si(OH) ₄ , Biofilms	[110], [112], [113], [114], [115], [116], [117], [118]
Ultrafiltration	Cellulose Acetate	Porous	Biofilms	[117]

Various sectors of industry and scientific research require solids in the crystalline state, and many products daily used are formulated as crystalline powders. Among these we find crystalline solids, for example, in products such as additives for cosmetics, hygiene and personal care, pharmaceutical products, fine chemicals, pigments and for the manufacture of microelectronic devices. In the medical field they are used for medical promotion through the rational design of new structure-based drugs [119]. This is because the solid state makes these products more stable for storage and more functional to manage by users. In the case of proteins, their structure is of fundamental importance for biofunction [120,121]. An example is human serum albumin, which carries small molecules in the blood and its structure information, essential for understanding the drug delivery process [122,123]. The protein crystals (100 nm at least in two dimensions) are therefore mandatory for the determination of the structure at the atomic level by X-ray crystallography [124-128]. These crystal structures are also very important for the next generation techniques: serial femtosecond crystallography (SFX) using free X-ray electron lasers (XFEL) [129,130], serial crystallography (SX) using synchrotron radiation sources and neutron diffraction [131,132].

3. Membrane condenser for water vapor capture

Membrane condenser is a new membrane operation recently introduced by Drioli and co-workers [13,135,136,137]. This process uses microporous hydrophobic membranes, for the selective recovery of evaporated waste water

through condensation from industrial gases [13,135,136]. By sending a flow of air with very high relative humidity on the surface of the membranes, their hydrophobic nature prevents the penetration of the liquid into the pores, allowing the dehydrated gases to pass through the membrane [10,13,136]. Therefore, the liquid water is blocked and recovered on the retentate side, while the other gases pass on the permeate side of the membrane unit. Figure 2 shows the membrane condenser concept [138]. The main advantages of membrane condenser are: clean operation, low energy consumption and no corrosion problem. The amount of recovered water can vary depending on the cooling of the gaseous flows up to a supersaturation state so that the part of the water vapor condenses, with the possibility to recover a great quantity of water [14]. This quantity can be calculated through the following relation:

$$\text{Water Recovery \%} = \frac{\text{Liquid water retained in the retentate side}}{\text{Total water contained in the feed stream}} \quad (2)$$

Figure 3 reports some data from literature in which experimental gas dehydration experiments were performed utilizing hollow fibers in PVDF and flat membranes in ECTFE [13]. The experiments were conducted under the same operating conditions: as feed was considered a saturated gas stream used at two different temperatures (55 °C and 65 °C, respectively) and cooling the feed of 10°C. ECTFE flat-sheet membranes presented excellent results, similar to commercial PVDF hollow fibers in term of amount of recovered water (between 40% and 60%) but at a much lower mean velocity.

Table 3
Membrane Assisted Crystallization performances in literature.

Membrane code	Membrane configuration	MCr operation mode*	Feed	Feed flow rate [L/h]	Permeate flow rate [L/h]	Temperature feed [°C]	Temperature perm [°C]	Flux [L/(m²*h)]	Ref.
AD40H_010	Flat sheet	DC	5.3 M NaCl	15	6	34	10.5	1.78	[81]
AD40H_045	Flat sheet	DC	5.3 M NaCl	15	6	34	10.5	2.54	[81]
CM-S	Hollow fiber	Vacuum	5.5 M NaCl	8.4	n.a.	50	n.a.	16.5	[4]
Virgin-PVDF	Flat sheet	DC	100 g/L NaCl + acid humic	0.2 m/s	0.4 m/s	60	25	15	[133]
PVDF	Flat sheet	DC	260 g/l NaCl	108	n.a.	50-60	20	20	[78]
PVDF	Hollow fiber	DC	26.4 wt% NaCl	0.5 m/s	1 m/s	70	17	20	[67]
DL-PVDF-PAN	Hollow fiber	DC	24 wt%	0.7 m/s	0.7 m/s	60-80	17	12	[134]
DL-PVDF	Hollow fiber	DC	24 wt% NaCl	0.7 m/s	0.7 m/s	60-80	17	8	[134]
SL-PVDF	Hollow fiber	DC	24 wt%NaCl	0.7 m/s	0.7 m/s	60-80	17	7.5	[134]

*DC= direct contact.

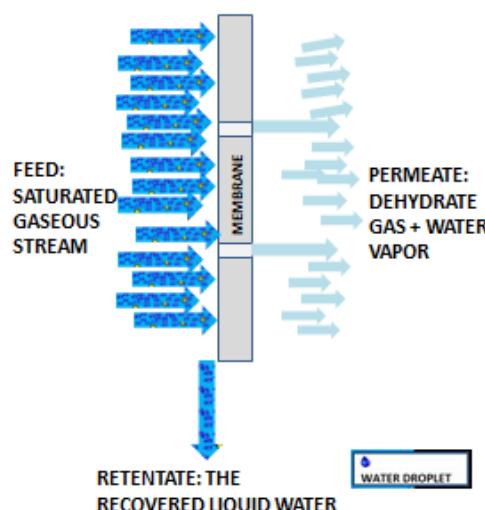


Fig. 2. Scheme of the membrane condenser process for the recovery of evaporated “waste” water from a gaseous stream.

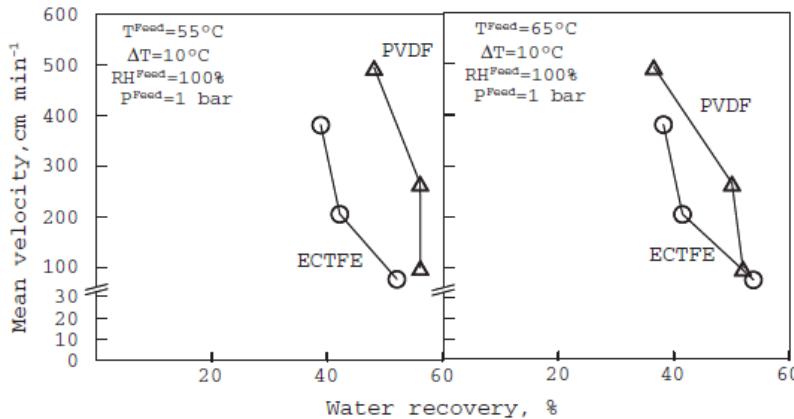


Fig. 3. Recovered water as a function of mean velocity for ECTFE flat-sheet membrane [13]. Reprinted with permission from Elsevier.

Moreover, considering waste gaseous streams can contain various pollutants and chemicals, membrane condenser can also be utilized for the removal and recovery (if of interest) of condensable compounds [11,13,135–138]. The concentration of components in the recovered liquid water can be modulated depending on the operating conditions, such as: relative humidity and temperature of the feed, temperature of the membrane module, and on the ratio between the feed flow rate and the membrane area. An example is reported in Figure 4 showing that the concentration of various contaminants in the recovered liquid water increases with the increasing temperature difference ΔT between the fed exhaust gas and the membrane module [138].

a reduction at higher $Q_{\text{Feed}}/A_{\text{Membrane}}$ ratios. Moreover, the analysis of membrane condenser process through the metrics mass and energy intensities showed that at low ΔT the rate-determining step of the water recovery is the temperature difference between the feed and the module. On the contrary, for high ΔT , the process is controlled by the ratio between the feed flow rate and the membrane area, which becomes the limiting factor. The indications provided by the metrics are useful to take into consideration in the design of the process. If, in fact, from the traditional analysis, a self-evaluation of energy consumption could lead to reducing the ΔT with purpose of reducing the energy duty required for cooling, a more comprehensive evaluation can drive the choice in a different direction, although the economic evaluations are, in the end, necessary to arrive at the final conclusion.

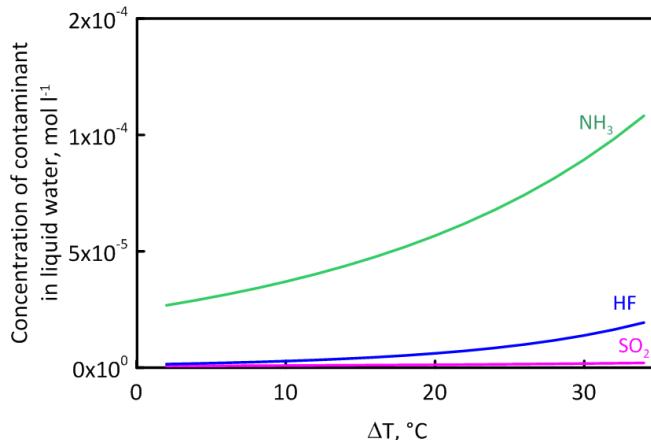


Fig. 4. Concentration of NH₃, HF and SO₂ in the recovered water as a function of the temperature difference ΔT between feed and membrane module [138]. Reprinted with permission from Elsevier.

To evaluate the performance of the membrane condenser, two fundamental parameters are the mass intensity and energy intensity. The first takes into account the water recovered on the retentated side with respect to the total mass fed, the second considers the power required by the system with respect to the recovered water [138]. Lower values of these indicators are linked to a more intense process. In the ideal situation, mass intensity and energy intensity tend to the lowest possible value. The main terms of energy entered are: the required power that drives the compression and heat needed to condense the steam or part of it [139].

$$\text{Mass Intensity} = \frac{\text{Total inlet mass}}{\text{H}_2\text{O mass recovered}} \quad (3)$$

$$\text{Energy Intensity} = \frac{\text{Energy duty for condensation}}{\text{H}_2\text{O mass recovered}} \quad (4)$$

It has been demonstrated [95] that the mass and energy intensities tend to

4. Current limitations

Water plays a central role in all activities and is, together with the energy supply, the exhaustion of raw materials and the protection of the environment, the foundations of modern society [85]. The discharge of inadequately treated waste water in many developing countries contributes negatively to pollution and to the degradation of limited water resources. As a result, salt water desalination can be one of the ways to increase fresh water production. Here, reverse osmosis is the main industrial source as it is able to maintain a high quality water standard. Suitable alternative methods to the traditional RO have been evaluated, such as thermal evaporators, crystallizers, spray driers and brine concentrators. Other innovative membrane based processes are membrane distillation (MD) and membrane assisted crystallization (MCR) [140]. The main obstacle that limits the broad applications of these membrane processes in industry and their commercialization are membrane wetting, temperature and concentration polarization, fouling, and scaling [141]. These phenomena lead to a higher frequency of chemical cleaning, higher operating costs, degraded membrane separation performance and reduced life of the membrane.

The polarization is a phenomenon mainly related to fluid dynamics, the only way to reduce it is to generate sufficient mixing and turbulence in the flow thus reducing the thickness of the boundary layer. Two different polarizations exist: temperature polarization and concentration polarization. To quantify the heat and mass transport resistance within the boundary layer with respect to the total transfer resistance of the system, the two fundamental coefficients (temperature polarization coefficient (TPC) and concentration polarization coefficient (CPC)) are defined with the follow equations:

$$\text{TPC} = \frac{T_{\text{fm}} - T_{\text{pm}}}{T_f - T_p} \quad (5)$$

$$\text{CPC} = \frac{C_{\text{Bm}}}{C_{\text{Bb}}} \quad (6)$$

where C_{Bm} is the concentration of the non-volatile solutes at the membrane surface; C_{Bb} is the concentration of the non-volatile solutes at the bulk feed. The increased concentration of non-volatile compounds next to the membrane surface would have the influence of reducing the transmembrane flux due to the establishment of concentration polarization (CP) layer at the feed side.

This acts as a mass transfer resistance for the volatile molecule species (water) [142]. Whereas concentration polarization is a limiting phenomenon in RO, MD permeate flux is only slightly affected by the concentration of the feedwater, and thus productivity and performance remain roughly the same for high concentration feed-waters. This means that, by membrane distillation, pure water can also be obtained from highly concentrated feeds with which RO cannot operate due to the increase of osmotic pressure. Therefore, MD can be preferentially employed whenever high permeate recovery factors or retentate concentrations are requested.

The wetting of the membrane pores involves a complex of physical and chemical interactions. The non-wetting of a liquid is the result of its high surface tension formed by the liquid in contact with the hydrophobic membrane surface [143]. This contact surface forms a convex meniscus which prevents the liquid from entering the pore of the membrane. Therefore, this balance remains until the pressure difference resulting from the surface tension of the curved interface balances the pressure drop caused by the partial pressures of vapors and air through the membrane. The pressure caused by the surface tension is called capillary pressure [144]. The primary parameter for measuring membrane wettability is liquid entry pressure (LEP) defined through Eq.7. The latter links the maximum capillary pressure for a hydrophobic membrane with the liquid surface tension, the free surface energy and the maximum pore size of the membrane.

$$LEP = \frac{-2B\gamma_L \cos\theta}{r_{\max}} \quad (7)$$

where B is a geometric factor determined by pore structure, γ_L the liquid surface tension and θ is the liquid/solid contact angle. When the hydrostatic pressure on the feed side of a MD membrane exceeds LEP, liquid penetrates the pores and is able to pass through the membrane. Once the wetting takes place, the membrane begins to lose its hydrophobicity locally. Membrane wetting can be distinguished into four degrees: non-wetted, surface-wetted, partially-wetted, and fully-wetted [143]. In the case of complete wetting, the membrane no longer acts as a barrier, resulting in a viscous flow of liquid water through the pores of the membrane, invalidating the MD [145,146].

Fouling is another extremely important factor, since it involves a greater energy consumption, longer downtimes due mainly to the continuous request for cleaning or replacing the membrane and is one of the causes of membrane wetting [147,148]. However, membrane fouling is less of a problem in MD than in other membrane separations because (1) the pores are relatively large compared (for example) to the pores in reverse osmosis and ultrafiltration, (2) the low operating pressure of the MD (which causes that the deposition of foulants on the membrane surface is less compact and only slightly affect the transport resistance), (3) there is not feed inside membrane pores (therefore foulants are deposited only on the membrane surface but not in the membrane pores).

In addition to these problems, desalination, and similar process, involves serious concerns about the potential environmental impact. In fact, although desalination plants produce large volumes of clean water, they also produce almost the same amount of concentrate (i.e. brine) and consume energy. The costs of disposal of this brine represents a cost that varies from 5% to 33% of the total cost of desalination [149], depending on the type of treatment of disposal and concentration of brine. Moreover, the brine disposal costs of the internal plants are higher than those of coastal plants [150]. However, these additional problems do nothing more than encourage the research of this sector with the development of innovative technologies for the exploitation and re-use of the brine. Thanks to these technologies it is able to produce renewable energy, produce salts and chemicals for the industry [12].

5. Conclusions and future perspectives

Industrial development in the production of RO technology is the symbol of the growth of membrane processes. This success is possible above all due to lower energy consumption compared to thermal technologies. Fouling, scaling and biofouling are the most critical problems for these technologies. Alternatives to RO, several emerging processes have been studied in the research field. Membrane distillation is a promising innovative technology which can be used for the concentration of solutions such as brines, fruit juices, acids, proteins and radioactive components [151], separation of mixtures [152], removal of heavy metals and dyes [153], etc. In the last years, several studies have been conducted to improve the design of membrane distillation process [154, 155]. The key factors to improve MD process are: the reduction in energy consumption and cost, the decrease in the simultaneous risk of wetting, scaling and fouling, the preparation of membranes specifically designed for MD applications and the coupling with renewable energy systems. In literature, there are new researches developed in

these fields. These include, for example, a porous hydrophobic/hydrophilic composite membrane prepared using surface-modification fluorescent macromolecule (SMM) and polyetherimide [156]; modification of the CF4 plasma surface of hydrophilic membranes in hydrophobic ones [157,158]; preparation of TiO₂ surfaces structured with nanotubes with superomniphobic characteristics [159]; manufacture of hybrid graphene/PVDF membranes [53]. Graphene is a material that has attracted considerable interest for countless applications, including those for water treatment and purification, especially the anti-fouling property [160–163]. The possibility of a more economical synthesis of a large area of graphene, as recently reported, makes it more interesting for modern use [60]. In addition to graphene, two-dimensional (2D) materials of atomic thickness represent the materials of the new-generation membrane with an extraordinarily high permeability. 2D membranes with well-defined transport channels and ultra-low thicknesses have demonstrated exceptional performance for liquid and gas separation applications. Potential materials for 2D membranes include zeolites, mixed-organic structures, molybdenum disulfide, etc. [41].

Membrane-assisted crystallization has been evaluated to provide important advantages against traditional crystallization due to easy scalability and good control of crystal nucleation growth [142]. This process arises, in fact, from the need to produce substances in the solid crystalline state required in various sectors of industry, technology and scientific research. The solid crystalline state makes these products more stable for storage and more functional to manage by users, where morphology is the dominant feature with a consequent safe interest in countless applications. In fact, as mentioned above, many daily products are formulated as crystalline powders [9]. The potential of membrane crystallization is addressed from a point of view of intensification and integration, with particular attention to present and future applications, such as the green economy and value-added production [25,164,165]. Other, but not less important, applications have been developed for the treatment of waste water for the recovery of high purity silver [108] or sodium sulphate [166], CO₂ capture [95,167,168], the synthesis of BaSO₄ and CaCO₃ particles [169,170], the recovery of antibiotics [119] or of polystyrene microparticles [171]. Membrane crystallization is a process with the potential to achieve the goal of zero discharge in desalination plants. In principle, MCr could overcome not only the limitations of thermal systems but also those of traditional membrane systems such as RO. Thanks to its characteristics, the integration of MCr with RO brine offers the possibility to produce high quality solid materials and controlled properties, with important added values, transforming the traditional problem of brine disposal into a potential new profitable market [6].

Finally, membrane condenser as an alternative for the production/purification/reuse of water from industrial waste gaseous streams has recently been developed. The quality of the recovered liquid water can be limited by the possible condensation of contaminants, if the latter are present in the gaseous stream. In this context, it should be emphasized that membrane condenser can be considered as the pre-treatment phase of another membrane unit for CO₂ separation. In fact, the performance of these units can be severely damaged by the presence of contaminants such as SO₂, NH₃, HF, NOx, etc. So the membrane condenser, in addition to the recovery of clean water, can be also developed for minimizing the contaminant content and as a pre-treatment step in post-combustion capture, forcing the retention of most contaminants [138]. Currently there is no commercial technology available for the recovery of waste water evaporated from industrial processes.

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