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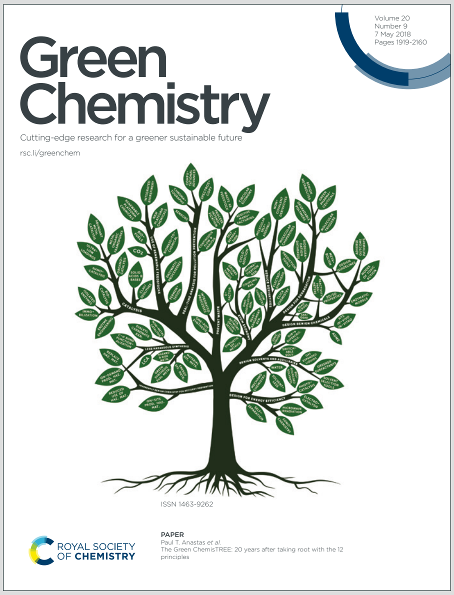

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How to make membrane distillation greener? A review on environmentally friendly and sustainable aspects

Emilia Gontarek-Castro [a*], *Roberto Castro-Muñoz* [b]

[a] Department of Environmental Technology, Faculty of Chemistry, University of Gdansk, 80-308 Gdansk, Poland

[b] Gdansk University of Technology, Faculty of Civil and Environmental Engineering, Department of Sanitary Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland

*** Corresponding author:**

E-mail: emilia.gontarek-castro@ug.edu.pl; (E. Gontarek-Castro)

Abstract

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There is an urgent need for the development of new water resources in order to solve the problem of the world's growing demand for clean water. Membrane distillation (MD) is a promising alternative to conventional seawater desalination. Although MD itself is often defined as sustainable desalination technology, there are many aspects within the membrane manufacture and process operation that make it far from being green. For instance, non-biodegradable polymers, toxic solvents and fluoroalkyl silanes are typical chemicals that unfortunately are used in membrane fabrication protocols. Additionally, the huge amount of wastewater generated from membrane fabrication processes makes solvent-free methods more attractive and desired for extensive investigation. Apart from this, the low energy efficiency of MD process can be effectively overcome by integrating the MD systems with low-grade waste heat. *This review critically addresses and discusses the recent advances in methods and strategies to improve the sustainability of MD technology*, which is not a common scope of study among the research community. Here, our attention has been devoted to main aspects in MD membrane fabrication, such as polymers, solvents (and its costs), nonsolvents, additives, solvent-free fabrication procedures, fluoro-free post modification, and MD operation (energy consumption). This review intends to introduce inspiration for membrane scientists for the development of the next-generation MD process, by promoting the sustainable transformation of today's approaches into a greener way. In this latter scenario, we provide some punctual considerations that could be followed by the researchers in the field.

Keywords: Membrane distillation; Green chemistry; Sustainability; Desalination; Energy efficiency.

1. *Introduction*

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Over the past century, the population of the world has increased, as has the demand for water. This global challenge of water supply will become even more serious due to further expansion in population and economic growth, followed by a continuing increase in demands on water resources. The World Water Council estimated that by 2030 a few billion people will suffer from water scarcity or poor water quality [1]. Thus, it is not surprising that governments and industry have tried to develop alternative water sources, water recycling, water imports, and desalination to face the concern of the world's growing demand for clean water. In general, desalination techniques can be divided into two groups: thermal-based and membrane-based. The former ones, thermal technologies, including multi-stage flash, multi-effect distillation, and vapor compression distillation [2], require the supply of thermal energy to induce the evaporation of water molecules from seawater; the vapor is subsequently condensed to give drinking water. Despite its versatility and ease of operation, thermal desalination has one significant disadvantage, its high energy consumption, as it is costly, and environmentally unfriendly method. For this reason, alternative methods to thermal desalination are sought, mainly to reduce the costs of the process.

Currently, one of the most dynamically developing desalination techniques are membrane-based technologies. Membrane technologies are becoming more popular due to their lower energy expenditure, compact modular construction, possibility of scaling-up, lower environmental footprint, and the possibility of spending investment recovery [3]. Among membrane-based technologies, the dominant one used for desalination (in terms of the amount of treated water) is reverse osmosis, which, according to the literature, produces up to 60% of the world's desalted water [4]; however, the costly installation and maintenance represent the main drawbacks of this technology. This has encouraged researchers to seek for new membrane desalination alternatives, such as membrane distillation (MD), which is a potentially promising technique for seawater desalination. The driving force of the process is based on a vapor pressure gradient across the membrane. This gradient is induced by the temperature difference between the feed and permeate solutions. The solutions are separated by a hydrophobic microporous membrane that allows the diffusion of vapor while preventing the permeation of the aqueous phase.

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Water evaporates at the solid/liquid interface on the heated feed side of the membrane, then diffuses through the air trapped in the membrane pores, and finally condenses at the cooler permeate side. Simultaneously, non-volatile substances remain in the aqueous feed solution. MD seems to be an effective method of seawater desalination as it successfully deals with high salinity content, high oil content, and high surfactant content feed. Despite the great progress in MD membrane preparation and performance improvement, their fabrication approaches and implementation procedures still need to be revised in terms of toxicity and pollution generation [5][6]. For instance, the typical materials used for membrane manufacture are perfluorocarbon-based non-biodegradable polymers, while toxic organic solvents are mostly applied at several membrane manufacturing stages, producing more than 50 billion liters of contaminated wastewater yearly and contributing to various of health and environmental risks. Due to the fundamentals of the MD process, more and more emphasis is being placed on the fabrication of superhydrophobic or even omniphobic membranes, however, typical substances applied for the post-fabrication modification of membrane surface properties are toxic fluoroalkyl silanes (FAS). Another aspect relies on the energy expenditure, the low energy efficiency of the standalone MD system significantly reduces its potential application. Due to the constant growth of environmental pollution problems, improving the sustainability of MD and developing green manufacturing protocols are a must around all aspects. **Figure 1** illustrates a comparison of the current scenario of MD and the aim of pursuing the green and sustainable scenario soon. This latter panorama can be reached by following the updated ¨Twelve Principles of Green Chemistry¨, developed by Anastas and Warner [7] and proposed by United States Environmental Protection Agency. The idea represents the design of safer chemical processes and products that reduce or eliminate the use or generation of hazardous chemicals.

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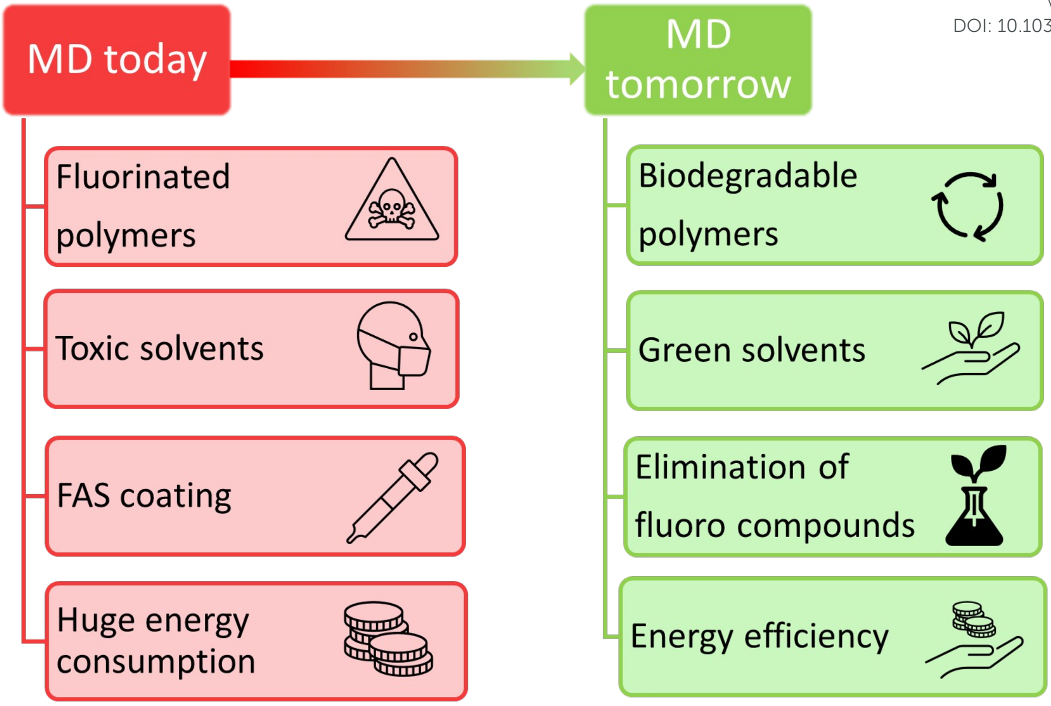

Figure 1. The transformation of the MD process to green and sustainable in the future.

In the light of green chemistry principles, the most often used definition of sustainable development is the one proposed by the Brundtland Commission in 1987 as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [8]. **Thus, to be really "sustainable"**, MD process should not only be free of the use of hazardous substances in membrane fabrication but also in the operating step process. *We believe that these aspects need to be reviewed and discussed exhaustively; and to the best of our knowledge, there is no report discussing these aspects so far*. Therefore, in this review, the latest advances related to the greener approaches of MD are described in detail. We highlighted different ways to improve the sustainability of the membrane manufacturing process, such as the use of biodegradable polymers, green solvents and FAS-free modification. The strategies for the solvent-free fabrication have been discussed together with the possibility to reduce the amount of solvents at various manufacturing stages. Finally, to reduce the energy consumption and make the MD process more competitive to RO, the energy efficient routes given by integrating MD systems have been addressed.

2. Polymer membrane fabrication

2.1. Biodegradable and perfluorocarbon-free polymers

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As for MD process, only water-repellent membranes, such as the ones made of petroleum-based polymers (polytetrafluorethylene (PTFE) and polyvinylidene difluoride (PVDF)), or coated with perfluorosilanes have been extensively investigated [9][10]. In the case of fluorocarbon membranes, they are expensive and prone to partial wetting during a long-term use, due to the interactions between membrane surface and contaminants [11][12][13]. These membranes owe their commercial interest their suitable properties in terms of their high porosities, low thermal conductivities, stability and hydrophobic nature [14]. Despite their many advantages, one of the main concerns of using and disposing of these polymer materials is their low biodegradability. This latter feature refers to the materials which once disposed in nature undergo degradation via microorganisms. Owning their high thermal and chemical stability they are resistant to microbial attack as their carbon linkages cannot be broken by enzymes and microorganisms. On the other hand, biodegradable polymers are originated from three plant (for example cellulose acetate and starch), animal (collagen and sericin), and sometimes synthetic resources (poly (butylene succinate) or poly (ε-caprolactone)). The application of these materials is rapidly growing, especially in the packaging industry, however, an increased interest is also observed in biodegradable membrane fabrication [15]. Although efficient MD membranes made from biodegradable and low-cost materials are highly desired, they are still not commercially available.

Recently, few studies proved the possibility to use cellulose for MD membrane preparation [16]. Cellulose is a renewable polymer that is found abundantly on Earth. Cellulose fibers can be extracted from various sources, including underutilized biomass feedstocks such as agricultural residues, recycled cellulosic products, and industrial waste. These fibers possess unique structural and mechanical properties, and they are abundant, cost-effective, and environmentally friendly. Thus, it has been found attractive to explore the use of cellulose fibers as a material to create permeable MD membranes. The presence of hydroxyl groups on the cellulose surface makes it hydrophilic, therefore a major concern of applying this material for MD membrane preparation is to create the hydrophobic surface with a green and sustainable approach. Several studies demonstrate different approaches for the creation of hydrophobic cellulosic surfaces, such as chemical modification with fluoropolymers or silanes and

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processing methods, namely chemical vapor deposition, plasma treatment, and electrospinning **(see table 1)**.

For instance, Leitch et al. [17] fabricated a novel fibrous nanocellulose aerogel membrane from bacterial nanocellulose, which met the requirements of MD process (e.g., high porosity >98%, and low thermal conductivity <0.03Wm^{-1} K^{-1}). Due to their isotropic fibrous structure and easily tunable fiber diameter between 15 nm and 7 μm, these biomembranes may become a natural substitute for electrospun polymer membranes [18][19]. The authors compared the direct contact membrane distillation (DCMD) performance of nanocellulose aerogel membrane and commercial PVDF membrane. The high void fraction of nanocellulose aerogel membrane led to the reduction of conducted heat flux, thus improved membrane thermal efficiency and temperature polarization coefficient (see **Figure 2a, 2b**). On the other hand, smaller average pore diameter and higher thickness, compared to the commercial PVDF membrane, increased the mass transport resistance of nanocellulose aerogel membrane. Dizge et al. [23] fabricated a superhydrophobic and oleophobic membrane by a three step process; the preparation of cellulose nanofibers by electrospinning, modification with silica and surface fluorination. The membrane system displayed exceptional resistance to wetting and maintained a high and stable performance. The water vapor permeability against 1 M NaCl feed solution was found to be very high and reached 46.3 L/m^{2}h, which was 1.7 and 1.6 higher when compared with the water vapor flux rate of commercial available PVDF and PTFE membranes, respectively.

Cellulose itself is the basic building block of plant fibers, proving mechanical support to specific growing parts of the plants. This molecule also provides mechanical integrity which makes it an attractive material for membrane reinforcement [20]. Lalia et al. [21] fabricated polyvinylidenefluoride-co-hexafluoropropylene membranes containing different loadings of nanocrystalline cellulose (NCC) by electrospining technique. The polymer membrane modified with NCC was found to have 30% higher tensile strength and 45% higher Young's modulus values than that of nonmodified one. Additionally, the incorporation of NCC into the membrane resulted in enhancement of its liquid entry pressure (LEP) from 19 psi up to 27 psi. This high LEP led to the effective DCMD performance with a water flux of 11.5 L m^{-2} h^{-1} and salt rejection of 99%. Hou et al. [22] have fabricated a cost-effective membrane directly from a sustainable wood material. In contrast to nanocellulose-based membranes, this membrane was made by directly removing lignin and hemicellulose from the wood samples via chemical treatment and freeze-drying. The prepared membrane had high porosity (~90%) and hierarchical pore structure, while the presence of crystalline cellulose nanofibrils and xylem vessels and channels across the structure led to the facilitated water vapor transport. This innovative plant-based material demonstrated potential for MD water desalination, and the performance comparable or better than that of commercially available membranes derived from fossil resources. For instance, the intrinsic permeability of nanowood membrane was 2.5 times higher than that of commercial polypropylene (PP) membrane, with exceptional thermal efficiency exceeding 70% (see **figure 2c, 2d**). Although nanowood membrane can be fabricated by a scalable top-down approach, it needed the FAS (perfluorodecyltriethoxysilane) treatment to become hydrophobic.

Recent studies proved the possibility to use cellulose for fabricating dual-layer membranes combining both hydrophobic and hydrophilic polymers. This type of membrane is supposed to eventually reduce the vapor transport path, thus improve the mass transport across the membrane. Owning their surface properties those membranes can be used for treating oily waste waters. For instance, Arumugham et al. [23] fabricated a dual-layered membrane made by coating the cellulose substrate with novel perfluorooctanoic acid-modified melamine nanofillers embedded in PVDF. The long perfluoro chain in hydrophobic fillers increased membrane surface roughness by randomly overlapping with PVDF backbone, resulting in higher water contact angle. Results indicated that the 1% PFOM membrane demonstrated high flux and rejection ratio, making it a promising candidate for seawater desalination.

Nassrullah et al. [24] used zeolite nanoparticles to open-up the cellulose structure, and thus to increase the porosity in dual layered membrane. Their process involves, initially the preparation of casting solution using nano zeolite and microcrystalline cellulose and the subsequent utilization of this solution to coat electrospun polymer membrane. Finally, each of the cellulose coated membrane was physically stacked on the top of unmodified electrospun membrane to form a double-layer membrane. The results showed that the addition of nano zeolite to the cellulose coating can effectively enhance the membrane performance without compromising the membrane selectivity. In the study of Joshi et al. [25], the

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superhydrophobic cellulose-based membranes containing a dual-layered structure have been fabricated using a straightforward method. The superhydrophobic properties have been achieved by the surface microstructure modification with inorganic filler followed by a hydrophobic sizing agent treatment, which both are a common additive in papermaking. Cellulosic membrane was tested for desalination of water using the DCMD configuration and exhibited high-water flux (23.0 ± 0.06 kg L/m^{2}h) and high salt rejection (97.5 %), comparable to the performance of commercial PTFE membranes.

Table 1. Comparison of the properties and MD performance of cellulose-based membranes obtained by various methods

Form of cellulose used	Fabrication method	Pore size (µm) porosity (%)	Thickness (µm)	contact angle (deg)	Flux rejection	Pros and cons	Ref.
microfibrillated cellulose	vacuum filtration of microfibrillated cellulose with additives followed by hydrophobic/hydrophilic treatment	0.50 55.7%	295 ± 12	147	23.0 ± 0.06 kg L/m^{2}h 97.5 %	+ membrane manufacturing based on papermaking techniques - large average pore size	[25]
cellulose acetate	Electrospinning of cellulose nanofibers followed with silica grafting and surface fluorination	1 90.2%	52	150.6 ± 4.0	46.3 L/m^{2}h ~100%	+ high permeate flux + strong antiwetting properties	[26]
cellulose nanocrystals	Electrospinning of PVDF-HFP/cellulose solution and hot pressing	~0.3 60-75%	200-300	132.2	11.5 L/m^{2}h 99%	+ tensile strength improvement - porosity and hydrophobicity reduction	[21]
cellulose sheet	Polymer solution casting on cellulose sheet	~0.005 nm 75.1%	200	112	6.9 L/m^{2}h 99.9%	+ excellent long-term rejection - utilization of fluorinated polymers	[23]

microcrystalline cellulose	Coating electrospun polymer membranes with cellulose-based solution	0.2-0.3 49.71%	86-105	0	20.52 L/m^2h 100 %	+ high oil and salt rejection - multi-step preparation procedure - nanoparticles leaching problem	[24]
bacterial nanocellulose (BNC)	Hydrophobization of dired BNC gels via CVD using trichlorosilane	0.115 98.0%	257 ± 45	156	22.92 L/m^2h 99.95	+ high porosity + low thermal conductivity	[17]
wood cellulose fibers	The treatment of wood slices followed by their fluoriantion	0.28 89%	502 ± 35	144	20.8 ± 0.8 L/m^2h 99.8%	+ membrane preparation directly from wood - high thickness	[22]

Das et al. proposed the application of perfluorocarbon-free MD membranes derived from silica and poly(methyl methacrylate) (PMMA) that are both water-wet materials. Inspired by the cuticles of springtails and hairs of sea skaters, they developed a two-step drilling process to create biomimetic gas-entrapping membranes (GEMs). Interestingly, the resulting GEMs comprised vertically aligned cylindrical pores with reentrant inlets and outlets, which effectively entrapped air on the membrane surface upon immersion in wetting liquids and gave it omniphobic character. To some extent, MD test proved robust separation of salt solutions from deionized water, yielding a stable and high flux of desalinated water permeation of 1 L m^{-2} h^{-1} for over 12 h.

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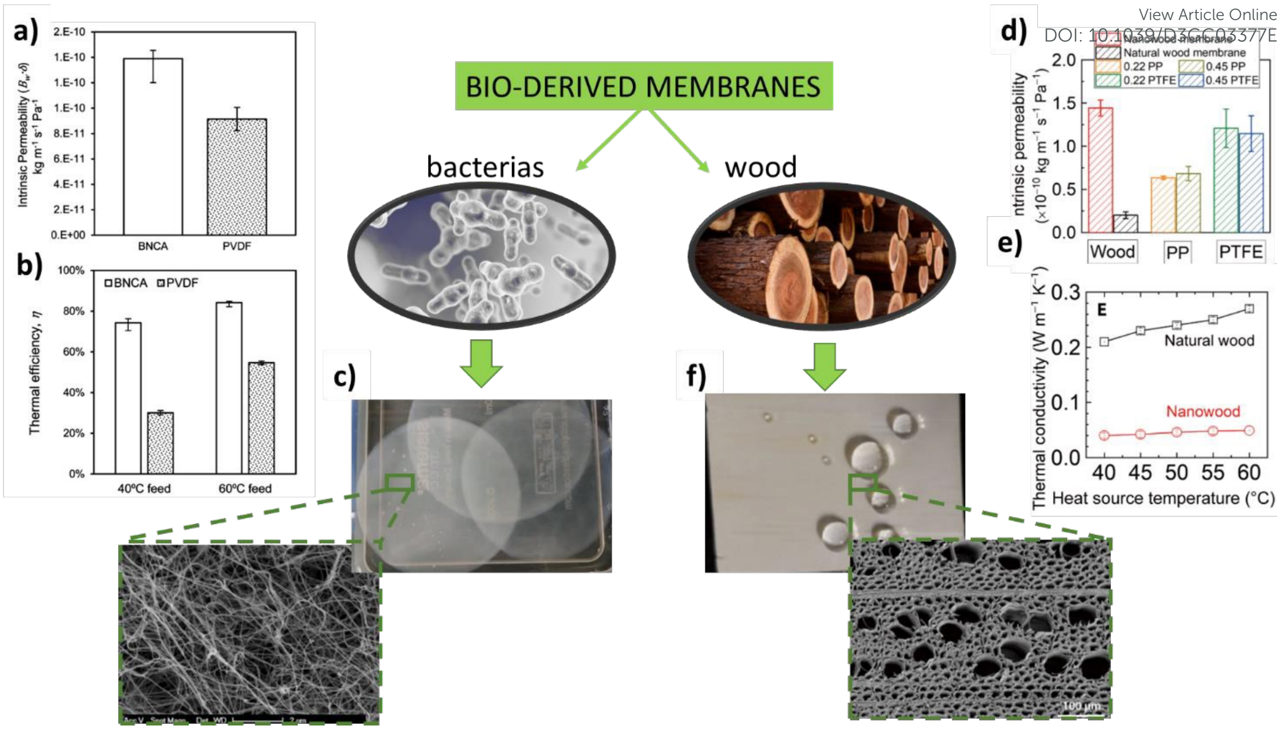

Figure 2. Bio-derived MD membranes and their performance, a) enhanced permeability of bacteria-derived membranes over commercial phase-inversion PVDF membranes, b) high thermal efficiency of bacteria-derived membranes, c) bacteria-derived membrane and its cross section, d) permeability of the nanowood and commercial membranes, e) thermal conductivity of the wood and nanowood membranes, f) nanowood membrane and its cross section. A, b, c reproduced from ref. [17] with permission from American Chemical Society, copyright 2016. D, e, f reproduced from ref. [22] with permission from American Association for the Advancement of Science, copyright 2019.

Remark. A significant number of publications have been devoted to minimize the environmental impacts of membrane manufacture and to develop polymers with environmental sustainability and minor disposal concerns. Nevertheless, the work on bio-based and biodegradable membranes is much more widespread for membrane processes other than MD. Polylactide, poly(lactide-co-glycolide), polyhydroxyalkanoates, chitosan and chitin, starch and poly(vinyl alcohol) are common biodegradable membrane materials that have been extensively studied towards enhanced membrane separation via microfiltration, ultrafiltration, nanofiltration, electrodialysis, and reverse osmosis [15]. Although the low cost of bio-based membranes may facilitate the dissemination of technology for water desalination in various areas, it is important to notice that for MD operation, one side of the membrane must be modified

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to become hydrophobic. So far, chemical vapor deposition method to cover the hydrophilic fibers with hydrophobic silane [9], and FAS (perfluorodecyltriethoxysilane) treatment [22] have been proposed. Therefore, it is apparent that the above mentioned membrane preparation procedures are often not environmentally friendly. The development of chemical-free methods of tailoring the structure of biodegradable membranes should be more explored.

2.2. Sustainable and green approaches for porous membrane preparation

Porous MD membranes can be prepared by various methods, including stretching, template leaching, track etching, phase inversion, and electrospinning, which are widely described and explained elsewhere [27][28][19]. Among them, phase inversion stands out as the most applied for the manufacture of commercially available membranes, and it attracts the continuously growing attention of researchers, as reflected in the growing number of publications (see **Figure 3a**). The basis of the phase inversion process is the preparation of a thermodynamically stable polymer solution which subsequently is transformed from a liquid into a solid state (coagulation) in a controlled manner. This coagulation is preceded through a so-called liquid–liquid demixing. In general, polymeric solution is used to form the shape of the membrane, what is followed by membrane immersion into a liquid coagulant also called nonsolvent. Then the demixing starts, separating the polymer solution into a polymer-rich and a polymer-lean phase. The higher polymer concentration phase starts to coagulate and leads to the solid membrane matrix, while the polymer-lean phase leads to the pore formation. The membrane immersion in a nonsolvent bath is called a non-solvent induced phase separation (NIPS), however, the demixing process may be induced as well by controlled evaporation of the volatile solvent from the polymer solution (evaporation induced phase separation, EIPS), thermally induced phase separation (TIPS) or by placing the cast film in a vapor phase consisting of nonsolvent - vapor induced phase separation (VIPS).

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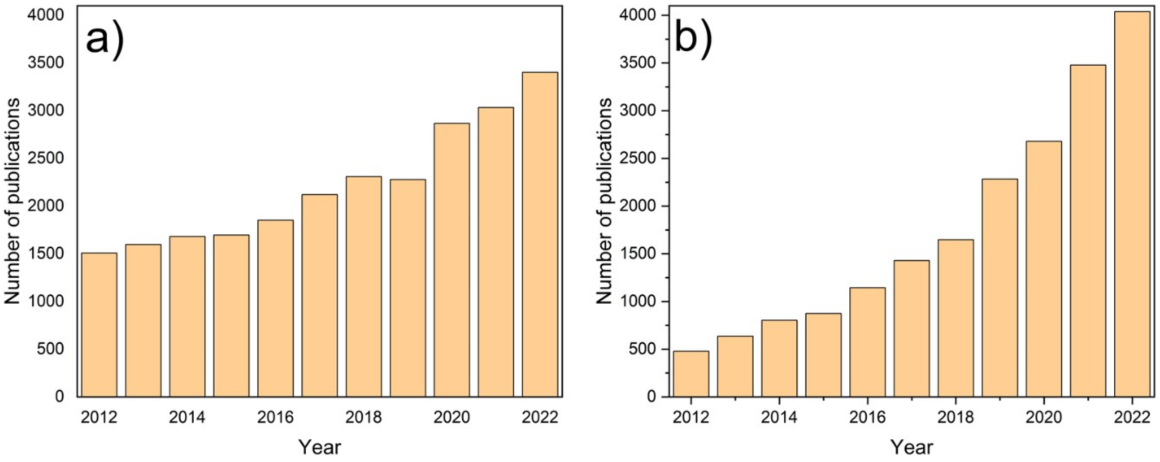

Figure 3. Publications on a) phase inversion membranes, and b) electrospinning membranes. Data taken from sciencedirect.com (30.08.2023).

The other membrane preparation method is electrospinning. It is known as a simple and reliable technique for the nanofiber preparation from a variety of polymers and is extensively used by research community for the design of nanostructured matrices for different applications (see **Figure 3b**). It involves the application of a high electric field to create nanofibers from a charged polymer solution or melt. By varying electrospinning parameters and polymer solution properties, different morphologies of the membrane can be produced. Despite the universality of phase inversion and electrospinning methods, their ease and the feasibility to produce membranes with the intended properties, they require the preparation of a polymer dope solution in order to form a membrane shape. Usually, hydrophobic polymers, such as PTFE, PVDF, PP and/or polyethylene (PE)[29], exhibit low polarity requiring to be dissolved in conventional non-polar (or nearly non-polar) solvents, such as N-Methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc). Although these chemicals are considered as fine universal solvents, with great abilities to dissolve both amorphous and semi-crystalline polymeric materials, they have an adverse effect on living organisms due to their serious toxicity according to multiple reports (see **Table 2**) [30]. For instance, the DMF is considered as a carcinogenic compound, that according to the International Agency for Research on Cancer, gives rise to mutation in mammalian somatic cells. On the other hand, DMAc is deemed to be responsible for the

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human reproductive toxicant and the promotion of congenital malformation in the fetus, while NMP brings an adverse effect to human fertility or to the unborn child.

Table 2. Classification and toxicity of common solvents used in MD membrane preparation.

Solvent	Chastrettes's report classification [31]	Pfizer classification – reason [32]	General Classification [33]
DMF	aprotic highly dipolar	undesirable - toxicity, classified as a HAP in the US, strongly regulated by EU solvent directive	hazardous
DMAc	aprotic highly dipolar	undesirable - strongly regulated by EU solvent directive, toxicity	hazardous
NMP	aprotic highly dipolar	undesirable - strongly regulated by EU solvent directive, toxicity	hazardous
Tetrahydrofuran	hydrogen bonding	usable	Problematic/ hazardous
Chloroform	miscellaneous	undesirable - carcinogen, classified as a HAP in the US	Highly hazardous
1,4-Dioxane	electron pair donor	undesirable - Carcinogen (CMR category 3), classified as HAP in the US	hazardous
Toluene	aromatic apolar	usable	problematic

Abbreviations: CMR- carcinogenic, mutagenic, or toxic for reproduction, HAP - Hazardous Air Pollutant

Therefore, to fabricate sustainable membranes, one must refrain from using these toxic and dangerous solvents by applying one of two common approaches. One of them is to employ green solvents for polymer solution preparation (as discussed in next subsection) and the second requires the use of a solvent-free method.

2.2.1. Green solvents

Non-toxic solvents are harmless and environmentally friendly substances that according to the principles of green chemistry don't pose any risks to both human health and the environment. Nevertheless, the affinity between solvent and polymer must be consider prior to polymer solution preparation, as it influences the phase separation mechanism and the performance of the resulting membranes. Therefore, it is crucial to select a suitable green solvent with proper affinity with the polymer. This affinity is defined by the R_a value, which can be estimated by the Hansen solubility parameters, given by the following equation [34]:

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$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + \left(\delta_{p1} - \delta_{p2}\right)^2 + (\delta_{h1} - \delta_{h2})^2}$$

where δ_d, δ_p, and δ_h are the parameters for the dispersion, polar and hydrogen bonding interactions, respectively. R_a value must not exceed the R_0 value of the polymer if solubility has to be maintained. These dependencies are often presented graphically in the form of Hansen solubility sphere of the polymer (based on R_0 value) in a three-dimensional coordinate system. Knowing the Hansen solubility parameter values of the solvents, it is possible to assess whether the solvent will be suitable for a given polymer, as described in **Figure 4a**. Due to its simplicity, this method has been widely used in combination with experimental results. For instance, **Figure 4b** shows the three-dimensional Hansen solubility parameter sphere of common polymer used for MD membrane preparation – PVDF, and the position of solvents (both conventional and green ones) reported in the literature to dissolve this polymer.

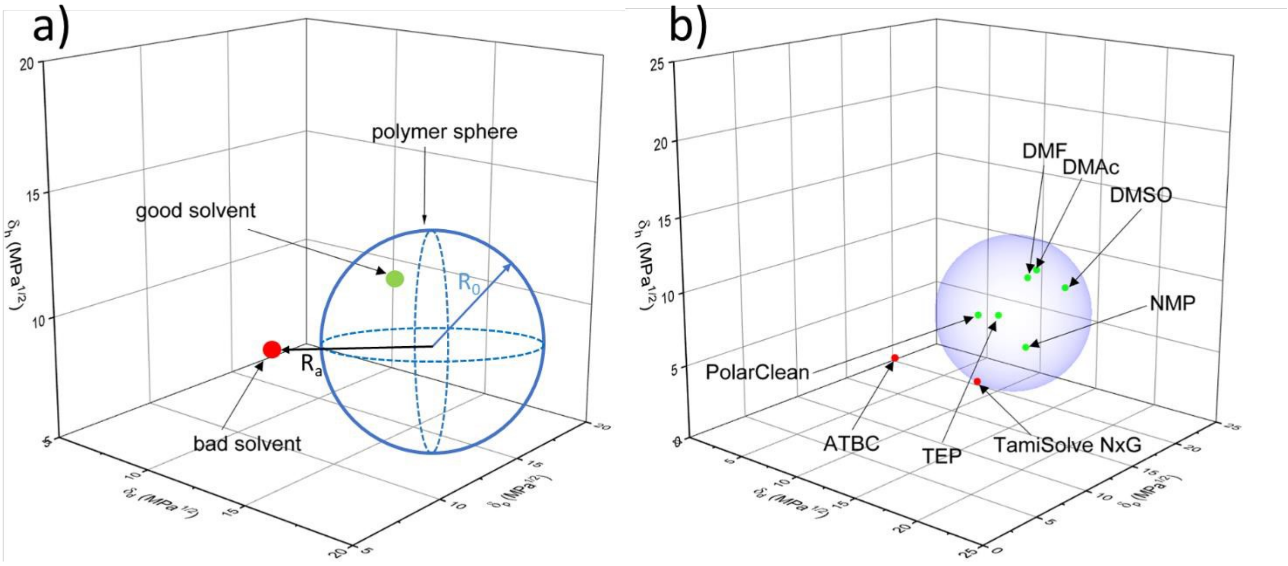

Figure 4. a) Three-dimensional Hansen solubility parameter sphere of specific polymer and the position of a good and a bad solvent, b) Three-dimensional Hansen solubility parameter sphere of PVDF and various solvents (red dots are outside the sphere, green dots are inside the sphere).

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To date, several green solvents have been widely employed for porous MD membranes preparation with good affinity to water as well (see **Table 3**). Most of the reports regard PVDF membranes [35][36][37][38], however, poly(ethylene-chlorotrifluoroethylene (ECTFE) [39], [40], PP [41], [42], and PU [43] MD membranes were also prepared by employing harmless solvents. For instance, Ding et al. (2021) [43] developed environmentally friendly PU/PTFE nanofiber membranes via electrospinning using ethanol and diacetone alcohol as a polymer solvent. Zou et al. (2022) [44] fabricated porous PVDF membranes via NIPS method using PolarClean. The membrane was tested in various MD systems and presented higher flux than that found in the literature, indicating that this green membrane showed good MD performance towards saline water and food extracts. Triethyl phosphate (TEP), as a green solvent, has been used to prepare both flat sheet and hollow fiber membranes [45],[46],[47]. Since TEP has a good affinity with PVDF (see **Figure 4b**), the research on this green solvent has basically focused on PVDF membrane fabrication. As an example, Chang et al. (2017) [47] fabricated MD hollow fiber membranes using TEP and compared its phase inversion kinetics to the conventional NMP/PVDF polymer solution system. The TEP/PVDF system presented a less rapid phase inversion rate and resulted in a more porous sponge-like membrane structure than NMP/PVDF system. Moreover, PVDF/TEP solution produced fibers with robust mechanical properties, high LEP and great porosity over 83% for all conditions studied, proving that green solvent TEP is able to replace commonly used NMP in membrane manufacture. Liu et al. [39] used trioctyl trimellitate (TOTM) as an environmentally friendly solvent to prepare porous ECTFE membranes by TIPS method. They analyzed the effect of ECTFE content on the membrane morphology and structure. Importantly, the 15 wt% ECTFE membranes presented the continuous structure without the production of dense layer, however, the further increase in the content of polymer resulted in the spherulite structure and denser surface. Xu et al. [40] introduced the green diluent acetyl tributyl citrate (ATBC) for preparation of ECTFE membrane and investigated the effects of polymer concentration and quenching temperature on the membrane properties. Here, together with the polymer concentration growth, the membrane became more integral, what resulted in a reduction of pore size, porosity and pure water flux but improved mechanical strength and hydrophobic properties.

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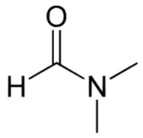
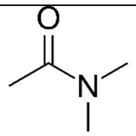
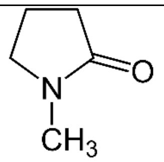
Importantly, several studies have proven that membranes obtained with the use of green solvents are not only a "current hot topic", but also a real competition for materials obtained in a traditional way. Very recently, Meringolo et al. [48] prepared PVDF membranes with dimethyl sulfoxide (DMSO) as the solvent via a combined VIPS and NIPS method without using any chemical additive as pore forming. The resulting membrane exhibited MD performance comparable to that presented by commercial PVDF membranes. Importantly, the cost of DMSO is almost at the same level as traditional solvents and is lower compared to other green solvents (see **Table 3**), which makes it a good candidate for a large-scale membrane preparation. In a different approach, Marino et al. [49] employed a TamiSolve NxG to prepare poly-(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) membranes. Preliminary MD tests showed comparable pore size to commercial PP membranes and promising performance during desalination [49]. The list of green solvents used in MD membrane fabrication together with membrane performance in MD process is enlisted in **Table 4**.

Table 3. The basic parameters of conventional organic solvents and green solvents applied for MD membranes preparation.

Solvent	**Boiling point (ºC)**	**Flash point (ºC)**	**Water Solubility (g/L)**	**Molecule structure**	**Cost**	**Ref.**
DMF	153	58	Miscible		2−4 USD/kg	[50] [30]
DMAc	166	64	Miscible		2−4 USD/kg	[30]
NMP	202	91	Miscible		1-3 USD/kg	[50][30]

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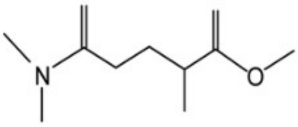
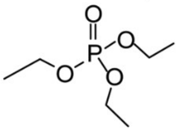
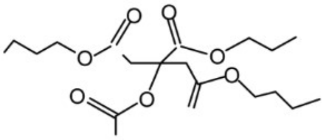
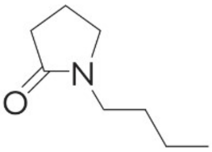
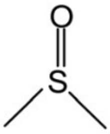
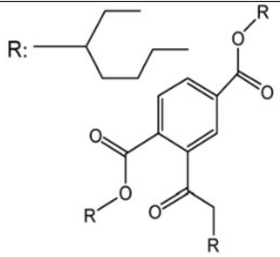
PolarClean	280	145	Miscible		7.3 USD/kg	[5]
TEP	215	112	Miscible		2.6 USD/kg for	[51][35]
ATBC	343	204	0.0045		1.9 USD/kg	[51]
TamiSolve NxG	241	108	Miscible		34USD/kg	[49]
DMSO	189	95	Miscible		1.6 USD/kg for	[5][51]
TOTM	414	>240	<0.00001		69.5 USD/kg	[39]

Recently, the green plant-based binary diluents have been applied to prepare PP microporous membranes, such as carnauba wax and soybean oil [42] and soybean oil and castor oil [41]. The binary diluents ratio significantly influenced the phase separation behavior and membrane morphology. Adding a so-called poor diluent into the polymer/good diluent system induced liquid-liquid phase separation, which favors the membrane formation with a continuous sponge-like pore structure and increases the membrane elongation at break. The PP membranes fabricated using non-toxic binary diluents show the

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potentiality in VMD desalination of 10 g/L NaCl leading to a water flux up to 18.4 kg m^{-2} h^{-1} [41], and 41.2 kg m^{-2} h^{-1} [42].

Table 4. Prepared membranes using green solvents and their performance in MD process.

Solvent	**Features**	**Polymer**	**Fabrication method**	**Membrane type**	**Configuration, performance**	**Reference**
Ethanol + diacetone alcohol	- preferred solvents according to Pfizer solvent selection guide	PU	Electrospinning	Electrospun fiber	DCMD 44 L/m^{2}h 99.96 %	[43]
TOTM	- better high-temperature resistance and less volatility than other solvents for ECTFE	ECTFE	TIPS	Flat sheet	VMD 23.09 L/m^{2}h 99.9 %	[39]
PolarClean	- an ecofriendly biodegradable solvent with no reported health hazards - miscible with water - nonflammable with very low vapor pressure	PVDF	NIPS/N-TIPS	Flat sheet	DCMD ~37 L/m^{2}h 99.9 %	[44]
TEP	- only harmful when being swallowed - high resistant to many organic and inorganic acids - good thermal stability	PVDF	NIPS	Flat sheet	VMD 36 L/m^{2}h 100 %	[45]
		PVDF	wet-spinning	Hollow fiber	DCMD 20 L/m^{2}h 99.99 %	[47]
		PVDF-HFP	NIPS	Flat sheet	DCMD 16.1 L/m^{2}h 99.3 %	[35]
		PVDF	TIPS	Hollow fiber	VMD 30.6 L/m^{2}h	[36]
		PVDF	TIPS	Hollow fiber	DCMD 61.6 L/m^{2}h 99.99%	[37]
ATBC	- non-toxic and eco-friendly - high boiling point	ECTFE	TIPS	Flat sheet	VMD 22.3 L/m^{2}h 99.9 %	[40]

TamiSolve NxG	- nonreprotoxic and biodegradable solvent - similar properties with NMP	PVDF-HFP	NIPS	Flat sheet	DCMD ~25 L/m^{2}h 99.5 %	[49]
DMSO	- polarity similar to those of DMF, DMA and NMP - nonhazardous, biodegradable, and recyclable - good solvent power for many polymers	PVDF	VIPS/NIPS	Flat sheet	DCMD 12.1 L/m^{2}h 99.9 %	[48]
Soybean oil	- edible oil - limited solubility, thus it is used as a one component of binary solvents	PP	TIPS	Flat sheet and hollow fiber	VMD 18.4 L/m^{2}h 99.99%	[41]
		PP	TIPS	Flat sheet	VMD 41.2 L/m^{2}h 99.95 %	[42]

Remark. Based on recent studies, it can be concluded that the substitution of traditional solvents with greener ones is possible. However, there are two aspects to consider before implementing them in large-scale productions. First, the membrane performance must be maintained or improved if possible. The second aspect is the economical estimation, as the price of green solvents is usually higher than that of traditional ones (see **Table 3**), however, researchers need to focus on the cost-benefit ratio as today there is a greater need to avoid the negative impact of conventional solvents on the environment. Although some research proved the feasible to achieve both goals simultaneously, this is only a small part of the overall research conducted on membrane fabrication using green solvents. Finally, some of the novel green solvents have not yet been investigated as dissolving systems to prepare MD membranes. For instance, deep eutectic solvents, which depending on their precursors, are considered low toxic, biodegradable, eco-friendly, and cheap [52]. It is worth exploring other possible solvents, like deep eutectic solvents, but always considering the physicochemical properties of the precursors (e.g., volatility) [53] during the membrane preparation.

2.2.2. Solvent-free methods

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The solvent-free method assumes membrane fabrication without the aid of any organic solvents. It involves processes, such as melt-spinning and stretching or cold-pressing; nevertheless, the publication record of solvent-free method for MD membranes fabrication is relatively less compared to the green solvents application.

Melt-spinning and stretching (MS-S) technique is a green and simple membrane preparation process, given that it does not require the use of any diluents and solvents, and does not involve any phase separation. To fabricate the membrane via this process, the polymer melt is spun at a temperature close to its melting point, while the pores are formed through the stretching force acting on the material in a further cold-stretching step [54]. In general, the formation mechanism of the microporous structure by MS-S method is possible due to the presence of stacked crystalline lamellar in the crystalline polymers. During stretching step, the crystalline lamellar is gradually separated, the large number of voids is formed, which are subsequently interconnected, and the micropores are then created. Therefore, MS-S is suitable for preparation of microporous membranes from highly crystalline polymer membranes, such as PE [55], PP [56] and semi-crystalline, for example PVDF [57]. The PVDF membranes fabricated by MS-S exhibited excellent mechanical properties, much better than that made by phase inversion method. Unfortunately, the porosity of those membranes was poor, as a consequence of PVDF semi-crystallinity, what lead to low pure water flux [58]. To increase the porosity of the membranes formed from semi-crystalline polymers, Hu et al. [59][60] proposed interfacial pore theory during the membrane preparation process via MS-S, which states that the blend of polymers with poor compatibility would form an interface layer between the polymer matrices. During the stretching step, this interfacial layer with low adherent strength facilitates the formation of the pores between matrix phases. Following this hypotheses, the authors prepared polyurethane/PVDF blend hollow fiber membrane, and observed improved pure water flux of 2174 L m^{-2} h^{-1} under the pressure of 0.1 MPa.

Although recent studies on MS-S membranes refer to membrane fabrication for oil/water separation [61], microfiltration [62], and membrane emulsification [63], there are several studies showing the possibility to apply MS-S for MD membrane fabrication [64][65]. Chen et al. [65], for instance, fabricated poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) hollow fiber membranes through

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melt spinning and stretching method. Similar to PTFE, FEP poses excellent thermal and chemical resistance and strong hydrophobic nature. The authors investigated the effect of different stretching ratios on membrane structures and thus performances. Together with the stretching ratios, the membrane's porosity increased, while the membrane stretching had a negative effect on the mechanical properties and LEP value. The VMD tests proved that the FEP hollow fiber membranes exhibited satisfying salt rejection (99%) and stable but relatively low permeate flux (ca. 8.4 LMH). In another study, Shao et al. [64] fabricated PP hollow fiber membranes made by MS-S method. When observing the membrane microstructure, the results indicated that the slit-like micropore size between 0.05– 0.3 µm have been formed during the MS-S. During the VMD test, the water flux reached 7.8 L m^{-2} h^{-1} while hindering the salt passage (rejection 99.9%).

The innovative solvent-free methods found to be useful in fabrication of PTFE porous membranes. Besides its superior properties, this polymer is difficult to process and challenging to prepare membranes by common phase inversion or melt spinning method, due to its ultrahigh melt viscosity and its insolubility. Therefore, the PTFE hollow fiber membranes are today fabricated via emulsion spinning, paste extrusion and stretching technology [66]. Interestingly, Zhu et al. [67] fabricated the PTFE hydrophobic hollow fiber membranes through a cold pressing method, including paste extrusion, stretching and sintering, and investigated the effect of stretching ratios on membrane performance. An increase in stretching ratio significantly improved the permeation flux in VMD desalination. The salt rejections for all the fabricated PTFE hollow fiber membranes achieved 99.9%. In the same research group, Wang et al. [68] observed that the increasing of stretching ratio endowed the membrane with higher porosity and larger pore size. Their PTFE membranes were tested in VMD during the treatment of seawater reverse osmosis brines. The results showed that the increase in stretching ratio and heating temperature significantly improved the permeation flux. Although the permeate flux of as prepared PTFE hollow fiber membrane was much lower than that of other hollow fiber membranes, the authors stated that membranes fabricated through cold pressing method are promising for practical application.

Remark. Compared with TIPS and NIPS, the MS-S process is more difficult to control in terms of pore formation and its size. It also requires crystalline polymers as the precursor materials for preparing the

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microporous membrane. However, the use of solvents and diluents in the phase separation processes results in the generation of huge amount of waste solvent. Thus, the solvent-free processes are more environmentally friendly. Recent studies investigated the green and sustainable preparation of polymeric membranes using MS-S method, unfortunately, none of them have been tested in MD process [69][70][71].

2.2.3. Novel and sustainable approaches for nonsolvent induced phase separation

As mentioned in the previous section, phase inversion method is a main approach to produce PVDF MD membranes. The NIPS method requires at least three components: polymer, solvent to dissolve the polymer, and nonsolvent to coagulate the membrane. In a typical NIPS process, a polymer dope solution is cast into a thin film and subsequently immersed in a nonsolvent bath (see **Figure 5a**). Water is frequently used as a nonsolvent, due to its availability, versatility and economic and environmental reasons. However, if the polymer solvent is water-soluble (what is very common for MD polymer solvents, see **Table 2**), it will lead to a dense membrane formation during the NIPS process, due to the fast solvent/non-solvent exchange rate. Consequently, these membranes will have a lower water permeance, as one of the prerequisites for effective vapor flux in MD process is microporous structure of the membrane. The phase demixing process is highly affected by the system components and their concentrations. In fact, the nonsolvent is considered as a strong one when its affinity with the polymer is low and the exchange rate between the solvent and nonsolvent is fast. In this case, rapid demixing of the polymer solution takes place and the formed membrane is characterized by a dense and asymmetric structure [72]. On the other hand, while the nonsolvent affinity with the polymer grows, the precipitation is slower and delayed demixing occurs, resulting in formation of porous and a more symmetric structure of the membrane. Therefore, the precipitation rate is strongly influenced by the affinity of the nonsolvent with both the polymer and the solvent. Thus, different combinations of the system components can lead to very dissimilar morphologies and structures of the membrane. For instance, few studies proposed the use of alcohols, such as methanol [73], ethanol [74] or isopropanol [38], as nonsolvent phases during coagulation bath, to fabricate hydrophobic PVDF membranes by NIPS method. In this regard, Munirasu et al. [73] fabricated highly porous and superhydrophobic PVDF membranes using methanol as nonsolvent, and compared them with the membranes fabricated through water phase inversion. When using this latter method, the membrane exhibited a particulate-like dense top layer with an asymmetric structure. On the contrary, the methanol induced phase inversion showed distinct sponge-like morphology, uniform throughout the whole PVDF film. Another approach is the solvent addition to the coagulation bath which lowers the nonsolvent activity and its diffusion rate into the polymer film, and consequently leads to the delayed demixing. Ghosh et al. [75] showed that by adding a small amount of polymer solvent to the coagulation bath (3% NMP/water solution), the membrane permeability increased by more than 25%. However, considering the environmental issues, those approaches are far from being green and sustainable. For instance, Razali et al. [76] calculated the amount of wastes generated from membrane manufacturing plants, and their estimation shows that approximately 100–500 L of wastewater per square meter of membranes is produced after coagulation step. Thus, the use of solvents, or alcohols as nonsolvent phases, may be environmentally unfriendly and costly.

Another solution preventing the formation of dense membranes is the addition of pore-forming agents in the polymer dope solution, such as (PVP)[77][78][79], polyethylene glycol (PEG)[80][81], Pluronic [77], and LiCl [80]. The addition of pore-forming agents induces a sponge-like membrane structure, prevents finger-like macrovoid formation, enhances both pore formation and interconnectivity. For example, Jung et al. [77], aiming to prepare porous membranes from PVDF/PolarClean solution, investigated the effect of three different sets of casting solution additives (Pluronic F-127, PVP, and LiCl & glycerol). To some extent, the pore-forming additives improved the water permeability, however, greatly decreased the mechanical strength of the resulting PVDF membranes. Among the tested additives, Pluronic was found to be the most effective pore-former. The membrane prepared with Pluronic showed narrow pore size distribution and water permeability up to 2800 L m^{-2} h^{-1} bar^{-1}.

Accordingly, it is highly important from environmental and practical perspectives to utilize a simple and green polymer system with only a water bath at room temperature to fabricate porous membranes without any dense layer for MD. Recently, an interesting method was proposed by Tian et al. [82], who produced a porous PVDF membrane by using co-casting method. During the fabrication process, they

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first cast a PVDF layer on the glass plate and then immediately cast another isolation polyethersulfone (PES) layer onto the PVDF layer. After being immersed in the water coagulation bath, they found out that the PES and PVDF layer separated automatically, as a result a porous PVDF membrane surface has been formed without adding any pore forming agents. Thus, the PES layer acted as an isolation layer which decreased the exchange rate of solvent and non-solvent, resulting in the formation of porous membrane surface. The porous PVDF membrane exhibited steady fluxes during a long-term DCMD test for 48 h using a 3.5 wt% NaCl solution as the feed, along with continuous high salt rejection of above 99.95%. Zou et al. [44] fabricated high-flux and stable PVDF membrane that was produced using co-casting method, as illustrated in **Figure 5b**. They applied two different green casting fluids including acetyl tributyl citrate (ATBC) and polyethylene glycol 400 (PEG 400). As prepared PVDF membrane top surfaces were highly porous and presented good performance during the concentration of saline water and ginseng extract in the MD process (99.99% rejection and ~37 kg m^{-2} h^{-1} flux). Therefore, co-casting method is a green approach to produce porous membranes, using water as a coagulation bath, without the need for adding any pore-forming agents.

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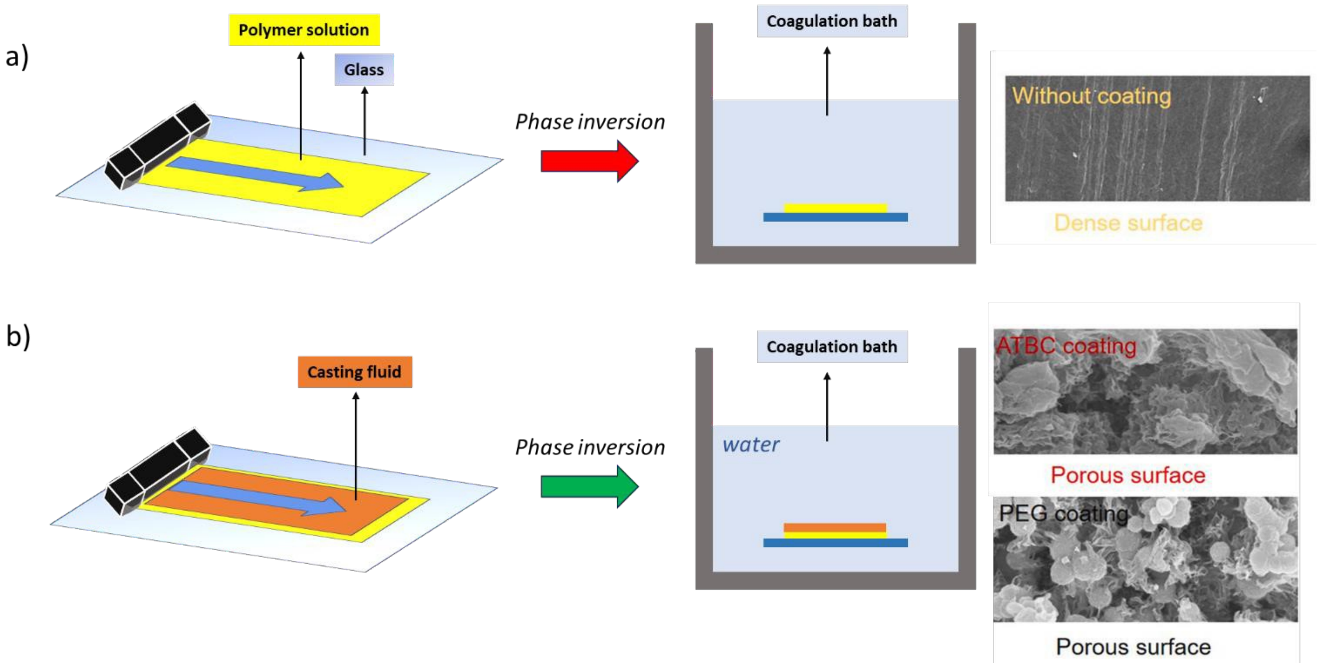

Figure 5. Membrane fabrication method using a) traditional phase inversion, b) co-casting method, and their morphology (SEM images reproduced from ref. [44] with permission from Elsevier, copyright 2022).

Delayed phase inversion not only prevents dense structure formation, but significantly enhances the membrane roughness and water contact angle. At this point, Zhang et al. [83] introduced saturated NaCl-H_2O solution to the PVDF casting solution, which was supposed to serve as green additive for controlling the phase inversion process and hydrophobicity enhancement. The results showed that salt crystals acted as nucleus for the pre-gelation and crystallization of polymer chains. Optimum amount of NaCl-H_2O solution conducted to the formation of superhydrophobic membrane with micro-nano spherical structure. The membrane exhibited great DCMD performance with permeate flux 1.6 times higher compared to the one without NaCl-H_2O addition.

Lu et al. [84] proposed a facile and green method to fabricate superhydrophobic PVDF membranes via pure rheological spray-assisted nonsolvent induced phase separation (SANIPS). Unlike conventional NIPS, compressed air or a designated solution was sprayed on the glass cast membrane, prior to

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immersion in water. This method did not require any further modification, as spraying was adopted to manipulate the morphology of the membranes by controlling the phase inversion speed. The exceptional anti-wetting and self-cleaning properties of the SANIPS membranes have been demonstrated in DCMD tests, while treating hypersaline wastewater, comprising 10% sodium chloride and Rose Bengal dye. The high and stable vapor flux of 36.0 kg m^{-2} h^{-1}, and a salt rejection over 99.9% during the long-term test of 100 h, proved the SANIPS method to be effective for the fabrication of highly porous, hydrophobic and rough structures.

Remark. When the nascent membrane is transferred into water coagulant, the exchange rate between the polymer solvent and water is fast and the undesirable dense layer is formed. Different studies proposed green approaches to delay the demixing during phase separation when the water is used as a nonsolvent, and thus to produce porous and rough structure. Some of them require the use of a multi-stage procedure or the use of additional professional equipment. The most preferred methods demonstrate one-step *in situ* construction of superhydrophobic membranes using only non-toxic and environmentally friendly additives.

3. Membrane modification - substitution of FAS

Fluoroalkyl silanes (FASs) are a group of substances commonly applied in the fabrication of MD membranes in order to create superhydrophobic or omniphobic surface [85]. FASs are composed of long hydrophobic carbon and fluorine chain and functional groups that may form strong covalent bonds with membrane material [86]. Since omniphobic surface can repel almost any liquid that comes in contact with, membrane modification has been studied extensively in order to achieve this property [87], as reported in **Table 5**. It is believed that cooperation of the multi-scale re-entrant topography and low surface energy material is the best solution for the creation of omniphobicity [88]. Within recent years, several studies have been carried out on omniphobic surfaces for MD application. For instance, various studies reported the use of FASs in order to lower the surface energy of membrane material [89][90]. Lee et al. [88] have fabricated omniphobic electrospun PVDF-HFP membrane for DCMD operation. To create multi-scale reentrant structures, silica nanoparticles were attached to the polymer via electrostatic interaction. Then, low surface energy heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (FDTS)

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was grafted on the silica modified PVDF-HFP nanofibers, which provided excellent omniphobic properties. Recently, Deng et al. [91] fabricated nanofibrous PVDF membrane with self-roughened fluorosilane omniphobic coating, without the use of any auxiliary nanoparticles. The preparation method included the electrospinning of PVDF nanofibers, followed by fiber functionalization with long-chained fluorododecyltrichlorosilane (FTCS) via simple solution immersion. The morphologies of those materials revealed the presence of hierarchically re-entrant structures that exhibited the characteristics of high omniphobicity.

Table 5. Some examples of recent studies using FASs for MD membrane fabrication.

Membrane base	Modification method	FASs	References
PVDF-HFP	attaching silica nanoparticles (SiNPs) followed by FAS grafting	(Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (FDTS)	[88]
PVDF	electrospinning followed by solution immersion treatment	1H,1H,2H,2H-perfluorododecyltrichlorosilane (FTCS)	[91]
PVDF	spray coating of the nano/microspheres onto a commercial PVDF porous substrate	1H,1H,2H,2H-perfluorodecyltrimethoxysilane	[89]
PVDF-HFP	attaching silica nanoparticles (SiNPs) to the fibers, followed by surface fluorination	1H,1H,2H,2H-Perfluorodecyltriethoxysilane	[90]
PDA/PEI/PI	electrospinning technique, electrostatic attraction, and FAS fluorination	(Heptadecafluorotetrahydrodecyl)-triethoxysilane	[92]
Alumina	dip-coating on porous ceramic support followed by post-grafting process with PFOTES	1H,1H,2H,2H-Perfluorooctyltriethoxysilane	[93]
PVDF	indirect fluorination over CNT intermediate layer previously coated on PVDF substrate	1H,1H,2H,2H-perfluorodecyltriethoxysilane	[94]
PA6 (polyamid 6)	surface fluorination followed by PVDF grafting	Trichloro(1H,1H,2H,2H-perfluorooctyl)silane	[95]
Cellulose	the attachment of SiNPs and chemical	(Heptadecafluorotetrahydrodecyl)-triethoxysilane	[96]

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	vapor deposition of fluoroalkylsilane		
PET	graft polymerization of triethoxyvinylsilane (TEVS) and fluorination	1H, 1H, 2H, 2H-perfuorododecyltrichlorosilane (PFDTS)	[97]
GO	fluorination through the thiol−ene click reaction	1H,1H,2H,2H-perfluorodecanethiol (PFDT)	[98]

An important aspect in the application of FASs is their cost, these chemical reagents are typically expensive feedstock. For example, 1 g of commonly used 1H,1H,2H,2H-perfluorodecyltriethoxysilane can cost between 28–40$ [99]. Furthermore, FASs may pose a negative environmental impact. Because of the difficulty of breaking the carbon-fluorine bond, per- and polyfluoroalkyl substances are persistent in the environment. Based on their chemical properties and various studies suggesting potential human toxicity and emerging water pollutant concerns [100][101], researchers began to look for replacements for long-chain per-fluorinated additives in lowering surface energy of the membrane.

A CF_4 plasma treatment has been proved to be an effective method to enhance membrane hydrophobicity (Yang et al., 2015[102], 2014 [103]). It provides a suitable membrane etching that increases surface roughness, and the formation of CF_2-CF_2 and CF_3 bonds that decreases surface energy of membrane. While this treatment imparted omniphobic characteristic of the membrane and significant improvement in transport properties [104], it still required the use of fluorinated additive that is CF_4 gas, with the potential negative impact on the environment and human body. Lee et al. [105] proposed a two-step electrospinning-electrospray method to fabricate a superhydrophobic surface without fluorinated additives. They created polymeric microsphere coating through electrospraying a polymer mixture of PVDF and poly(dimethylsiloxane). Although pure microsphere-coated membrane showed superhydrophobic properties with 156.7° contact angle, it was needed to add the silica-based aerogel particles to strive towards omniphobicity. The 30% aerogel-assisted microsphere-coated membrane presented a high and stable resistance to wetting by relatively low surface tension solution of 3.5% NaCl containing 0.1 mM sodium dodecyl sulfate. Nevertheless, such a surface coating method requires a more complicated two-step process, which leaves internal pores unmodified and poses a risk of

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inhomogeneous surface coverage. Guo et al. [106] adopted one-step biaxial electrospinning and electrospray method to fabricate a hybrid monolayer nanofiber and nanosphere superhydrophobic PVDF-HFP membrane without the use of any long-chain perfluorinated additive. The surface roughness of the nanosphere-nanofiber membrane increased 3.58 times, while good surface stability was achieved thanks to its single layer structure. The fabricated membrane exhibited excellent resistance to wetting and fouling when operated with saline feed water, which consisted of dissolved low surface tension surfactants and organic matters, confirmed with a 7-day MD test (rejection rate of 99.8% and 30 LHM flux). Zheng et al. [107] fabricated hierarchically-structured membrane by grafting octavinyl-polyhedral oligomeric silsesquioxane on PVDF membrane via UV-induced thiol-ene click reaction. Although this method requires chemical preparation of PVDF support (the hydroxylation and sulfhydrylation pretreatment), it offers a fluoride-free, green and cost-effective strategy for superhydrophobic membrane preparation. The fouling and anti-wetting properties of as-prepared membranes were found to be superior compared to the peer membrane reported in literature before. In study of Zhang et al. [108], fatty acids, as naturally occurring compounds, have been proposed as a cost-effective and more environmentally friendly alternative for hydrophobic modification. The carboxylic groups of the fatty acids can be involved in the creation of chemical bonds with the membrane surface, while the long carbon chains are supposed to contribute to the hydrophobicity enhancement. Authors studied two different fatty acid chlorides of palmitoyl chloride and stearoyl chloride with different carbon chain lengths. Due to the presence of acyl chloride group, these chemicals are supposed to easily react with functional groups on ceramic membranes. Both fatty acid chlorides with different carbon chain lengths formed strong covalent bonds on the membranes with the high water contact angle and LEP values, comparable to the hydrophobic membranes prepared through silanization. The comparison of as reported FAS-free MD membranes has been included in **Table 6**.

Table 6. The properties and performance of the FAS-free MD membranes as reported in literatures.

polymer	modification	WCA_0/WCA	LEP_0/LEP	Performance	WSA	Ref.

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PVDF	CF$_4$ plasma treatment	130°/162°	-	DCMD 41.37 LMH	-	[102]
PVDF	CF$_4$ plasma treatment	130°/162°	2.4/3.1 bar	DCMD 32.8 LMH 99.98%	-	[103]
PVDF	CF$_4$ plasma treatment	133°/160°	142.7/186.7 kPa	AGMD 15.3 LMH ~100%	51-52°	[104]
PDMS/PVDF	electrospraying of the polymer/aerogel solution	128°/162°	105.2/129.1 kPa	DCMD 20 LMH 97%	3.4°	[105]
PVDF-HFP	biaxial electrospinning	139°/153°	1.21/2.17 bar	DCMD 32.7 LMH 99.2%	-	[106]
PVDF	octavinyl-polyhedral oligomeric silsesquioxane grafting	136°/155°	-	DCMD 10.5 LMH 99.9%	7.5°	[107]
PVDF	solvent-thermal induced roughening	132°/164°	83/182 k PA	DCMD 20 LMH	8.1°	[109]

WCA$_0$ – initial water contact angle, WCA- water contact angle after modification, LEP$_0$ – initial liquid entry pressure, LEP – liquid entry pressure after modification, WSA- water sliding angle.

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Remark. The elimination of fluoroalkyl silanes from the procedure for obtaining omniphobic membranes is in fact problematic due to their extremely low surface energy, which is unprecedented in other substances. Above mentioned studies on FAS-free synthesis of omniphobic membranes, applied other fluorine materials instead, e.g., CF_4 or fluoropolymers, to achieve low surface energy membranes. Therefore, those methods of obtaining omniphobic surfaces cannot be described as environmentally friendly. On the other hand, attempts have been made to replace FASs with naturally occurring compounds, e.g., fatty acids, giving promising results. However, in the field of MD membranes, this topic is still in its infancy.

4. Design for energy efficiency

According to the 6th principle of green chemistry, the energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure. The MD process meets this regulation in two ways. First of all, it operates at low temperatures as compared to the conventional thermally-driven desalination processes, namely multi stage flash and multiple-effect distillation. Unlike conventional pressure-driven membrane processes, such as reverse osmosis, MD can operate at atmospheric pressure. On the other hand, since MD is a thermally-driven process, it remains an energy demanding technology. The overall estimations of the cost of energy on water production clearly emphasis the economic weakness of the standalone MD systems. Energy consumption accounts for 30% of the total cost of water price using MD (see **Figure 6**), and at the same time, it is the highest contributing factor among others, such as the cost of heat exchangers, storage and membrane modules, and other devices. The high energy consumption in MD systems is due to the need to heat the feed to high temperatures (even up to 70 °C) to provide high driving force for vapor permeation through the membrane. Moreover, MD systems are prone to the heat loss by conduction that occurs in the membrane during the mass transport of vapor [110]. However, based on the analysis and economic evaluation made by Usman et al. [111], MD systems may show better economic potential than reverse osmosis systems (**figure 6**). Due to relatively low operating temperatures, alternative energy sources can be applied to run the MD process. For instance, the integration of renewable energies into the MD process

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significantly reduces the contribution of energy consumption in the total cost of water price and makes the process environmentally friendly and sustainable. As shown in **Figure 6b**, the implementation of waste heat recovery into MD systems decreases the water price from 6.78 \$/m^3 to 4.63 \$/m^3. In addition, as shown in **Figure 6c**, the effect of using solar energy further reduces the price of the water to 1.60 \$/m^3. The cost breakdown is a result of the reduction of energy impact on the total cost of water price to only 2%, which is a significant decrease when compared to conventional standalone MD systems (30%).

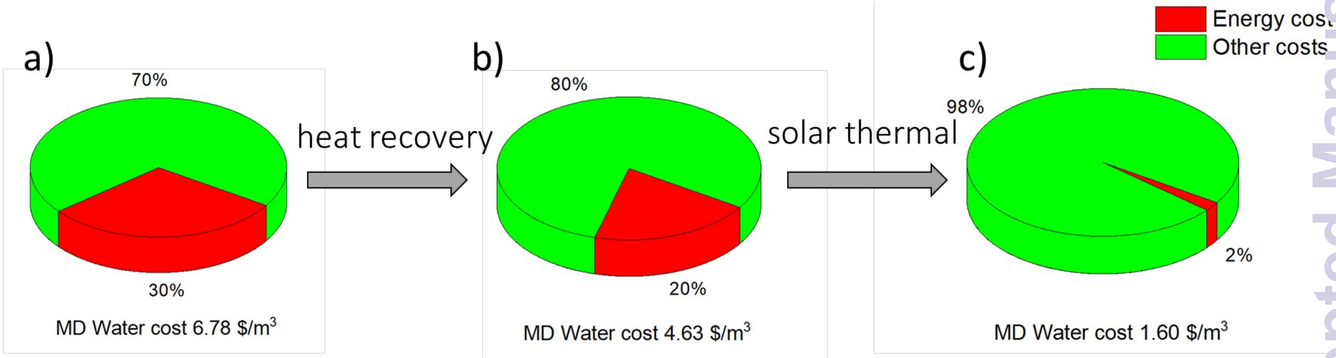

Figure 6. The contribution of energy consumption in total cost of water production price for a standalone MD process a) operating with electricity from the grid, b) assisted by heat recovery (40%), and c) powered by solar thermal and heat waste recovery.

The utilization of low-grade waste heat as driving force has gained considerable attention, as it significantly reduces operating costs [112], giving MD promising potential as a viable technology for future desalination [113]. Recent studies examined the suitability of the MD systems for integration with different types of low-grade heat sources [114], such as solar energy, geothermal energy [115] and waste heat [116]. Among all low-grade types of heat applied in MD systems, solar energy seems to be the most studied so far. However, the use of solar energy requires advanced control strategies [117][118]. Furthermore, an instability of solar radiation and its limited supply time needs to be overcome using technically and economically feasible systems [119]. Nevertheless, various studies confirm the possibility to implement the integrated modules in different MD configurations. For instance, Ma et al. [120] recently built a small scale VMD unit to provide drinking water in remote areas and provide electricity via direct solar heating. Concurrently, Soomro et al. [121] investigated the performance and

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economical comparison of solar power plants integrated with DCMD. Interestingly, water production cost was found to be 0.314 USD/m^3 for the solar powered plant integrated with the DCMD system. Moore et al. [122] developed a comprehensive process model and designed an economically optimal system. Thermal energy for distillation was provided by solar thermal collectors and electricity was provided using photovoltaic collector. Recently, reported studies on MD systems using low-grade heat energy and their desalination performance are summarized in **Table 7**.

Table 7. Recent studies on the MD systems using low-grade heat energy and their desalination performance.

Source of low-grade heat energy	**MD configuration**	**Membrane module**	**Membrane material**	**Permeate flux**	**Salt rejection**	**Ref.**
Ship engine	VMD	Flat sheet	PTFE	13 L/m^{2}h	99.99 %	[123]
Waste heat from ship engine	WGMD	Flat sheet	PTFE	13.08 L/m^{2}h	99.99 %	[116]
Waste heat from ship engine	AGMD	Flat sheet	PTFE	6.73 L/m^{2}h	99.99 %	[116]
Solar energy	VMD	Hollow fiber	PVDF	17.68 L/m^{2}h	Not available	[124]
Waste heat from diesel engine	Multi effect MD	Flat sheet	PTFE	2.61 L/m^{2}h	> 99 %	[125]
Effluent-waste heat	DCMD	Flat sheet	PTFE	14 L/m^{2}h	>99.89 %	[126]

WGMD: water gap MD

Baghbanzadeh et al. [127] have demonstrated the innovative concept of a zero-waste and energy efficient, thus sustainable MD strategy. Since the main energy concern of conventional MD desalination is its requirement of large quantities of thermal energy to heat up the feed, they have established the zero thermal energy input MD. The proposed process implies the use of naturally occurring temperature difference between the surface of seawater (at 30 °C) and the bottom (at 10 °C) as the process driving force. The results show the feasibility of producing pure water with a flux reaching 11.3 L/m^{2}h and a

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cost equal to \$0.28/m^3, which is significantly lower than that offered by the currently dominating membrane desalination technology, reverse osmosis (\$0.45–2.00/m^3).

Although above mentioned studies are praised for significant reduction of water cost production, MD process still cannot withstand large production rates while maintaining energy efficiency. Various hybrid systems have been already thoroughly discussed in terms of water production and energy efficiency [128][129]. For instance, MD integration with conventional desalination processes, such as reverse osmosis, multi-stage flash and multi-effect distillation may result in nearly zero liquid discharge and higher performance. The integration of reverse osmosis system with MD led to reported water recovery higher than 80% [130], which is twice as much as the value for the conventional reverse osmosis. Various integrated desalination systems have been evaluated by González-Bravo et al. [131]. It has been showed that MD desalination systems coupled with multi-stage flash or multi-effect distillation techniques achieved the maximum economic and environmental advantages among other MD integrated systems. The interest of integrated systems grows also within emerging processes. The combination of forward osmosis with MD enables simultaneous production of clean water and regeneration of the draw solution, ensuring process sustainability. The study of Wang et al. [132] demonstrated the prospective of employing the forward osmosis–MD hybrid systems for sea water desalination with a high vapour flux of 6/32 LMH (FO/MD). Kim et al. [133], used the low vacuum pressure naturally created by adsorbents during the adsorption desalination cycle to drive a VMD system without the need for a vacuum pump. The authors noticed a 23% increase in water recovery ratio and a 21% increase in water production compared to a standalone VMD. More recent, MD hybrids in which the electrodialysis [133] or electrocoagulation [134] modules were used for wastewater pretreatment, have emerged. Pretreatment of the feed streams is essential when developing large-scale MD processes, as it significantly reduces the susceptibility of the membrane to fouling and wetting and removes chemicals potentially harmful for the membrane.

Remark. By using low-grade heat energy, it is possible to implement and improve MD for the water supply situation. Current literature suggests that inexpensive energy sources, such as solar energy, geothermal energy, and waste heat, play a crucial role in the water-energy nexus, making the MD process

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more sustainable and cheaper. Although the techno-economic analysis estimates that the utilization of energy from low-grade heat sources makes MD process competitive to conventional desalination techniques, an important factor that has a significant impact on MD economics is its ability to create hybrid systems using the strengths of two or more processes. An extensive evaluation of each hybrid energy demand is needed in order to minimize their specific energy consumption.

5. Conclusions

In the future, the definition of green MD membrane process should be expanded, including sustainability considerations. This transformation requires the innovation of science and technology coupled with new emerging systems design, resulting in a positive impact on a global scale. In the past decade, most research mainly focused on treating wastewater using membrane technology but ignoring the wastewater production itself during membrane preparation process. According to the literature, the wastewater contributed to more than 95 % of the total waste produced during the membrane fabrication process. To achieve completely green and sustainable development of membrane technology, the research on green preparation process should be paid more attention. Designing for a circular economy, which requires the establishment of a series of interconnected closed-loop processes, is crucial. This idea states that no waste streams are generated, but materials are recycled or repurposed to retain or increase their value. This transition, applicable to membrane science and engineering as well as other domains, calls for innovative engineering solutions that enable new ways of designing. In general, some unsolved scientific and technical problems mentioned in the remark at the end of each section are pending and still need to be investigated.

Abbreviations:

AGMD: air gap membrane distillation

ATBC: acetyl tributyl citrate

DCMD: direct contact membrane distillation

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DAMc: N,N-dimethylacetamide

DMF: N,N-dimethylformamide

DMSO: dimethyl sulfoxide

ECTFE: poly(ethene-co-chlorotrifluoroethene)

EIPS: evaporation induced phase separation

FASs: fluoroalkyl silanes

FEP: poly(tetrafluoroethylene-co-hexafluoropropylene)

FDTS: Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane

FTCS: fluorododecyltrichlorosilane

GEMs: gas-entrapping membranes

LEP: liquid entry pressure

MD: Membrane distillation

MS-S: melt-spinning and stretching

NCC: nanocrystalline cellulose

NIPS: non-solvent induced phase separation

NMP: N-Methyl-2-pyrrolidone

PE: polyethylene

PEG: polyethylene glycol

PES: polyethersulfone

PMMA: poly(methyl methacrylate)

PP: polypropylene

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PTFE: polytetrafluorethylene

PVDF: polyvinylidene difluoride

PVDF-HFP: poly-(vinylidene fluoride-hexafluoropropylene)

SANIPS: spray-assisted nonsolvent induced phase separation

TEP: Triethyl phosphate

TIPS: thermally induced phase separation

TOTM: trioctyl trimellitate

VIPS: vapor induced phase separation

VMD: vacuum membrane distillation

WGMD: water gap membrane distillation

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