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Progress of nanomaterials incorporation into PVDF membrane distillation: characteristics enhancement, nanomaterials leaching and stability: A review

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HIGHLIGHTS

- Nanomaterials such as metal oxides, MOFs, and carbon-based materials are incorporated and coated onto PVDF membranes
- The leaching of nanomaterials into the permeate flux can lead to secondary contamination
- The long-term stability of nanomaterials in flat-sheet PVDF membranes is crucial for sustained operation

Keywords:
Membrane distillation; Modification membrane; Nanomaterials; leaching; Hydrophobicity; Stability

ABSTRACT

Membrane distillation (MD) faces challenges in the form of diminished permeate flux attributed to the loss of hydrophobicity with time. Nanomaterials play an essential role in enhancing the performance of MD through membrane modification during formation or surface modification. Numerous nanomaterials have been investigated, particularly for flat sheet polyvinylidene fluorides (PVDF). These nanomaterials have provided unparalleled opportunities for the MD process application, such as increased water desalination efficiency, improved membrane durability, and reduced energy consumption. Adding nanomaterials changed the MD membrane properties, such as the size of the pores, porosity, and hydrophobicity, which significantly enhanced MD efficiency. However, some are sometimes exposed to peel-off or release to the distillate, which causes second contamination (leaching of nanomaterials). This review provides a comprehensive insight into the impact of different nanomaterials on the performance of flat sheet PVDF membranes and their stability over extended operations in MD for water desalination.

1. Introduction

Water, a fundamental resource for human activities, is facing a serious scarcity issue. Despite covering 72% of the planet, only 3% of the total water resources are fresh water, with the rest being saltwater in the oceans, [1]. Rapid urbanization, industrialization, climate change, and a growing global population have all contributed to an irreversible decline in the availability of freshwater resources [2]. The demand for global water use is presently about 4600 km^3/year in 2019 and will increase to 6000 km^3/year by the year 2050. Figure 1(a) displays the global water, the gross domestic product (GDP) per capita, and the population around the world since 1900, and Figure 1(b) displays the graphical representation of water scarcity [3]. In this context, desalination has emerged as a crucial solution, driving the exploration of efficient and reliable water purification technologies [4]. The desalination process can be classified into two types: thermal processes and membrane processes. Thermal processes employ heat source energy, such as fossil fuels, for water evaporation from seawater. Various thermal desalination processes are used to turn the condensate collected into fresh water, such as multi-effect distillation (MED) [5], mechanical vapor compression (MVC) [6], low-temperature thermal desalination (LTTD) [7], multistage flashing (MSF) [7,8], and freeze desalination (FD) [9]. While effective in producing freshwater, these processes can be costly due to the

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high energy requirements. Another part of the desalination process is membrane processing like forward osmosis (FO) [10,11], reverse osmosis (RO) [12], electrodialysis (ED) [13], and membrane distillation (MD) [10]. Though less energy-intensive than thermal processes, these processes also have cost considerations, particularly regarding membrane replacement and maintenance. For reference, the energy consumption associated with these processes varies: MSF requires 10-16 kWh/m^3, MED uses 5.5-9 kWh/m^3 [11], MVD demands 7-12 kWh/m^3, and ED consumes 2.6-5.5 kWh/m^3 [12]. In comparison, FO requires 21 kWh/m^3 [13], while RO consumes approximately 3-4 kWh/m^3 for seawater and 0.5-2.5 kWh/m^3 for brackish water [11]. It is important to note that these processes are continually evolving and improving due to ongoing research, which is encouraging for the industry's progress and the future of desalination technologies.

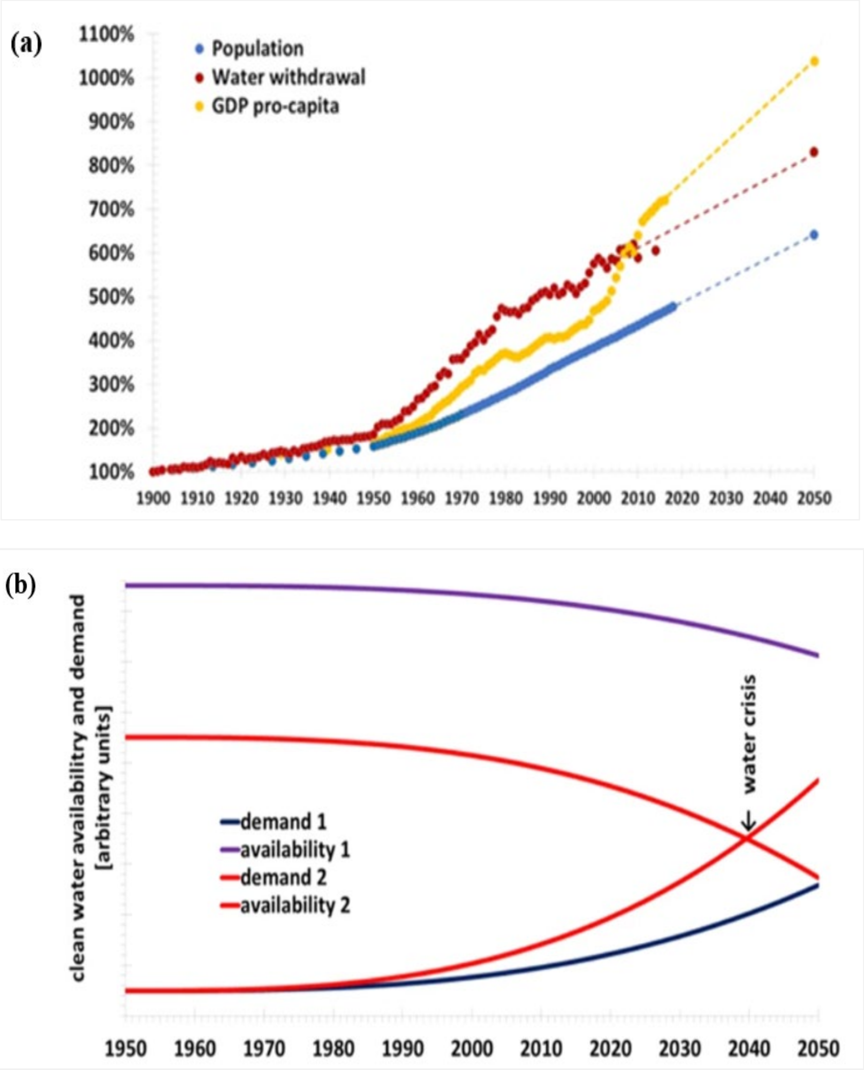

Figure 1: (a) The withdrawal of water globally and the gross domestic product (GDP) per capita, (b) graphical of water scarcity [3]

Membrane distillation (MD) has received significant attention, paving the way for the second generation of membrane processes [14]. Thus, scientists have extensively explored the MD approach for seawater desalination, offering a high salt removal rate, fewer pretreatment requirements compared to pressure-driven membranes, and efficient utilization of low-grade waste heat [15][16]. When compared to other conventional distillation techniques, MD has several attractive features, including low operational pressures (1 atm) and low temperatures (30–80 °C) [17,18], and high rejection of non-volatile pollutants [19]. Its economic efficiency is a major advantage over other thermal desalination technologies, highlighting its cost-effectiveness [20]. MD membranes are available in various configurations, including hollow fiber, spiral wound, and flat sheet membranes. These are typically made from hydrophobic polymers such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP) [18-20]. Among these, PVDF, a thermoplastic fluoropolymer characterized by its inert properties and a repeating unit of -(CH_2CF_2)n, is a popular choice due to its strong mechanical properties, high thermal stability, chemical resistance, and excellent aging resistance [21,22].

The main disadvantages of these polymers are their low permeation flux and unavailability over long-term operation due to their relatively low porosity and hydrophobicity [17]. Table 1 summarizes the essential properties of membranes used in MD processes. Conducting benchmark studies to achieve optimal performance is crucial, as these studies play a pivotal role in guiding the development of more efficient and reliable MD processes.

Table 1: Typical requirement of the characteristic membranes used in the process of MD

Property	Typical values	Ref.
Tortuosity [τ]	1.1-3.9	[19]
Porosity (%)	30-85	[23]
Pore size (μm)	0.1-1	[23]
Operating temperature (°C)	50-70	[24]
Contact angle [θ](º)	>90	[25]
Liquid Entry Pressure (LEP)(kPa)	>250	[26]
Thermal conductivity [W/m.K]	0.1-0.5	[26]
Tensile strength [MPa]	3.4-54.9	[27]

High porosity and a suitable pore structure are essential for enhancing permeate flux and preventing pore wetting in membrane distillation (MD) [27,28]. The wetting properties of membranes can be enhanced by increasing their hydrophobicity, where the membrane is considered hydrophobic if the static water contact angle (WCA) of its surface is greater than 90°, while for the superhydrophobic membranes, WCA is greater than 150° and the water sliding angle is less than 10° [17]. Hydrophobic surfaces can be found in nature, and artificial ones can be made through micro and nanostructure roughness on the surface, as proposed by Wenzel and Cassie-Baxter theories [24]. Researchers have used various methods to achieve hydrophobic surfaces, i.e., plasma etching, laser etching, anodic oxidation, the sol-gel method, and electrochemical reaction and deposition. While effective in enhancing the hydrophobicity of membranes, these approaches present several challenges that underline the complexity and depth of the research in this field. These challenges, such as harsh operating conditions, complex process control, special equipment requirements, and poor durability, are significant and require careful consideration [24]. Recently, nanomaterials have been used to increase hydrophobicity and contact angle of membrane surfaces. Nanomaterials can be integrated into the polymer solution before membrane fabrication or coated onto an existing membrane surface. The latter method is more desirable for MD membrane synthesis, as the membrane surface in contact with the liquid feed must be hydrophobic [28].

This review focuses on using nanomaterials in MD, a process that has shown promise in enhancing the permeate flux and significantly improving the efficiency of the separation process. We specifically concentrate on loading nanomaterials into flat sheet polyvinylidene fluoride (PVDF) membranes prepared by phase inversion. The MD process chooses this polymer due to its attractive properties for water desalination, such as high hydrophobicity and simplicity of fabrication. This article also addresses a frequently overlooked aspect: the stability of nanomaterials within the membrane structure in membrane distillation.

2. Membrane distillation (MD)

Membrane distillation (MD) is a thermal process that relies on a hydrophobic microporous membrane to separate nonvolatile compounds [29]. This process takes advantage of a temperature gradient between a hot side solution and a cold permeate solution on either side of the composite membrane, creating a difference in vapor pressure [30][31]. Mass transfer and heat transfer phenomena occur on the same side, from the hot to the cold side. Subsequently, vapor molecules diffuse across the membrane due to the difference in vapor pressure, following condensation on the cold side (permeate) [32]. Mass transport can occur through three diffusion types: Knudsen diffusion, molecular diffusion, and/or Poiseuille's type of flow [11, 33], whereas heat transport can happen through conduction and convection, leading to loss of energy in the process [26]. Compared to other desalination processes, MD has several advantages, such as operating at lower operating temperatures and requiring less pressure than reverse osmosis (RO) [34,35]. The ability to treat high-salinity water demonstrates promise for the use of low-grade heat energy heat and renewable energy sources for treating water at high salinity with the ability of 100% rejection of nonvolatile components [36,37]. Nevertheless, MD has a number of limitations, such as poor permeate flux, membrane pore wetting, and restricted long-term stability[20, 38,39]

The first patent for MD was granted to Bodel [40], and the first research publication on the subject dates to 1967. Asymmetric membranes designed for MD applications were first developed in 1960 [41,42]. The development of MD membranes is still a scoped application in the desalination industry; utilizing the MD process involves integrating it with different processes, such as forward osmosis (FO) [43], and employing more economical energy sources to make the process more environmentally friendly and cost-effective [44]. For example, DCMD was installed on the island of Pantelleria in Italy, and an integrated power station for diesel engines used waste heat from diesel engines for seawater desalination from the Mediterranean Sea at 35,000 ppm. In contrast, the Amarika Namibia Etosha basin used thermal solar energy for groundwater at 28,000 ppm from well drilling, and the Gran Canaria Spain Test Site of ITC used solar thermal for seawater Atlantic Ocean desalination at 35,000 ppm [45]. Figure 2 displays the growing number of publications for membrane distillation.

Membrane distillation (MD) can be classified into four standard configurations based on the method used to condense water vapor [46,47]. These include direct contact membrane distillation (DCMD), where the membrane is in contact with cold water on the permeate side; air gap membrane distillation (AGMD), where the membrane on the downstream side is in contact with stagnant air which is connected to a cold plate [48]; sweeping gas membrane distillation (SGMD), which consists of sweeping an inert gas on the downstream side of the membrane; and vacuum membrane distillation (VMD), where the downstream side of the membrane is kept under vacuum pressure or lower pressure compared to the upstream side of the membrane. VMD, in particular, has been gaining interest for its versatility in various applications beyond seawater desalination [49,50,51,52].

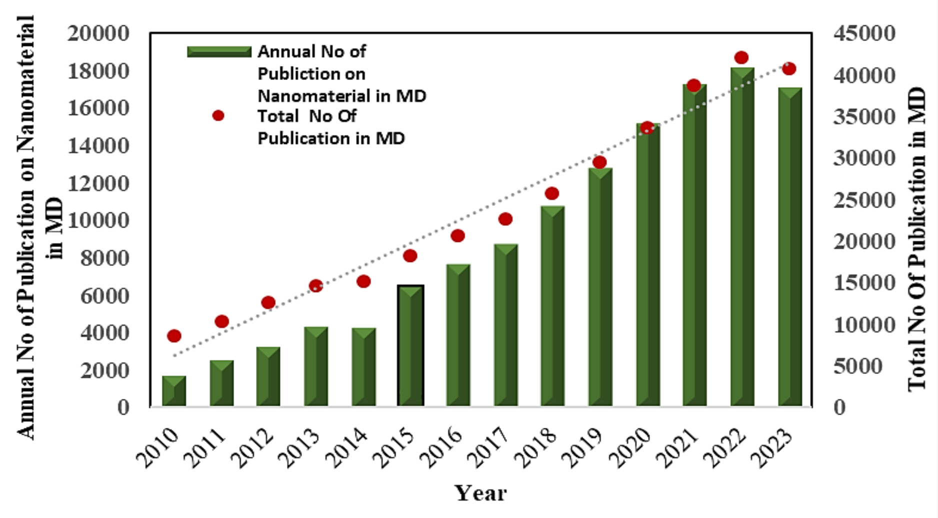

Figure 2: Number of studies on membrane distillation and nanomaterials in membrane distillation in the last 10 years (Google Scholar)

In addition to the main configuration, there are some modified configurations, such as multi-effect membrane distillation (MEMD), material gap membrane distillation (MGMD), permeate gap membrane distillation (PGMD), vacuum-multi-effect membrane distillation (V-MEMD), liquid gap membrane distillation (LGMD), solar vapor gap membrane distillation (SVGMD), pressure-retarded membrane distillation (PRMD), water gap membrane distillation (WGMD), and vacuum-enhanced direct contact membrane distillation (VE-DCMD) [53]. These modified configurations play a pivotal role in expanding the application of membrane distillation. Achieving optimal performance requires an ideal membrane structure and favorable physicochemical characteristics. Characterizing different properties, such as membrane thickness, pore size, contact angle (CA), sliding angle, the roughness of the surface, and liquid entry pressure (LEP) measurements, provides insight into the membrane's hydrophobicity and material composition [54]. According to the configuration of MD, the transport mechanism of vapor is mass and heat transfer; it requires the latent heat of vaporization to change phase from liquid to vapor. Therefore, the thermal energy required for mass transfer is significant. Despite this, the heat sources in the MD process are available for free; however, the energy required to circulate the feed and permeate pumps across the module is required high flow to create high turbulence and produce high flux and high thermal efficiency. Even so, the pump's energy can be ignored in calculating the total energy efficiency [37]. For these reasons, economists view the MD process as more economical than conventional desalination methods, especially because it can utilize low-grade heat sources like solar energy, geothermal energy, and waste heat [55,56].

3. Membrane distillation modification methods

Hydrophobicity is a leading property that significantly improves the water flux. Electrochemical reaction, deposition, anodic oxidation, sol-gel technique, plasma etching, and laser etching are some methods that researchers have used [57,58]. However, these methods often encounter challenges, such as the need for specialized equipment and complex operating conditions and processes [24]. Recently, nanomaterials have emerged as effective means of enhancing the hydrophobicity of membrane surfaces through two primary approaches. Firstly, the method involves blending nanomaterials with the polymer solution during membrane fabrication [59,60]. Secondly, the method involves coating the membrane surface [35].

3.1 Embedded nanomaterials (blending modification)

Nanomaterials blended polymers are composite materials that integrate the properties of nanomaterials with polymers, such as high reactivity, high surface area, and magnetic and optical properties. With their remarkable efficiency, these materials hold immense potential for a wide range of applications in the field of membrane preparation. Embedded (inorganic or organic) nanomaterials are one of the most efficient modification methods for preparing MD membranes with appropriate properties such as hydrophobicity and morphology [61]. Nanomaterials can be embedded in a single stage and are typically used to obtain the required functionality for the membrane production process [26]. Most nanomaterials are dispersed uniformly in the polymeric solution, and a minimum amount of nanomaterials are exposed to anti-fouling properties [56].

Zhou et al. [62] prepared a nanocomposite membrane by blending multi-walled carbon nanotubes (MWCNTs) and additives MWCNTs/ SiO_2 (three additives with hydrophobic, superhydrophobic, and hydrophilic properties) with PVDF for desalination by (VMD). The study investigated the impacts of MWCNTs and MWCNTs/SiO_2 on the structure and efficiency of the membrane. It was found that when loading MWCNTs as the additive, the pore size decreased, and the finger-like layer extended and increased the porosity. It also increased the size and number of macro voids, increasing VMD flux to 5.6 $kg/(m^2 \cdot h)$, but the mechanical properties deteriorated. When the SiO_2 to MWCNTs ratio increased, the membrane structure gradually collapsed, resulting in a membrane with compressed microvoids (low porosity), and the permeate flux exhibited 4.55 $kg/(m^2 \cdot h)$. Besides, embedded nanomaterials greatly influence the diffusion of water molecules through membranes. Lee et al.

[63] described the diffusion of water molecules through blended polymer/carbon nanotubes (CNTs) mixed matrix membranes (MMMs) following three mechanisms: direct diffusion through the polymer matrix, diffusion inside the inner wall of CNTs, and surface diffusion through the outer wall of CNTs , Figure 3. Additionally, some molecular simulations have further proved the accelerated flow (increased permeate flux) in MMMs due to hydrogen bonds forming between water molecules as molecules move through the CNTs' interior structure. These connections and the weak interactions between water and the hydrophobic CNT walls create nearly frictionless pathways, resulting in increased flux.

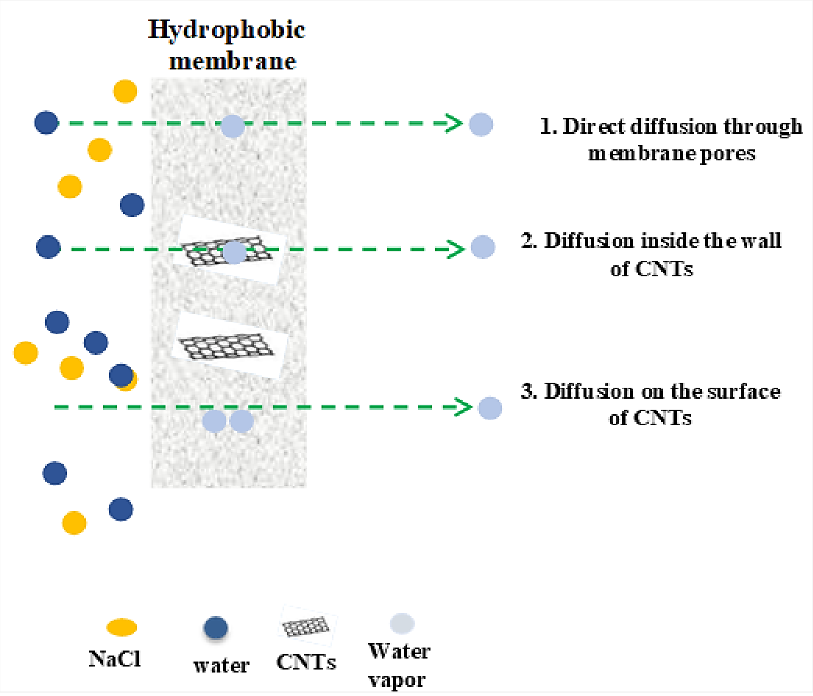

Figure 3: Schematic diagram of the mechanism of diffusion in MMM [63]

3.2 Surface coating

Surface coating, the simplest and most effective method for enhancing the performance of MD membranes, is a field of diverse approaches. By altering the surface characteristics such as roughness, surface energy, and hydrophobicity, a thin functional layer is deposited on the membrane's outer surface. The main challenge is the potential instability of the deposited layer (nanomaterials), which can be released during cleaning and long-term operation in MD due to the relatively poor physical adsorption connection between the coated layer and the membrane surface. Therefore, chemical modification, such as cross-linking, is often used to ensure the stability of nanomaterials [26]. This modification is preferred for fabricating membranes in MD, as the membrane surface in contact with the liquid feed must exhibit hydrophobic or superhydrophobic properties. The field employs a variety of methodologies, such as dip coating, electro-spraying, spray coating, and vacuum filtration, each with unique advantages and challenges [19]. Figure 4 illustrates the publications on surface modification methods, showcasing the diversity of approaches in this field.

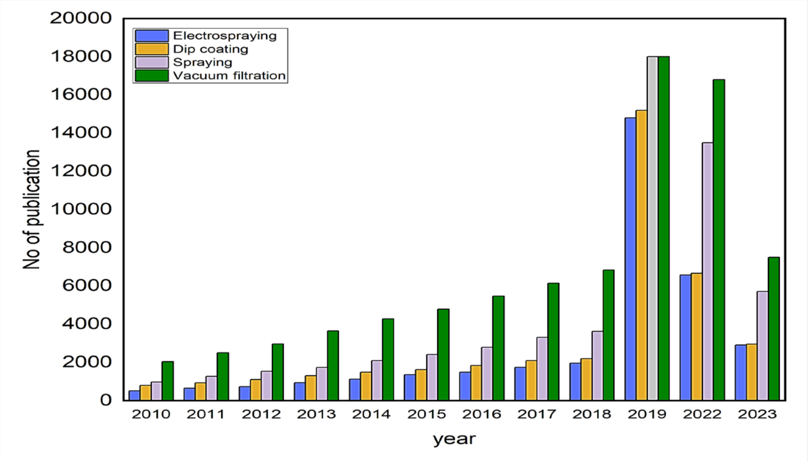

Figure 4: Number of publications using surface modification in MD (according to Elsevier database)

3.2.1 Dip coating

The dip coating method is a simple method to deposit nanomaterials on the MD membrane and involves three stages: immersion and duration stay, accumulation, evaporation, and outflow from the solution, as shown in Figure 5 (a) [64]. The coating layer's thickness, the pores' size, and the membrane structure are significantly influenced by various process factors, such as dip coating concentration, the concentration of crosslink, and the dipping time [65]. This method creates a rough surface and increases hydrophobicity [66]. However, it is essential to note that dip coating may have several disadvantages despite its ease of use. These include low coating quality and non-uniformity, depending on the types of samples and processing circumstances, as well as the clogging of membrane pores by nanomaterials over a long period of operation in the MD process, which limits the usage of dip-coating on the surface of the modifying membrane [57, 67]. The dip coating method is also susceptible to many types of defects caused by contamination, aggregation of precursors, air bubbles microscopic in the solution, and variations in the supporting substrate surface. However, the dipping is performed in a clean (controlled) environment and repeated numerous times, ensuring the reliability and consistency of the coating process [58, 68].

3.2.2 Electro-spraying

Electro-spraying is a versatile and economical technique for preparing nanocomposite–nanofiber membranes. In this process, homogeneous nanomaterials are generally dispersed in the polymeric dope solutions [69]. High voltage is used to eject the liquid jet, and different types of nanomaterials are introduced to create nanofibers [11]. After adding the nanoparticles, the solution becomes more viscous, and the size and quantity of beads decrease, improving the membrane's surface roughness and, subsequently, its hydrophobicity and tensile strength [25,70].

3.2.3 Spray coating.

Spray coating, an effective and robust process, instills confidence in its application for minimizing wetting and pore penetration, making it ideal for preparing inorganic porous membranes. It employs a spraying device (based on an airbrush of air, such as a spray gun) to deposit nanomaterials onto the surface of the membrane through the air, as shown in Figure 5 (b) . It can be applied to any kind of material, flexible or solid, and this approach can be used to coat any flat materials. The thin film homogeneity formed by this process (spray coating) is contingent upon the spray pressure, necessitating optimization.

3.2.4 Vacuum filtration

Vacuum filtration is a physical coating technique in which the solution is filtered through the membrane surface. Before filtering, the coating solution is frequently agitated to provide a uniform surface layer [25]. It can significantly decrease the defects of the pores, contributing to the tortuosity of the membrane required for the MD process. This approach typically yields a homogeneous thin film; the film thickness may be adjusted by varying the filtered suspension's volume and the solution's concentration as shown in Figure 5 (c). It is not scalable and is limited to the filter membrane's size (increased filter size, effective area of evaporation to enhance the flux) [71,72].

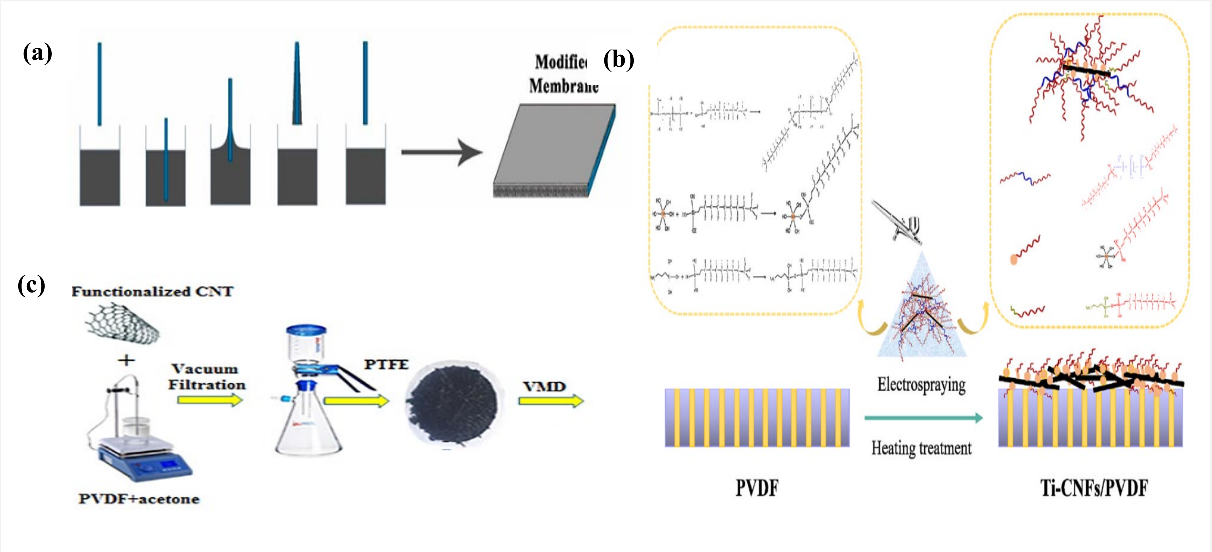

Figure 5: Surface modification method a) dip coating [16] ,b) electrospraying, [73] c) vacuum filtration [74]

4. Types of nanomaterials for membrane modification

Nanomaterials, such as metal oxide nanomaterials, metal-organic frameworks (MOFs), and carbon-based nanomaterials (carbon nanotubes, graphene, and quantum dots), are increasingly recognized for their potential to enhance MD membranes. They are instrumental in monitoring the change of the characteristics of the PVDF membrane and determining the proper loading range based on specific criteria (such as porosity, hydrophobicity, thickness, and roughness) for achieving superior outcomes compared to the virgin membrane in terms of water flux and salt rejection. The use of nanomaterials in MD is a promising area of research with significant potential. Figure 6 illustrates the growing interest in nanomaterials for MD, as evidenced by the increasing number of published papers on different types of nanomaterials over the last few years. This trend highlights the potential of nanomaterials in MD, with metal-organic frameworks (MOFs) being an up-and-coming area of research.

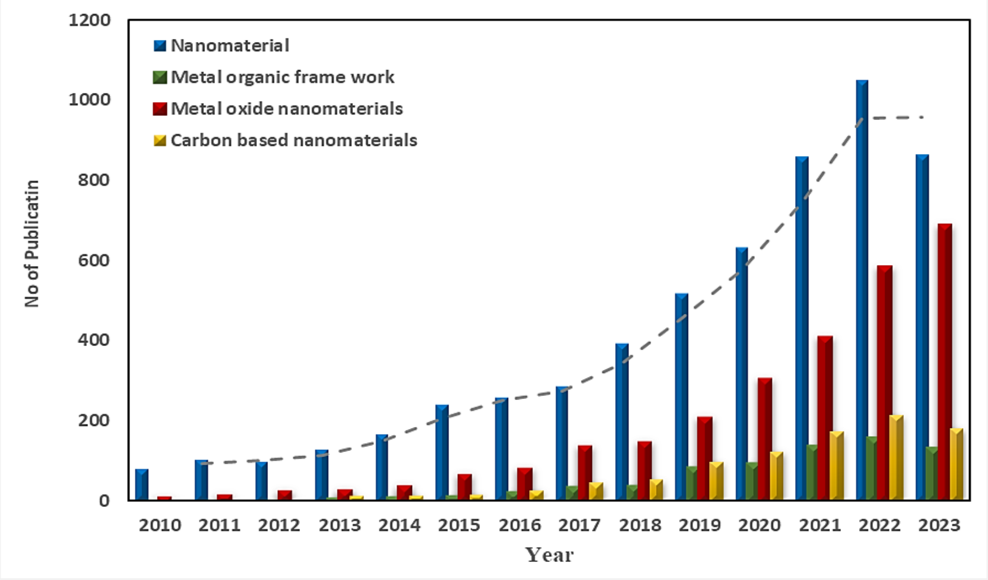

Figure 6: Number of Publications about all types of nanomaterials (metal oxide nanomaterials- metal-organic framework- carbon-based nanomaterials- Metal oxide nanomaterials) for water desalination by MD research at the word (according to Elsevier database)

4.1 Hydrophobic metal oxide (TiO_2, SiO_2, and ZnO) on PVDF membrane

In recent research, different metal oxide nanomaterials such as TiO_2, SiO_2, and ZnO are used to enhance the performance and maintain the stability of the water permeate flux over a long time of MD operation [75,76]. The metal oxide nanomaterials in the membrane can effectively reduce fouling and wetting, and modifying membrane surfaces with metal oxide nanomaterials can enhance operational performance and flux stability in long-term MD processes [2, 76]. Table 2 shows the effect of metal oxide nanomaterials on the MD membrane properties and the permeate flux.

4.1.1 Hydrophobic titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) is a commonly used metal oxide nanomaterial to enhance the performance of PVDF membranes in MD due to its low cost, commercial availability, chemical stability, low toxicity, and anti-fouling properties [77,78]. The rapid and inexpensive hydrothermal synthesis of TiO_2 nanomaterials can produce various morphologies, including nanorods and others [79][80]. Merging of TiO_2 in the MD could change the membrane from hydrophobic to hydrophilic due to the hydroxyl group, which caused the membrane to have high surface energy. As shown in Table 4, TiO_2-coated PVDF membrane reduced the permeate flux by 15% when coated with perfluoro dodecyl trichlorosilane (FTCS) and produced a superhydrophobic membrane, as shown in Figure 7 (a). The surface structure, porosity, and size of the pores of the PVDF membrane were not significantly altered by the accumulation of TiO_2. Due to the extremely thin layer of TiO_2 present on its surface, it was shown that the modification of the PVDF membrane after being coated with TiO_2 did not change the mean pore size, and the LEP was reduced by about 33% after the deposition of TiO_2 on the surface and enhanced 58% after modification because of the low surface free energy of fluorosilane (FTCS). In order to check the stability of the coating layer and evaluate the mechanical properties of the membrane, the contact angle was measured after being submerged in distilled water and sonicated for 15 min. at room temperature.

The results demonstrated that the contact angle of the FTCS-TiO_2-PVDF membrane decreased slightly from 163 to 160°, which indicates that the coating was mechanically stable due to the strong interaction between the hydroxyl group and TiO_2 in the PVDF membrane. When the temperature was increased to 90 °C, the contact angle reduced marginally to 156°, indicating the thermal stability of the coated membrane reduced the surface tension of water and the cohesive forces and enhanced molecular thermal activity and surface hydrophobicity [81]. On the other side, hydrophobically modified TiO_2 with a silane coupling agent can be embedded with PVDF, as shown in Figure 7 (b) , enhancing DCMD performance by 2.3%. The results demonstrated that the performance depends on the concentration of silane; increasing silane enhanced the membrane hydrophobicity by 21% and the rejection by 100% [82]. Fluorination of TiO_2 leads to covalent bonding between the PVDF membrane and the hydroxyl group (OH) of TiO_2, and then TiO_2-Silane is entangled in the membrane matrix. This modification and connection by the hydroxyl group, which acts as a bridge between the PVDF membrane and TiO_2, prevents aggregation and enhances the stability of nanomaterials [16].

4.1.2 Hydrophobic silicon dioxide (SiO_2)

The research on transforming silicon dioxide SiO_2, a naturally hydrophilic material, into a superhydrophobic material has immediate and significant practical implications for water desalination. This transformation can be achieved using hydrophobic binders like flourosilane [83] or by directly synthesizing the hexamethyldisiloxane precursor [84]. For instance, applying a fluorinated SiO_2 spray on the membrane increased the contact angle by 172% and effectively filled surface cavities by depositing material onto the membrane onto the membrane orderly after SiO_2 deposition. The FTIR image of the modified SiO_2 showed a functional group (-CH2-CH3), indicating the chemical stability of the nanomaterials in the PVDF membrane and their ability to enhance hydrophobicity for MD applications. The F-SiO_2@PVDF membrane demonstrated a 350% enhancement in water flux compared to the pristine PVDF membrane. Additionally, it exhibited salt rejection over 99.95% and a more stable flux, with only a 16% decrease during 24 hours of application. These results highlight the immediate and practical importance of the modified membrane for water desalination in AGMD [85]. In another study, Efome et al. [86] blended superhydrophobic silica nanomaterials (SiO_2) with polyvinylidene fluoride at different concentrations to enhance the efficiency of VMD. While increasing the concentration of nanomaterials led to larger pore sizes, the results from the SEM images indicated that the pore size remained consistent across all membranes. This phenomenon is attributed to the agglomeration of the hydrophobic nanomaterials, which, despite their stability, did not significantly impact the pore size, water flux, or salt rejection of the membranes at higher concentrations.

4.1.3 Hydrophobic zinc oxide (ZnO)

Another metal oxide nanomaterial, zinc oxide (ZnO), stands out for its high surface-to-volume ratio, excellent thermal resistance, and antibacterial properties. Its cost-effectiveness, non-toxicity, and mechanical and chemical stability have made it a subject of increasing interest. These nanomaterials are believed to offer a more economical and environmentally friendly alternative to TiO_2 for modifying membrane surfaces. When ZnO is treated with fluorosilane like 1H, 1H, 2H, and 2H-perfluorooctyltriethoxysilane (FAS), it may provide anti-wetting, anti-fouling, and anti-scaling properties with a higher water contact angle and lower sliding angles. These characteristics of ZnO with FAS provide a stable surface and super hydrophobicity, suggesting that these nanomaterials could be a promising solution for MD [87,88].

A study by Wang et al. [148], used ZnO nanorods with a pyrolysis-adhesion method and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PDTS) to modify the PVDF membrane and create a superhydrophobic membrane (P-ZnP), resulting in a remarkable 152° water contact angle. The size of the pores and porosity slightly decreased due to the filling of some pore sizes by nanomaterials, and the liquid entry pressure of the modified membrane was higher than that of the neat membrane at 277 kPa. The hydrophobicity was enhanced by 20% when modified with the low surface free energy of PDTS, a crucial property for the superhydrophobic membrane according to the Cassie-Baxter theory. Additionally, the high aspect ratio of the nanorods significantly lowered the adhesion force and contact area between the membrane and droplets [89]. The modified P-ZnP membrane maintained the same permeate flux as the pristine PVDF membrane while demonstrating high salt rejection, a benefit attributed to its anti-wetting properties and the micron gap between the membrane and the feed solution [89]. The findings indicated that the use of modified ZnO with PDTS resulted in enhanced stability of the nanomaterials, which improved the mechanical properties of the modified membrane due to the covalent bonds formed between Si-O-Zn (the chemical bonds connecting PDTS and ZnO).

Table 2: Some literature on metal oxide nanomaterials (SiO_2-TiO_2-ZnO)/PVDF membrane in MD

MD Conf.	Process parameter	Membrane type	Nanomaterial	Method of addition nanomaterials	LEP (bar)	Operating Time (h)	Contact angle (°)	Flux (kg/m^2h)	Rejection %	Ref.
DCMD	3.5 wt% NaCl	PVDF	PM		120	8	125	37	94	[81]
	Tf:70 ºC		F-TiO_2	Coating	190		163	32		
	Tp:25 ºC									
DCMD	Tf:60 ºC	PVDF	PM		78	--	97	3	99.9	[82]
	Tp:25 ºC		TiO_2	Embedded	90		84	13		
			F-TiO_2		140		118	10.10		
AGMD	3.5 wt% NaCl	PVDF	PM		--	24	98.5	5.7	99.54	[85]
	Tf:70 ºC		F-SiO_2	Coating			169.7	10.1	99.95	
	Tp:25 ºC									
VMD	35 g/L NaCl	PVDF	PM		489	6	76	0.7	99.98	[86]
	Tf:70 ºC		F-SiO_2	Embedded	448		94	2.9		
	Tp:25 ºC									
VMD	200 g/l	PVDF	PM		238	8	116	5.6-4.5	93	[89]
	Tf:60 ºC		F-ZnO	Coating	277		152	4.7-4.5	98.6	
DCMD	7-12 g/L NaCl	PVDF	PM		250	3	53	12	96	[90]
	Tf:80 ºC		F-ZnO	Embedded	100		67	18	96.8	
	Tp:25 ºC		F-ZnO-ZIF		100		70	25	98.9	

DCMD: direct contact membrane distillation; AGMD: air gap membrane distillation; VMD: vacuum membrane distillation; Tf: feed temperature; Tp: permeate temperature; NaCl: chloride sodium, PVDF: polyvinylidene fluoride; PM: Pristine membrane.

In another study by Salehi et al., blended functionalized ZnO with fluoro silane (F-ZnO) and functionalized ZnO-ZIF with PVDF Figure 7 (c). The liquid entry pressure (LEP) went down when F-ZnO and F-ZnO-ZIF were added due to the increase in the size of the pores and porosity of the membrane. This rise was a result of the rate of diffusion of solvent from the cast film, which reduced the thermodynamic stability of the cast film and the phase inversion when hydrophobic additives were added. The hydrophobic membrane (F-ZnO-ZIF-PVDF) showed higher distillate and high salt rejection than the pristine PVDF membrane [90]. Metal oxide nanomaterials are inherently hydrophilic, which decreases the contact angle of the membrane. Therefore, they are modified with different chemical reagents (fluorosilane) to enhance their stability and membrane performance in MD.

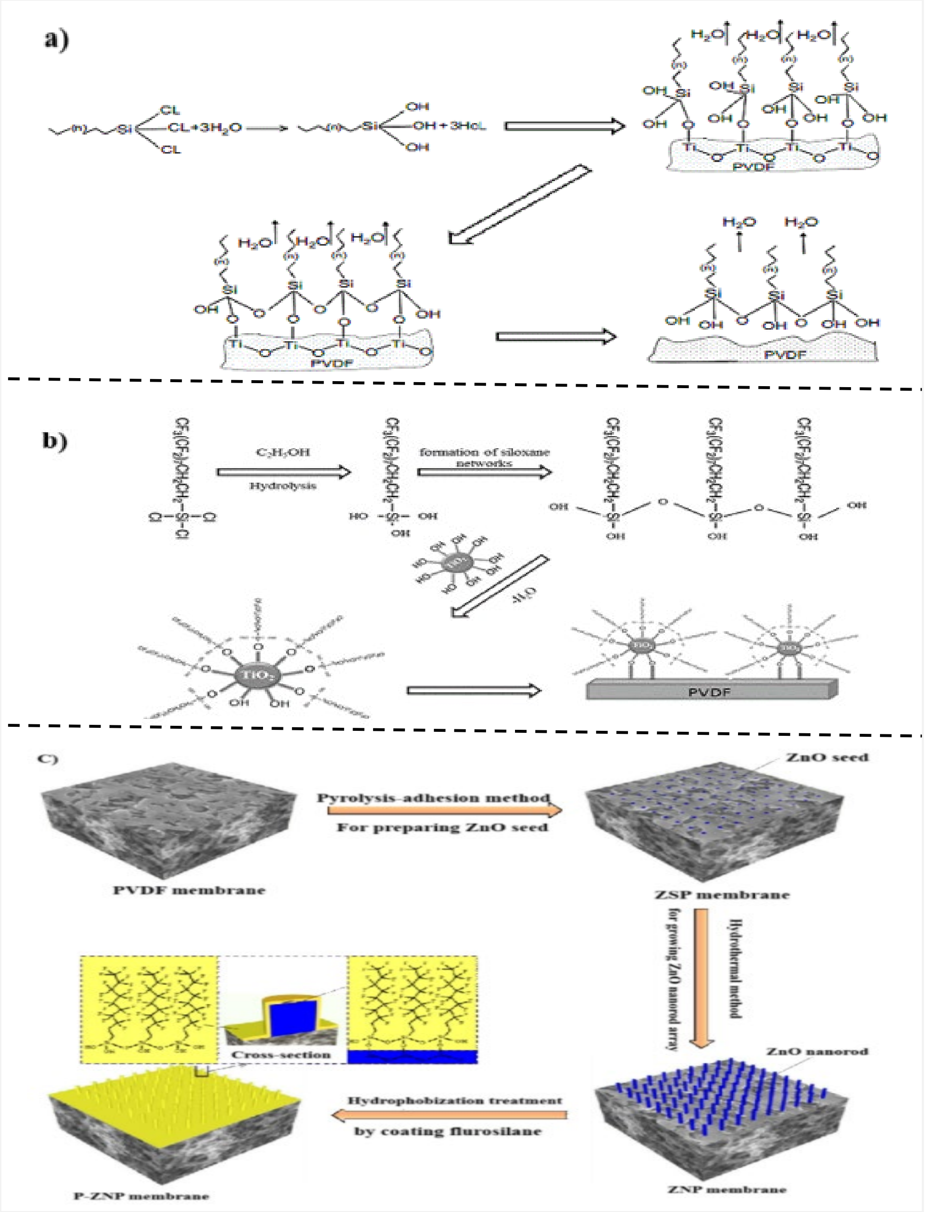

Figure 7: Schematic modification of metal oxide nanomaterials a, b) TiO_2 with silane (coated and blended) [81,82] c) ZnO coated PVDF(P-ZnP) membrane (PDTS-Zn-PVDF); ZSP membrane: seed fasted of Zno on PVDF membrane; ZNP: ZnO nanoroad PVDF membrane [89]

4.2 Metal-organic framework (MOF) on PVDF membrane

Metal-organic frameworks (MOFs) are crystalline porous materials that can be used to create highly customizable structures. They are made of metal ions connected to organic linkers by strong molecular interactions [91,92]. In the field of membrane technology, MOFs have been investigated for their potential to enhance membrane characteristics such as pore size, porosity, surface roughness, and mechanical stability, thereby improving membrane distillation performance [93,94]. The extensive research and development in this field is evident in the fact that more than thousands of different types of MOFs have been synthesized and used in various membrane processes, including separation gas [95], ultrafiltration (UF) [96], forward osmosis (FO) [97], reverse osmosis (RO) [98], and membrane distillation (MD). Some of the MOFs used in MD include aluminum fumarate (ALFu) [99,100], Cu-BTC [101,102], ZIF-8 [103,104], ZIF-71 [105], ZIF-CoZn [106], iron 1,3,5-

benzene dicarboxylate Fe-BTC [107], Silica Aerogel (SiAG) [108], Ui0-66 [109], MOF-808 [110], and MAF-4 [111] Table 3 shows the effect of MOF on the properties of the PVDF membrane for water desalination by MD.

Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, are known for their high thermal resistance, chemical stability [112,113], and high porosity. ZIF-8, a member of the ZIFs group, is made from zinc (Zn) ions and 2-methylimidazole (Hmim) linkers, presents a sodalite zeolite-type structure, and includes six-ring β cages with a small pore aperture of 3.4 Å [114,115]. Its hydrophobic properties make it a promising candidate for MD [116]. Kebria et al. [103] coated ZIF-8/chitosan on the PVDF membrane surface, thereby improving the performance of air gap membrane distillation (AGMD) for water desalination. The result demonstrated that coating ZIF-8/chitosan enhanced the surface effective porosity from 2279 nm to 3373 nm, whereas the mean pore size of the membrane surface reduced from 696 nm to 468 nm. and the water contact angle changed slowly (84.16- 83.2°) after the coating of this layer due to the addition of a hydrophilic chitosan layer.

The liquid entry pressure (LEP) increased considerably (300 kpa) due to the decreasing pore size of the surface, resulting in a higher water flux of about 350% higher than the unmodified membrane. The membrane also became more stable, with a 16% decrease in stability and a salt rejection of 99.5%, confirming its stability in MD. Yang et al. [107] developed superhydrophobic PVDF membranes by incorporating varying amounts (1%, 3%, and 5% by weight) of iron-BTC using an electrospinning method for water desalination via direct contact membrane distillation (DCMD). The results demonstrated that loading 5 wt.% of Iron-BTC enhanced the pore size of the PVDF membrane from 0.23 µm to 0.32 µm, porosity from 61.23% to 66.24%, thickness from 46.69 µm to 79.99 µm, and the contact angle to 138.06° The permeate flux reached 2.87 kg/m^2.h, with a salt rejection rate of 99.99% for water desalination at a concentration of 35 g/L using DCMD.

Cu-BTC is another type of MOF nanomaterial used in MD; it has a porous structure and a large surface area to improve mass transfer in MD. The rougher surface oil contact angle of 152.8° was produced by coating Cu-BTC on the surface of the PVDF membrane to prepare the CU-BTC@PVA/PVDF Janus membrane with superior capabilities in preventing oil fouling [102]. Another study used Cu-MOF to coat the PVMD membrane to improve the performance of photo vacuum membrane distillation (PVMD). The Cu-MOF photothermal layer has a hierarchical structure and operates as a transformer for vapor water, encouraging the addition of heat and feed solution to the area of vaporization in order to ensure continuous vaporization in PVMD. The result demonstrated that the Cu MOF-PVDF membrane had a 3.07 kg/m^2.h, and the salt rejection was 99.9% [117].

Table 3: Summary of metal-organic framework nanomaterials (MOF) /PVDF membrane in MD

					Membrane Properties								
MD Conf.	**Process parameter**	**Membrane type**	**Nanomaterial**	**Coating method**	**Porosity (%)**	**pore size (µm)**	**Thickness (µm)**	**LEP (bar)**	**Operating time (h)**	**Contact angle (°)**	**Flux (kg/m^{2}h)**	**Rejection %**	**Ref.**
AGMD	3.5 wt% NaCl ΔT= 40ºC FF: 0.5 L/min	PVDF	PM ZIF-8	Dip coating	--	0.468	12	300	--	84.16 83.2	2.5 7.2	99.6 99.5	[103]
VMD	NaCl $CaSO_4$ Tf = 60 ºC FF: 4 cm^3/s Pv=740 mmHg	PVDF	MOF-5	blended	--	--	--	--	--	--	14.4	--	[118]
PhVMD	3.5 wt% NaCl	PVDF	Cu-MOF	Coting	--	--	--	--	--	--	3.07	99.99	[117]

AGMD: air gap membrane distillation; ΔT: temperature difference between feed and permeate side; FF: feed flowrate; NaCl: chloride sodium; PVDF: polyvinylidene fluoride; PM: Pristine membrane.

4.3 Carbon-based nanomaterials for PVDF membrane

Carbon-based nanomaterials are hydrophobic nanomaterials, such as activated carbon (AC), carbon nanotubes (CNTs), graphene oxide (GO), and quantum dots (QDs), which are extensively employed in coating or embedding MD membranes with the appropriate properties [79], [80, 119]. Carbon nanomaterials have been demonstrated to enhance operational performance, stabilize flux in long-term MD processes, and reduce fouling and wetting of membranes [75, 120]. A summary of some literature on the effect of carbon nanomaterials on PVDF membranes in MD is shown in Table 4. It was demonstrated that coated nanomaterials have more effects than embedded nanomaterials on the efficiency of the PVDF membrane in MD (higher flux and rejection) due to their higher hydrophobicity and contact angle.

4.3.1 Carbon nanotube (CNTs)

Carbon nanotubes (CNTs) are one-dimensional (1D) nanomaterials that can modify membranes by reducing water permeability while increasing the movement of water vapor molecules [121,122]. Their superior chemical, mechanical, and thermal properties, self-cleaning and anti-fouling capabilities, high surface area, and hydrophobicity make them highly attractive for enhancing the performance of polymeric membranes in the MD process [123- 126]. Compared to traditional MD membranes, polymeric membranes incorporating CNTs demonstrate a greater capacity to increase vapor flux due to the nanotubes' slippage effect, smooth walls, adsorption capacity, and electrical conductivity [127- 128].

Baolei X. et al. [129], coated polyvinylidene fluoride (PVDF) with CNTs and found that this spray-coating significantly improved the performance of the DCMD membrane. The pore size of the CNT-PVDF membrane decreased, and the thickness increased slightly due to the deposition of CNTs. When compared to other polymers like PTFE, the increase in thickness for PVDF was more pronounced after depositing the same quantity of CNTs, which is attributed to the surface free energy of PVDF being higher than that of PTFE (13.4 mJ· m $^{-2}$ vs. 8.7 mJ· m $^{-2}$). The packing density of CNTs on the PVDF surface is also denser because the interaction between the PVDF surface and CNTs is influenced by the substrate's surface energy. In other words, PVDF, having a higher surface energy with more polar groups, generates a strong interaction force with CNTs. This increased interaction enhances the adhesion and stability of the CNTs on the PVDF membrane surface, ensuring that the nanomaterials maintain stable permeate flux and rejection rates over an extended period in DCMD [127].

In another study, MWCNT at varying concentrations was embedded to study the characteristics and efficiency of PVDF membranes. The finding demonstrated that the addition of MWCNT reduced the pore size due to the strong interaction between PVDF and MWCNTs, whereas the finger will expand and increase porosity as a result of the accelerated phase inversion, which makes the pore at the finger wider and longer, as shown in Figure 8. The high finger-like pores diminish the membrane's mechanical properties, as documented in previous research [130-133], which may damage the interaction between MWCNT and PVDF molecules and leakage of nanomaterials over time. Despite these properties, the enhanced permeate flux was 116% larger than the PVDF membrane (pristine), and salt rejection is stable in VMD [59].

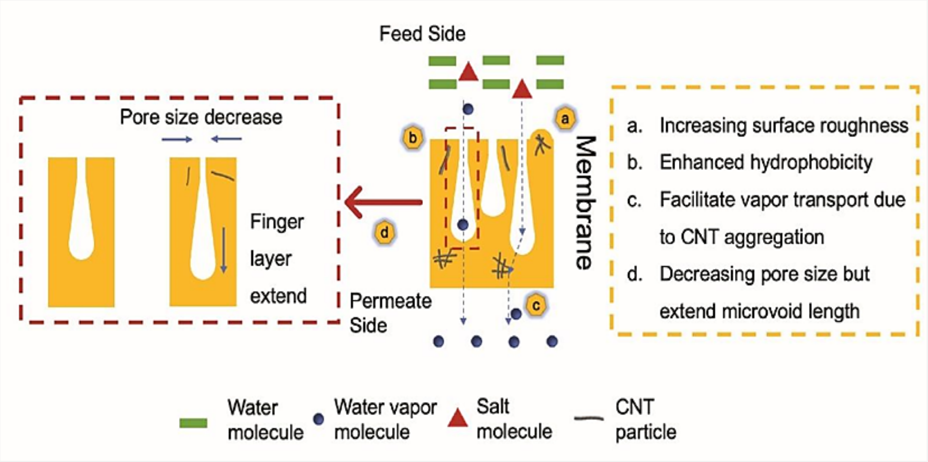

Figure 8: Effect of CNT on PVDF membrane and vapor transport [63]

4.3.2 Activated carbon (AC)

Activated carbon (AC) is a porous nanomaterial with internal channels for vapor transfer and enhanced permeate flux in MD. Compared with carbon nanotubes (CNTs), AC has channels in all directions and does not have to be aligned in the membrane matrices [134,135, 22]. However, due to agglomeration, direct blending with the polymer is unsuitable [134], while other modifications and grafting processes were proposed [135]. Aljumaily et al. [136], coated a polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) membrane with 10-30 mg of modified powder activated carbon (CNM/PAC) for water desalination by DCMD. As shown in Table 4, this approach significantly enhanced the porosity by 91%. The key factors were the higher porosity, uniform dispersion, and interaction of nanomaterials with the surface of the PVDF-HFP membrane.

The CNM/PVDF-HFP exhibited a contact angle of 124°, higher than the neat PVDF-HFP, and the pore size was reduced due to the partial filling of pores on the membrane surface by CNM/PAC, which enhanced the liquid entry pressure (LEP). Increased loading of CNM/PAC further enhanced the permeate flux to 77 L/m^2.h and the salt rejection to 99.9% due to the enhanced hydrophobicity and porosity, which increased water vapor transport without wetting. On the other side, CNM/PAC was embedded with PVDF-HFP to examine the effect of nanomaterials on membrane morphology at different concentrations. It was found that the pore size on the membrane surface increased when CNM/PAC was increased from 1-3%, and the sponge structure on the bottom side was increased, whereas the top surface finger-like structure diminished due to the delay in transport between solvent and non-solvent during the phase inversion of the membrane, which led to the formation of a sponge-like structure on the bottom side of the membrane. Reduced finger-like pores lead to enhanced mechanical properties and stability of CNM over a long time of operation in DCMD [137].

4.3.3 Graphene-based nanomaterials

Graphene-based nanomaterials are hydrophobic nanomaterials with a high surface area-to-weight ratio and good thermal and mechanical characteristics for enhancing membrane stability [138]. They can significantly improve the MD membrane properties, such as chemical, mechanical, thermal stability, permeate flux, and salt rejection [139]. Graphene oxide (GO) is a hydrophilic form of graphene consisting of pristine sp2 and sp3 hybridized oxidized regions. Owing to the unique water channels, GO is introduced in membrane composite fabrication to improve the membrane properties for water desalination

[140-143]. The hydrophilic properties of GO are due to functional groups such as carboxyl and hydroxyl; for this reason, functionalized graphene oxide is used before being used in membrane distillation. The functionalized group enhances the interaction between nanomaterials and PVDF and the stability of GO.

Zahirifar et al. [142] added octadecyl amine to graphene oxide (GO) to prepare a dual layer of the GO-ODA-PVDF, as shown in Figure 9. The result demonstrated that the flux of the GO-ODA-PVDF membrane was decreased from 18.2 to 16.7 kg/m^2.h, and the salt rejection increased from 88.5% to 98.3% for water desalination at 35 g/l in the AGMD process, as shown in Table 4. This enhancement in the performance of the membrane is attributed to the formation of interconnected channels with high surface area due to the presence of the GO-ODA coating on the surface of the PVDF membrane. In order to ensure the stability of nanomaterials on the membrane surface, they examined the mechanical and thermal stability of the modified membrane; GO-ODA-PVDF was sonicated at different times, and the contact angle was measured before and after sonication. It was found that the contact angle of the modified membrane after one hour of sonication changed slightly from the primary contact angle (146^o-141^o), confirming the nanomaterials' stability and mechanical properties. The thermal stability was examined by putting the modified membrane in deionized water (DI) at 80 °C at different times. Increased temperature increases the molecules' thermal activity, which results in a decline in the adhesion between intermolecular in water and a decrease in surface tension. As a result, it reduces the surface tension, which leads to a decrease in the hydrophobicity of the membrane surface (146°-138°). However, the GO-ODA hydrophobic and low surface energy layer form a fragile film for insulating air on the surface of the modified membrane, which reduces the wetting of the surface and ultimately resists profound decreases in surface hydrophobicity [144-146]. In another study, Athanasekou et al. [145] studied the influence of graphene (G) and graphene oxide (GO) mixed matrix membranes on the characteristics of PVDF and the performance of DCMD by adding different concentrations of G and GO. Table 4 summarizes the carbon-based nanomaterials/PVDF membrane for MD. It can be seen from Table 4 that the permeate flux of G/PVDF is 1.7 times higher than the unmodified membrane, with a rejection of 99.8%, demonstrating the potential for improved performance. Similarly, GO/PVDF had twice the water vapor permeate flux compared to the neat PVDF membrane, indicating enhanced characteristics. However, its salt rejection effectiveness was only modest (80%) due to pore wetting during the DCMD process [145]. Abdel-Karim et al. [146] examined the effect of the degree of reduction on membrane distillation performance. The addition of rGO affects the structure of the PVDF membrane, where adding 0.5 wt% rGO results in a wider and longer micro void structure, and the presence of a residual hydrophilic group on rGO may lead to quick diffusion by non-solvent during phase inversion. These macro void structures increase the porosity of the membrane; the higher porosity leads to higher permeate flux and conductive heat loss. However, the porosity of membranes limits the mechanical strength, therefore requiring a balance between mechanical stability and porosity.

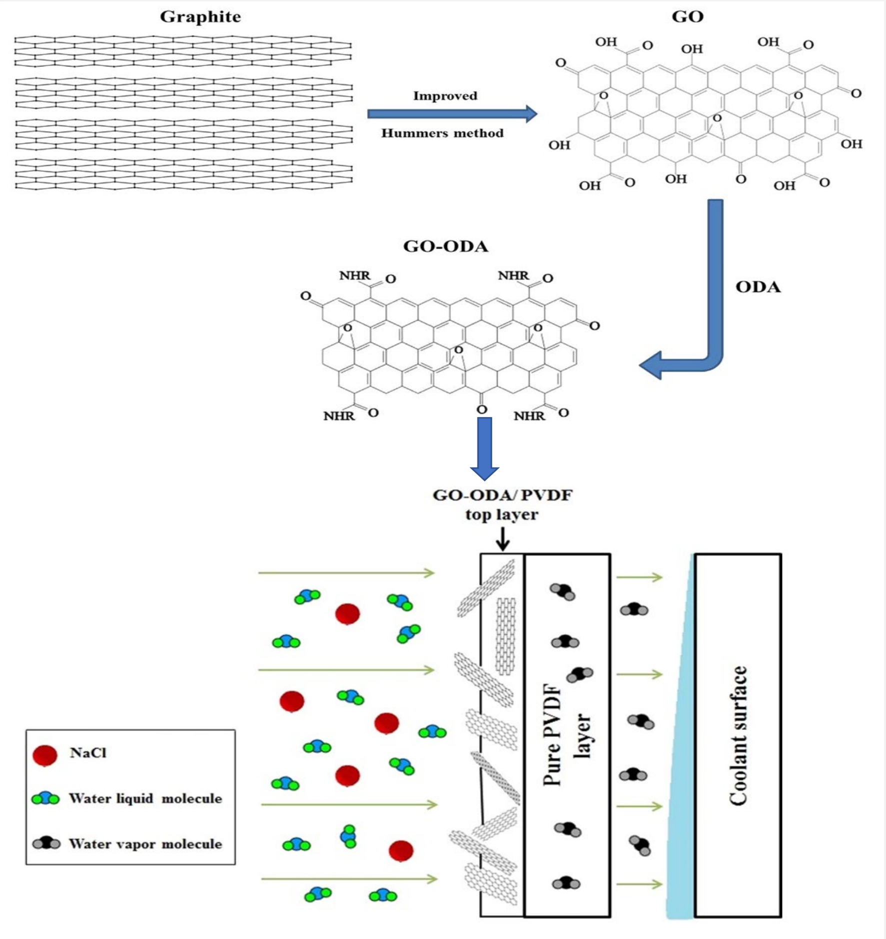

Figure 9: a) Schematic of functionalized GO (GO-ODA), b) prepared dual layer for AGMD [142]

Table 4: Summary of carbon-based nanomaterials /PVDF membrane for MD

					Membrane Properties								
MD Conf.	**process parameter**	**Membrane type**	**Nanomaterial**	**Coating method**	**Porosity (%)**	**pore size (μm)**	**Thickness (μm)**	**LEP (bar)**	**Operating time (h)**	**Contact angle (°)**	**Flux (kg/m^{2}h)**	**Rejection %**	**Ref.**
DCMD	3.5 wt% NaCl Tf:60 °C Tp: 20 °C	PVDF	PM MWCNT	coated	66 66	1 0.7	120 121	40 45	--	130 139.9	12 27	99.9	[129]
AGMD	0.5 M NaCl Tf:54 °C Tp: 9 °C	PVDF	PM SWCNT	coated	--	--	--	97 657	24	110 165	9.3 10.22	75 99.99	[147]
DCMD	DW	PVDF	CNT	coated		0.22 0.18	125 140	--	--	125 180	15 32	--	[148]
AGMD	35 g/L Tf:30 °C	PVDF	PM MWCNT	Embedded	81 86	0.14 0.114	92 85	620 510	24 h	81.79 86.68	1.2 2.6	99.98	[63]
DCMD	3.5 wt% NaCl Tf:60 °C Tp: 20 °C	PVDF	PM AC	coated	72 85	0.38 0.4	--	150 300	13 h	92 115	25 29.8	99.9	[135]
DCMD	3.5 wt% NaCl Tf:60 °C Tp: 20 °C	PVDF-co –HFP	CNM/PAC	Coated	45 86.9	--	--	--	--	90 124	35 77	99.9	[136]
DCMD	3.5 wt% NaCl Tf:60 °C Tp: 20 °C	PVDF-co –HFP	CNM/PAC	Embedded	45 96	--	210 165	--	--	83 133	10 16	99.9	[137]
AGMD	3.5 wt% NaCl Tf:80 °C Tp: 15 °C	PVDF	PM GO-ODA	Coated	60	0.108 0.057	73 60	185	5 days	77 146	18.2 16.7	88.5 98.3	[142]
DCMD	3.5 wt% NaCl Tf:80 °C Tp: 10 °C	PVDF	PM PVDF-F PVDF-F-G	Coated	--	0.03 0.13	--	5	35	71 73 61	3	99.9	[149]
DCMD	3.5 wt% NaCl Tf:75 °C Tp: 25 °C	PVDF	PM GO	embedded	70.73	0.4 0.29	--	217 210	3	90 73.9	9.84 18	95 80	[145]
DCMD	3.5 wt% NaCl Tf:75 °C Tp: 25 °C	PVDF	PM G	embedded	70 73.8	0.4 0.52	--	217 140	3	90 75.7	9.84 16.53	95 99.7	[145]
AGMD	3.5 wt% NaCl	PVDF	PM rGO	embedded	72	0.076 0.083	43	--	9	84 70	3 7	99.99	[146]
DCMD	3.5 wt% NaCl Tf:70 °C Tp: 20 °C	PVDF	G	embedded	-	0.13	-	5	35	-	3	99.9	[149]
DCMD	1 wt% NaCl Tf:65 °C Tp: 20 °C FF: 30L/h	PVDF/ PES	G	Embedded	88	0.37	142	132	-	132	19.35	99.9	[150]

DCMD: direct contact membrane distillation; AGMD: air gap membrane distillation; Tf: feed temperature; Tp: permeate temperature; NaCl: chloride sodium, PVDF: polyvinylidene fluoride; PVDF-co-HFP: polyvinylidene fluoride co hexafluoropropylene; PM: Pristine membrane; CNT: carbon nanotube; MWCNT: multiwall carbon nanotube; SWCNT: single wall carbon nanotube, AC: activated carbon, GO: graphene oxide, ODA: octadecyle, CNM/PAC: carbon nanomaterials powder activated carbon.

4.3.4 Quantum dots (QDs)

Quantum Dots (QDs) have garnered significant research interest for modifying membrane distillation (MD) membranes due to their unique physicochemical properties, chemical inertness, and the presence of various functional groups that enhance anti-fouling capabilities [151]. Chen et al. [152] developed Janus membranes for MD applications inspired by nanofiltration (NF), which have proven to be a highly effective way to reduce wetting and fouling. The PVDF-P-CQD membrane, composed of a hydrophobic PVDF membrane and a thin polydopamine/polyethylenimine (PDA/PEI) layer, hydrophilically enhanced by adding sodium-functionalized carbon quantum dots (Na-CQDs), demonstrates good resistance toward oil and surfactant-induced wetting in the (DCMD) method. Importantly, this membrane has shown the potential to enhance the permeate flux and salt rejection, with the permeate flux remaining stable over a long time of operation in MD.

5. Nanomaterials leaching and stability over a long time of operation in MD

Leaching nanomaterials is one of the formidable challenges facing composite membrane synthesis [153-155]. Leaching occurs due to the poor chemical interaction between nanomaterials and the membrane, consequently reducing process stability and raising environmental concerns, as releasing such materials can cause serious health issues for living beings [76,151]. For composite membranes, the bond between nanomaterials and the membrane structure is crucial and manageable for long-term stability [16]. Therefore, adding functional groups such as amine, hydroxyl, carboxyl, and carbonyl and using heat treatment or chemical cross-linking can significantly enhance this bond, thereby improving the overall stability of the membrane [16, 156-158]. In the MD process, the membranes are exposed to high operating conditions (feed temperature and feed flow rate), which could release weakly anchored nanomaterials. Therefore, the membrane should have high thermal and mechanical stability to ensure long-term operation [11]. The thermal stability of the TiO_2 was evaluated by sonicating a sample of the membrane at a high temperature of 90 ºC for 15 minutes. The results revealed that the contact angle decreased from 163° to 156° (see Figure 10 (a)), indicating that high temperatures can adversely affect the thermal stability of nanomaterials. To evaluate mechanical stability, the membrane sample was immersed in deionized water and sonicated for 15 minutes at room temperature. This led to a reduction in contact angle of 4.5% (from 163° to 161°) as shown in Figure 10 (b), suggesting that the nanomaterial-coated membrane is stable [81].

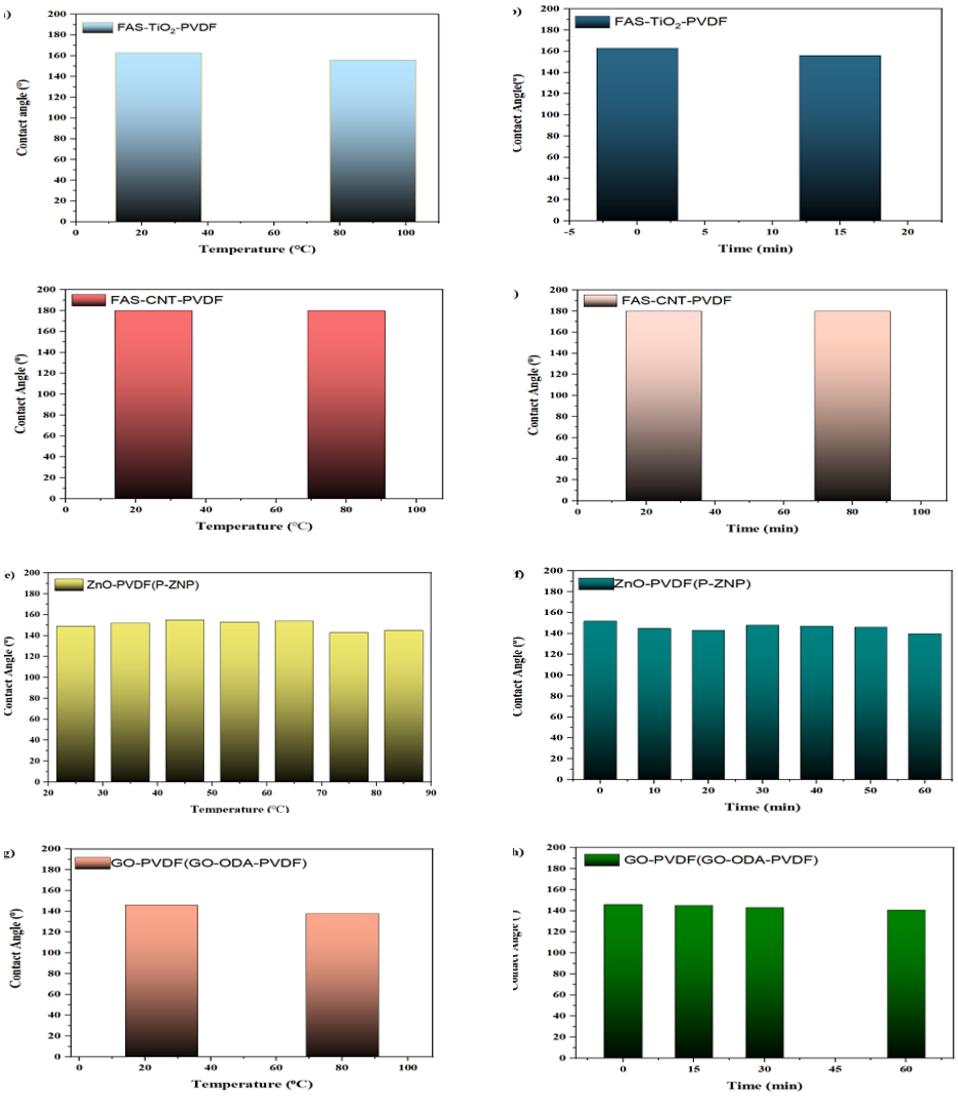

Figure 10: Variation of contact angle membrane with temperature (thermal stability test) and time (mechanical stability test) for different types of nanomaterials (a, b) FAS-TiO2-PVDF [81] ; (c, d) FAS-CNT-PVDF [148]; (e, f) P-ZNP [89]; (g, h) GO-ODA-PVDF [142]

In another study by Tung Wang et al. [148], the thermal stability of CNT as an intermediate layer was examined by grafting 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (FAS) (PVDF-CNT-FAS) with (PVDF-OH-FAS) at a high temperature (80 ºC) for one hour. The results indicated that the superhydrophobic PVDF-CNT-FAS maintained a constant contact angle of 180° , Figure 10 (c), demonstrating greater stability than PVDF-OH-FAS under severe operating conditions, attributed to the strong bonding between FAS and the membrane facilitated by the CNT intermediate layer. After one hour, the mechanical stability at room temperature was evaluated, and the contact angle for the superhydrophobic PVDF-CNT-FAS remained constant at 180°. This result indicates that the membrane is stable under harsh operating conditions for vacuum membrane distillation (VMD) (see Figure 10 (d)) [148].

Wang et al. [86] studied the thermal stability of ZnO-coated PVDF when exposed to a high temperature of 90 ºC; it was noticed that the contact angle dropped slightly by 2.7% after an hour due to the strong adhesion of ZnO on the surface of the PVDF membrane Figure 10 (e). The mechanical stability of ZnO was evaluated by measuring the contact angle every 10 min at room temperature for an hour. The P-ZNP membrane contact angle was found to be the same over time (Figure 10(f)), indicating that the mechanical stability and force of adhesion of ZnO nanomaterial is robust. Similarly, Zahirifar et al. [142], evaluated the thermal stability of GO at 80 ºC at different times (15, 30, and 60 min). The results demonstrated that the contact angle decreased by 5.7% (146º to 138º) after one hour (Figure 10 (g)). The mechanical stability tests at room temperature revealed a 3.5% decrease in the contact angle (from 146º to 141º) after one hour, as shown in Figure 10 (h).

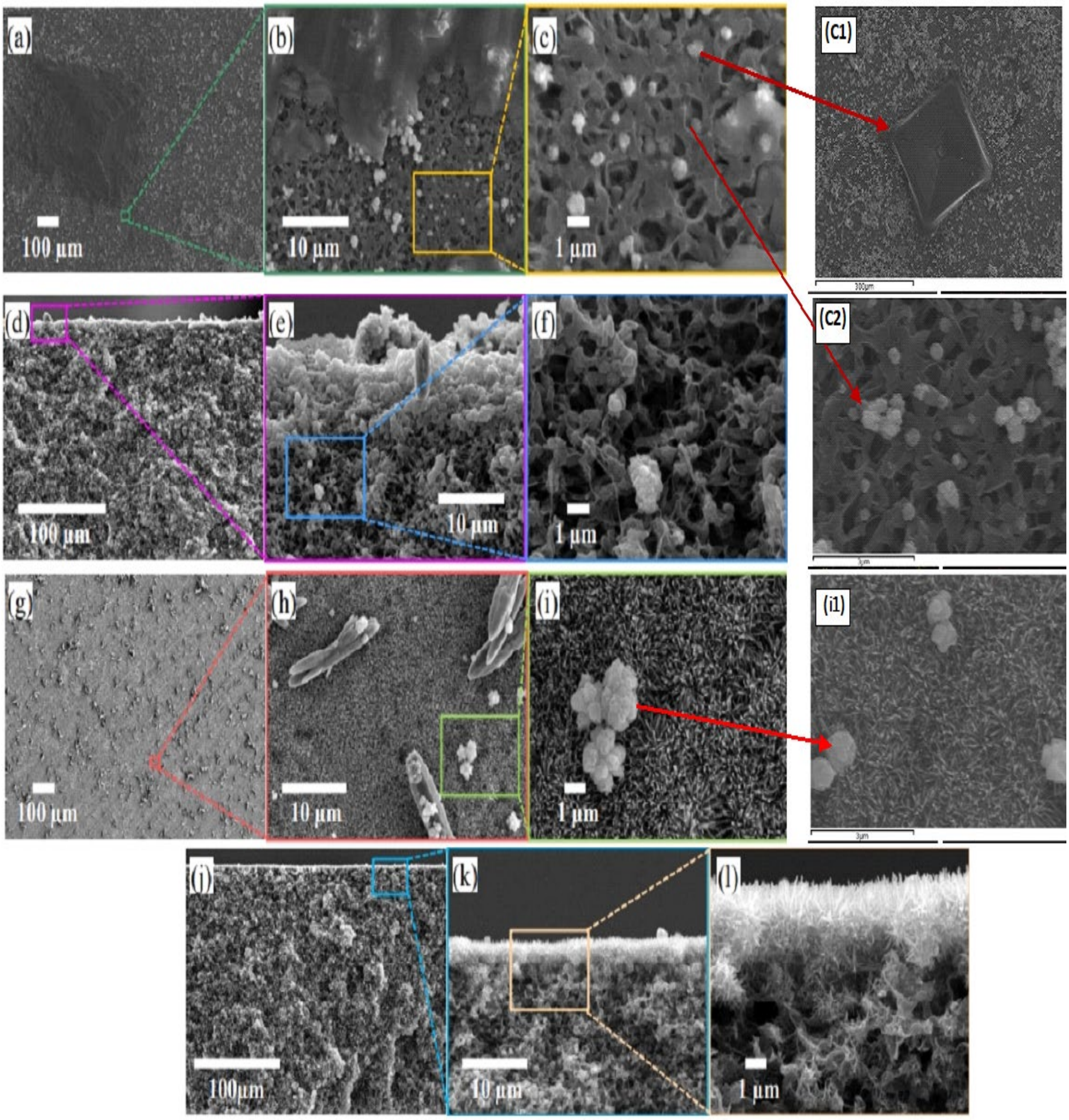

Figure 11: (a-c_2) SEM image surface and cross of the used PVDF membrane and (g-l) P-ZNP membrane surfaces and cross after 8h of operation in VMD [89]

Based on the above results, it was concluded that the temperature affects the stability of nanomaterials; the increment in temperature increases intermolecular thermal activity and reduces the force of adhesion between the nanomaterials and the surface tension and hydrophobicity, which leads to the release of some nanomaterials [145,146].

Figure 11 illustrates the stability of the neat and modified PVDF membranes. As depicted in Figures 11 (a-c), numerous NaCl salt crystals are observed on the PVDF membrane surface, with some crystals penetrating the pores of PVDF membranes after VMD operation Figures 11 (d-c_2). This observation suggests a decrease in membrane hydrophobicity due to fouling, leading to pore wetting. Figures 11 (g-i) showcase the superhydrophobic membrane, with salt deposition on the P-ZNP membrane surface. In contrast, Figures 11 (i-l) reveal no crystal salt inside the pore of the P-ZNP membrane, a clear indication of ZnO's effective role in preventing membrane wetting and enhancing its stability during VMD operation [89].

Like other membrane technologies, permeate flux and salt rejection are critical performance indicators for MD. The unmodified membrane with nanomaterials may experience wetting over a long period due to its large pore size and poor hydrophobicity, which lead to reduced mechanical characteristics. The modified membrane, on the other hand, was found to produce stable flux and rejection, as shown in the examples in Figure 12. Moreover, figure 12 displays the stability of the neat and modified PVDF membranes over a long time of permeation. Figures 12 (a) show that the pristine PVDF had an unstable permeate flux and salt rejection, where the salt rejection increased after time of operation. On the other hand, the modified membrane with nanomaterials (CNT) modified with FAS had stable permeate flux and salt rejection over 8 h of operation [148] . It is also shown in Figure 12 (b) the stability of the pristine PVDF and modified with ZnO over a long time of VMD operation for a salt solution at 200 g/L NaCl. As shown in Figure 12 (b), the permeate flux of both PVDF and modified with ZnO nanorods PDTS (PZNP) membranes gradually decreased over 8 h of VMD operation. However, the salt rejection of neat PVDF decreased from 8.75 to 142.70 s/cm whereas the salt rejection of the PZNP membrane reduced slightly from 0.18 to 12.89 S cm^{-1}[89]. Figure 12 (c) shows the stability of the PVDF membrane before and after modification with GO-ODA over five days of AGMD operation for a salt solution at 35 g/L NaCl. As illustrated in this figure, the continuous operation of the modified membrane exhibited stability in terms of permeate flux and salt rejection. This can be due to the enhanced hydrophobicity and the LEP of the modified membrane [142]. The difference in performance of the pristine PVDF and the modified membrane reveals that the modified membrane is more stable than the pristine PVDF membrane.

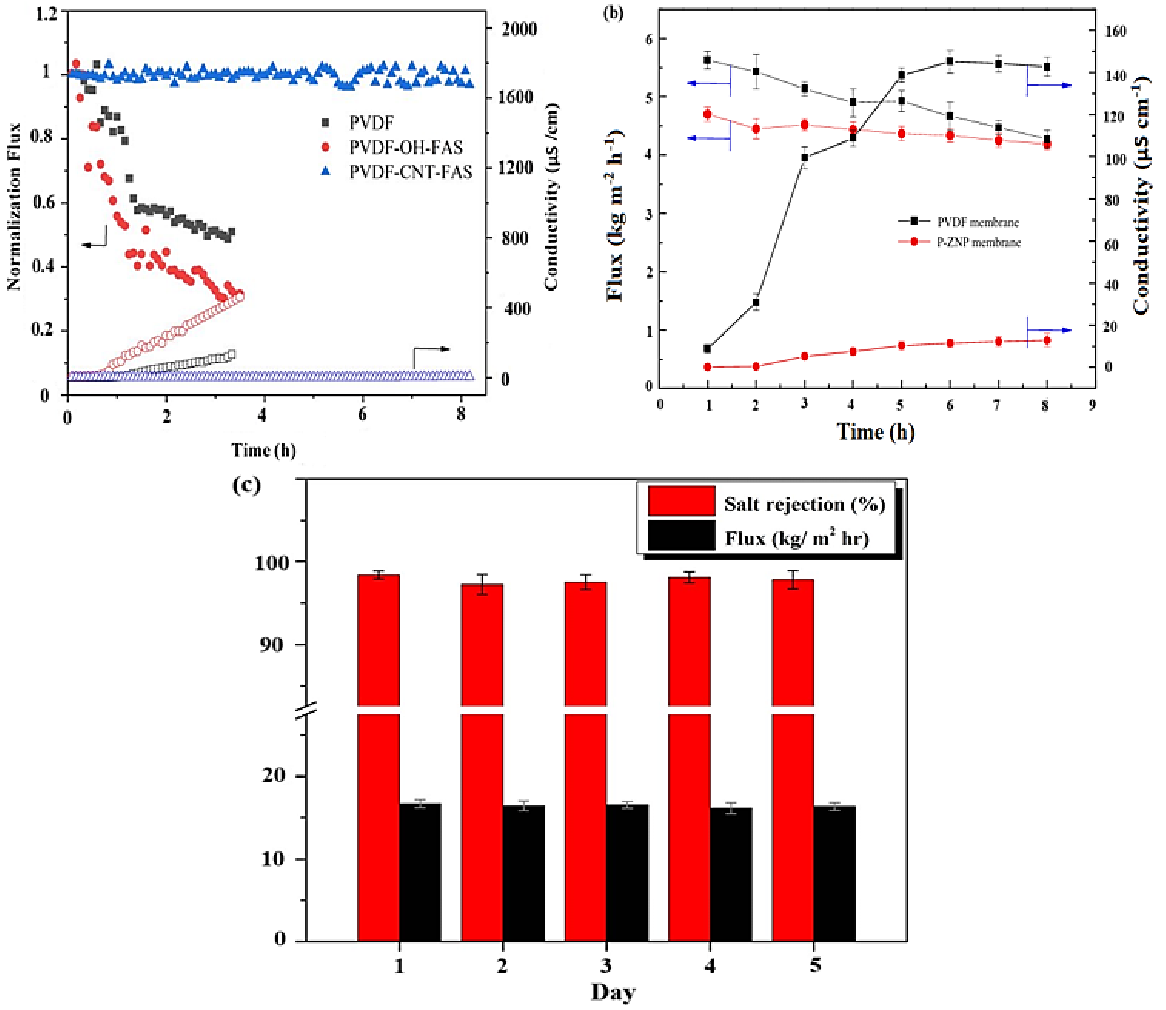

Figure 12: Stability of water permeate flux and conductivity for different types of nanomaterials coating PVDF membrane over period operation in MD a) FAS-TiO2-PVDF [81] ; b) FAS-CNT-PVDF [148]; c) P-ZNP [89]; d) GO-ODA-PVDF [142]

The successful integration of nanoparticles and their stability can only be validated through ex-situ sophisticated analytical approaches. The successful incorporation of nanoparticles can also be estimated through their effect on membrane performance. Ibrahim and Alsalhy [157] took the lead from these notions and developed a mathematical model to track the change in membrane characteristics through its performance. They validated their work with the utmost thoroughness, cross-checking their results against published experimental data from 135 studies. This study can be utilized to monitor the leaching and fouling development through the obtained experimental data where initial membrane characteristics are known.

Baghbanzadeh et al. [158] investigated the possibility of silica (SiO_2) leaching to the distillate from the SiO_2-PVDF composite membrane in the VMD process. The membrane was prepared at different SiO_2 loadings of 0, 2, 5, 7, and 9 wt% in the solution of the polymer. They found that the permeate flux of pure water at the M2 (2% SiO_2) membrane was higher than M0 (PVDF) after 1.5 h of operation and increased after 4.5 h. However, the rejection decreased due to the PVDF membrane degradation through repeated VMD testing, which resulted in SiO_2 leaching. The M2 membranes were tested in VMD for 4.5 h with $AgNO_3$ solution (1.0 wt.%) to investigate the membrane degradation. The membrane was washed with distilled water before being tested for silver distribution using EDS mapping. There was a small amount of $AgNO_3$ on the membrane surface and no silver in the membrane matrix (the membrane leaking was not caused by pore wetting). Moreover, when M7 (7% SiO_2) was used in VMD, high leakage was noticed after three hours, and the leakage was observed at 1.5 h for M9 (9% SiO_2). They suggested that mechanical properties failure might have occurred due to the reduction in the sponge layer with the increased concentration of nanomaterials, as shown in Figure 13, which eventually led to nanomaterials leaching.

To enhance the stability of CNT, Ding et al. [140] prepared an MWCNT/PVDF conductive membrane by the vacuum filtration cross-linking method and tested the effect of different concentrations of PVA on the stability of the MWCNT/PVDF membrane by measuring the mass loss rate of the conductive layer according to Equation (1).

$$\text{Mass loss rate} = \frac{M_1 - M_2}{M_3 - M_4} \times 100 \tag{1}$$

where M_1 and M_2 represent the mass of dry conductive membrane before and after ultrasonic (g), M_3 is the mass of MWCNT/PVDF before ultrasonic (g), and M_4 is the mass of neat PVDF membrane (g). It was found that the mass loss is very low, 10-4 g, and the average mass loss rate of the conducting layer was just 1.22% when sonicated for 30 min at 0.05 wt% PVA. This indicates that the conducting layer was extremely stable after the addition of a linker group such as PVA. Mpala et al. [159] evaluated the stability of capped silver (CNC-Ag) within polyvinylidene fluoride functionalized carbon nanotubes (PVDF/f-CNT) membranes over a long time of operation (72h) in DCMD, where the membrane was immersed in DI water and shaken at 140 rpm for 72h. The leachate samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) at different times. The result demonstrated that approximately 0.378 ± 0.0628 ppm was released from the membrane with a gradual decline as a function of time, (Figure 14). This indicates the reasonable stability of nanomaterials and explains the release of high concentrations at the initial stages of operation due to the weakly bound or excess Ag.

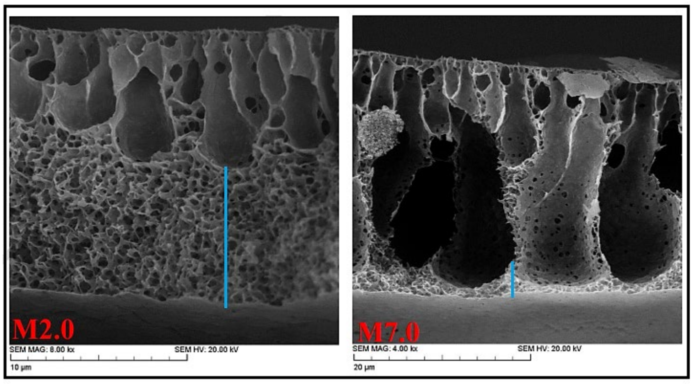

Figure 13: SEM image M2(2% SiO_2-PVDF),M7(7% SiO_2-PVDF)membrane [158]

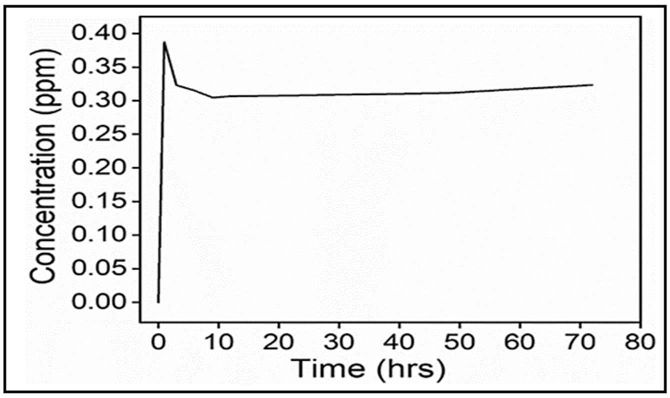

Figure 14: The concentration of CNC/AgNP leaching from PVDF membrane after a 72 h [159]

6. Improvement of the stability of nanomaterials

Leaching nanomaterials is one of the most challenging aspects of the application of MD membranes. Recently, scientific research aims to achieve a strategic enhancement of the stability of nanomaterials in polymeric membranes [160-162]. In 2021, Ding et al. reported that the structure of CNTs and PVDF polymers was unstable due to the weak force (van der Waals) between them, which was damaged easily by water flow; they enhanced the stability of CNTs by adding polyvinyl alcohol (PVA) as a cross-linker by covalent bonding between the (OH) groups on PVA molecules and the (COOH) groups on MWCNT-COOH (carboxylate multi-walled carbon nanotubes) [142, 163]. This type of nanomaterial linker will make the membrane more efficient and effective and enhance stability and life [16]. In another study, the quantity of –OH hydroxyl groups was enhanced, and the CNT was kept from leaching by using PVA; then, the membrane was immersed in the glutaraldehyde (GA) and hydrochloric acid (HCL) solution as an across-linker with PVDF in DCMD [152, 164]. Li et al. [163] applied polydimethylsiloxane (PDMS) to the membrane surface as a cross-linker agent and strong hydrophobicity to increase the stability of PDANPs and PVDF membranes in DCMD. Pouya et al. [74] functionalized CNT with oleic acid and formaldehyde, then mixed the mixture with PVDF polymer and coated it on the surface of the PTFE membrane by vacuum filtration.

7. Challenges and future work

Research on membranes that incorporate nanomaterials such as (CNTs, SiO_2, ZnO and TiO_2) is of great significance despite current limitations. These membranes, which have only been produced at the bench scale, have primarily been tested using synthetic samples with binary or well-defined contaminants. This indicates a strong potential for future commercialization. However, several technical challenges and knowledge gaps still delay the commercialization of membrane distillation (MD) composite membranes. Therefore, addressing these challenges is essential to fully unlock the capabilities of this technology. The challenges and future work can be summarized below.

1) Nanomaterials dispersion in the polymeric solution can be non-uniform, leading to agglomeration, which affects the membrane's characteristics, such as thickness, pore size, mechanical strength, stability, and overall efficiency in the MD process [139], [157]. Therefore, it is essential to determine the precise amount of nanoparticles required accurately. Researchers can use Hansen solubility parameters to explore surface interaction forces and compatibility of polymers with different nanoparticles (NPs). These parameters help calculate the theoretical affinity distance between the components of the composite materials [158]. Machine learning tools can be employed to simulate the extensive data on available materials, creating a database that can serve as a reference for scientists and engineers aiming to develop membranes with strong and stable structures.
2) The interactions between the nanomaterials (coating nanomaterials) and polymer are exposed to high temperatures in the MD process (over 50 ^{o}C), which could potentially affect the thermal stability of nanomaterials and their binding with the polymeric structure [17]. In this case, the thermodynamics of the binding reactions should be studied carefully, utilizing the computational chemistry tools to identify the tolerance range for different composites.
3) The mechanical strength of the MD membrane may be compromised at high temperatures and low to moderate pressures, such as in the case of VMD [34]. In such instances, the physical attraction forces between NPs and membranes should be tested through vigorous imposed forces before their use in actual testing. Reinforcement strategies like heat pressing and chemical cross-linking should be implemented if leaching occurs.
4) The cost of nanomaterials, along with the additional conditioning and pre-treatment processes, can negatively affect both the economic and environmental aspects of membrane synthesis. The incorporation of NPs into membranes should be guided by the 12th Green Chemistry principles, which emphasize the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. These principles encourage atom economy and the use of safe materials. The use of natural-based NPs should be explored more to mitigate the environmental and health risks in case of leaching. The researchers should, however, take heed of the environmental factor of the preparation and refining processes of such materials and avoid inadvertently promulgating greenwashing.

8. Conclusion

Membrane distillation (MD) has become a promising technology for desalinating water, attracting significant research interest in recent decades. This review provides insights into different methods for modifying MD membranes, specifically focusing on techniques that incorporate nanomaterials, such as blending and surface coating modifications. Surface modification is a crucial aspect of improving membrane performance. Various methods have been examined, including dip coating, electro-spraying, and vacuum filtration. A comparative analysis has been conducted to investigate how the loading of different nanomaterials, such as metal-oxide nanomaterials, metal-organic frameworks (MOFs), and carbon-based nanomaterials, affects flux performance in terms of coating and embedding.

The MD membranes are exposed to harsh environmental conditions. High temperature, feed flow rate, pressure, and stability of nanomaterials (coated or embedded) in the membrane are some challenges the MD membrane faces over a long period of operation. This may lead to degradation of membrane structure and second pollution of distillate with the nanomaterials. Nanomaterials-coated layers are more exposed to delamination or released easily from the surface. Various commonly used nanomaterials, such as metal oxide, MOF, and carbon-based nanomaterials, could be linked to membranes' surfaces by functional groups, such as OH, present on their surface or fluoro-silanization. This will lead to strong interaction, make the membrane effective and efficient, and enhance the membrane's thermal and mechanical properties.

Author contributions

Conceptualization, **S. Khalil**, **R. Al-Juboori**, **W. Lau**, **S. Low**, **Z. Jawad**, **S. Al-Saadi**, **S. Ibrahim** and **Q. Alsalhy**; data curation, **S. Khalil**.; formal analysis, **S. Khalil**, **R. Al-Juboori**, **W. Lau**, **S. Low**, **Z. Jawad**, **S. Al-Saadi**, **S. Ibrahim and Q. Alsalhy**; investigation, **Q. Alsalhy**; methodology, **Q. Alsalhy**; project administration **Q. Alsalhy**; resources, **Q. Alsalhy**; software, **S. Khalil**.; supervision, **Q. Alsalhy**; validation, **Q. Alsalhy**; visualization, **S. Khalil**; writing—original draft preparation, **Q. Alsalhy**; writing—review and editing, **S. Khalil**, **S. Ibrahim**, **R. Al-Juboori**, **W. Lau**, **S. Low**, **Z. Jawad**, **S. Al-Saadi** and **Q. Alsalhy**. All authors have read and agreed to the published version of the manuscript.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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