

A review of nanoparticle-enhanced membrane distillation membranes: membrane synthesis and applications in water treatment

Lebea N Nthunya,^{a,b*} Leonardo Gutierrez,^{b,c} Sebastiaan Derese,^b Edward N Nxumalo,^a Arne R Verliefde,^b Bhekile B Mamba^a and Sabelo D Mhlanga^{a,d*} 

Abstract

Membrane distillation (MD) is a thermally driven process that uses low-grade energy to operate and has been extensively explored as an alternative cost-effective and efficient water treatment process compared to conventional membrane processes. MD membranes are synthesized from hydrophobic polymers, e.g. polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) or polypropylene (PP), using various methods including phase inversion and electrospinning techniques. Recent literature on MD membranes clearly shows their important role in surface water/wastewater treatment and seawater desalination. Modification of MD membranes with nanoscale materials significantly improves their performance, preventing wetting and fouling. This review presents a critical assessment of the progress on the use of nanomaterials for the modification of MD membranes. The techniques commonly used to synthesize MD membranes, the modifications that have been adopted for the incorporation of nanomaterials onto membranes, and the unique properties these nanomaterials impart on the membranes are discussed. The use of modified membranes in different MD configurations and their application in groundwater, surface water, wastewater, brackish water and seawater treatment is reviewed. Finally, cost implications, commercial viability, environmental sustainability, and future prospects of MD are also discussed to elucidate promising approaches for a future and successful implementation of MD at an industrial scale.

© 2019 Society of Chemical Industry

Keywords: nanoscale materials; membrane distillation membranes; water treatment technology; modification; applications

INTRODUCTION

Water is an essential resource for living organisms and a key driver of various anthropogenic activities including irrigation, domestic and industrial applications.¹ Although water is an important component of the water–food–energy nexus, serious concerns regarding water security and scarcity still persist; specifically, ease of access, availability, and water quality.² Water security is highly affected by economic, social, and anthropogenic activities such as agriculture, industrial discharges, urban runoffs, and mine drainage of discharged brines.^{3,4} These activities introduce a wide array of organic [e.g. phenols, polyaromatic hydrocarbons (PAHs), and pesticides] and inorganic (e.g. sodium, magnesium, calcium, chlorides, fluorides, cyanides, sulphates and carbonates) pollutants into the water bodies.⁵ Most of these organic contaminants are carcinogenic and often cause illnesses and deaths when ingested.⁶ However, inorganic compounds (e.g. NaCl, NaF, KNO₃, MgSO₄, and FePO₄) increase the water salinity and consequently affect the quality of water for further drinking, irrigation, and industrial applications.⁷

Membrane technology has been extensively used as a separation technique to reduce the salinity of water from different sources. Additionally, membrane technology offers a relatively high rejection efficiency for particulate and dissolved organic matter from water.⁸ Membrane processes widely used in water desalination include reverse osmosis (RO) and nanofiltration (NF).⁹ These pressure-driven processes operate at high energy requirements

and operational/capital costs.¹⁰ Although NF is less energetically demanding relative to RO, this membrane process has low rejection efficiencies towards sodium and chloride (i.e. notwithstanding the fact that these monovalent ions are the main constituents of saline water).¹¹ Remarkably, the membrane distillation (MD) process has been found to counteract the operational challenges of RO and NF membrane technologies. Also, due to its significantly low energy requirement, MD could be a potential economically feasible technique comparable to pressure-driven membrane processes.¹²

* Correspondence to: LN Nthunya or SD Mhlanga, Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida, Johannesburg, South Africa. E-mail: lebea.nthunya@ugent.be (Nthunya); sdmhlanga1@gmail.com (Mhlanga)

a Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa

b Particle and Interfacial Technology Group, Department of Green Chemistry and Technology, Ghent University, Ghent, Belgium

c Facultad del Mary Medio Ambiente, Universidad del Pacifico, Guayaquil, Ecuador

d DST/MINTEK Nanotechnology Innovation Centre, Johannesburg, South Africa

The use of MD in water desalination and wastewater treatment has recently attracted the attention of numerous researchers. MD is a thermally-driven process in which water vapour molecules pass through a porous hydrophobic membrane. This process is enhanced by a vapour pressure induced by the temperature difference across the membrane;¹¹ thus, offering the possibility of solution saturation without causing a significant flux decline.¹³ The heat energy required in the MD separation process can be generated by solar energy, geothermal energy, or waste-grade energy.¹⁴ In theory, the membranes used in MD processes should strictly allow the passage of vapours and retain non-volatile substances. Therefore, the filtrate would be close to 100% pure from solids or non-volatile contaminants.¹⁵

However, the performance of MD is severely affected by two key factors: (i) wettability as a result of condensation of water vapour inside the pores of the membranes; and (ii) fouling due to the accumulation of biofilm, organic, inorganic, and colloidal substances on the surface or in the internal pore structure of the membranes.¹¹ These two limiting factors restrict the choice of suitable polymers for the synthesis of MD membranes. Briefly, hydrophobic polymers promote hydrophobic–hydrophobic interactions between pollutants and the membrane surface; thus, blocking the pores of the membranes and causing fouling.¹⁶ Furthermore, hydrophilic polymers enhance the wettability of the membranes; consequently, affecting the diffusion of water vapour through the membrane and compromising its rejection efficiency.⁸ As a result, numerous membrane modification studies have been conducted to concurrently overcome the fouling and wettability challenges associated with MD membranes.^{17,18} Although, MD is a promising technology widely tested at a laboratory-scale, its industrial implementation has yet been limited.

Therefore, the goal of this article is to provide a critical and comprehensive review of the state-of-knowledge regarding MD process with insights toward better understanding its shortcomings and limitations. Additionally, recent advancements in membrane modification by the embedment of nanoparticles (NPs) to enhance fouling resistance and tackle wettability are emphasized; whereby areas for further work are recommended. Finally, cost implications and environmental sustainability of MD are also discussed to elucidate promising approaches for a future and successful implementation of MD at an industrial scale for the desalination of brackish water/seawater at high recovery rates.

MEMBRANE SYNTHESIS METHODS

MD membranes are commonly prepared using solution-casting and nanofibre-electrospinning methods. In the casting process, a solution of a specific material is placed on a substrate to adopt the shape of the casting material and subsequently allowed to solidify under suitable conditions.¹⁹ Figure 1 shows an illustration of a membrane casting procedure using a casting knife. In this process, the polyvinylidene fluoride (PVDF) solution is casted on a non-woven fabric to adopt its flat shape. The membrane is then coagulated in a water bath and peeled off from the non-woven fabric. The PVDF nanofibre membrane was spin-coated using titanium dioxide nanoparticles (TiO₂NPs) to enhance the super-hydrophobicity of the membrane.²⁰

The most studied methods for the synthesis of MD membranes are phase inversion and electrospinning methods, involving interfacial polymerization, graft polymerization, and dip coating as membrane modification processes.

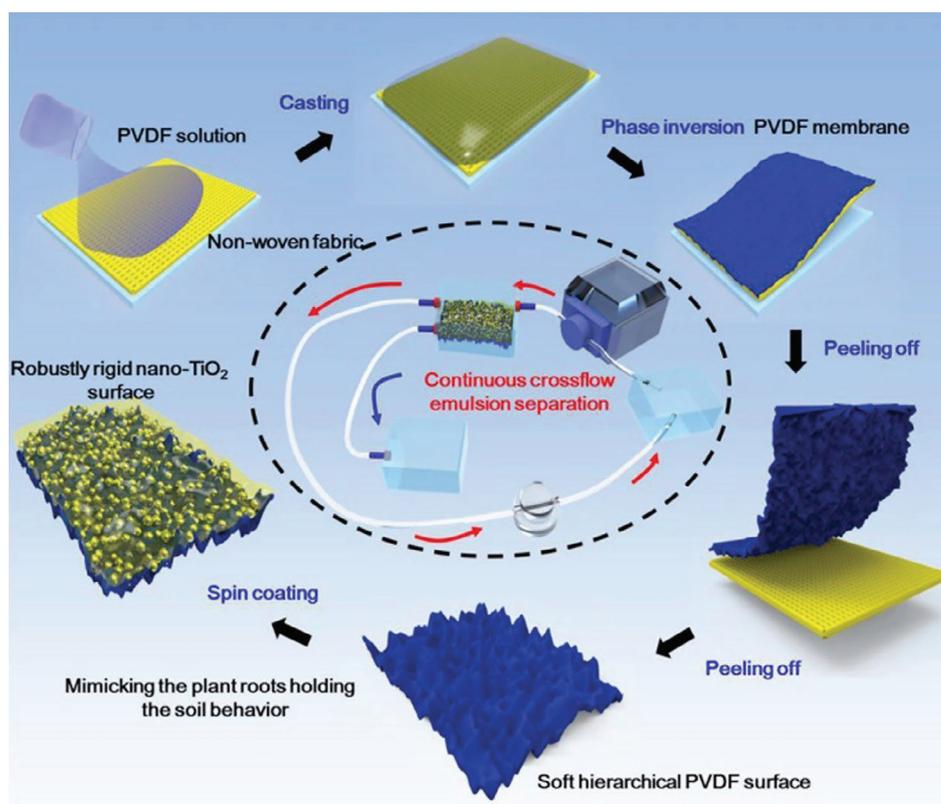


Figure 1. Casting of polymer films to prepare nano-titanium dioxide (TiO₂) surface coated membranes for membrane distillation.²⁰

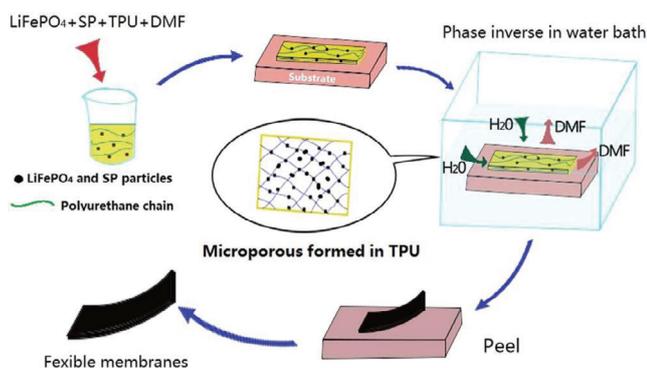


Figure 2. Phase inversion formation of membranes.²¹

Phase inversion

Phase inversion is a de-mixing process whereby a homogeneous polymer solution is transformed to a solid material under controlled conditions (see Fig. 2). This transformation process can be performed using the following techniques:¹⁰

- (i) immersion precipitation, where the polymer solution is immersed in a coagulation bath to allow the exchange of solvents to occur;
- (ii) thermally induced phase separation, in which the de-mixing process occurs by subjecting the membrane to high temperatures;
- (iii) evaporation-induced phase separation, which occurs through the evaporation of the volatile solvent used to prepare the polymer solution of interest.

The phase inversion method can be applied in the synthesis of flat sheet and hollow fibre membranes. For the preparation of flat sheet membranes, the polymer solution is casted on a flat support material (e.g. glass) and subsequently immersed in a coagulating bath. The structural properties of the resulting flat sheet membrane would depend on the rates of exchange of the solvent and non-solvent.²² An example of immersion precipitation phase inversion of super-phosphorus (SP) and lithium iron phosphate (LiFePO_4) NPs-modified thermoplastic polyurethane (TPU) is illustrated on Fig. 2. In this process, a solution of TPU and SP/ LiFePO_4

is casted on a flat polyfluorotetraethylene (PFTE) substrate using a casting knife. The casted solution on the substrate is placed in distilled water (coagulation bath at 25 °C) to remove the solvent from the liquid-solution (de-mixing process) for 4 h. The solidified membrane is peeled-off from the substrate and dried at 100 °C for 2 h.²¹

The phase inversion preparation of hollow fibre membranes involves the extrusion of the polymer solution, coagulation and sintering of the coagulated hollow fibre.²³ An illustration of the phase inversion preparation of hollow fibre membranes is provided in Fig. 3. The nanocomposite membrane is prepared through a solvent transfer-induced phase separation, followed by photopolymerization.²⁴ Bicontinuous interfacially-jammed emulsions are used for the formation of NP-functionalized hollow fibre membranes. The ternary fluid is composed of silicon dioxide nanoparticles (SiO_2 NPs)-doped monomers and the bore/sweeping fluid is water. The co-extrusion of these fluids results in the formation of hollow fibres.²⁴ To ensure the formation of uniform hollow fibres, the nozzle of the sweeping fluid is centred, and its viscosity is adjusted by the addition of high molecular weight polyethylene glycol (1%). Photopolymerization is induced by UV-light irradiation, resulting in hollow porous NP-modified membranes. The aligned hollow fibre membranes are collected in a water-filled rotating glass cylinder.²⁴

Electrospinning techniques

The electrospinning technique is a high voltage driven process, in which the polymer solution becomes electrically charged and induces electrostatic repulsive forces when subjected to an electric field (see Fig. 4). The polymer surface tension is broken by these forces; thus, leading to the stretching and thinning of the polymer jet.²⁶ The electrospinning and electrospaying techniques take place simultaneously under specific controlled conditions.²⁷ Electrospaying occurs when entanglements and molecular cohesion of the polymer solution are not strong enough to sustain stream break-down (i.e. a process where a polymer solution is ejected from the capillary nozzle and drops as a result of jet breakage) during the ejection of the polymer solution. However, under favourable molecular cohesion conditions, the droplets form charged jets, which stretch due to electrostatic forces to synthesize uniform nanofibres.²⁸ Simultaneous electrospaying and electrospinning can lead to the formation of beaded

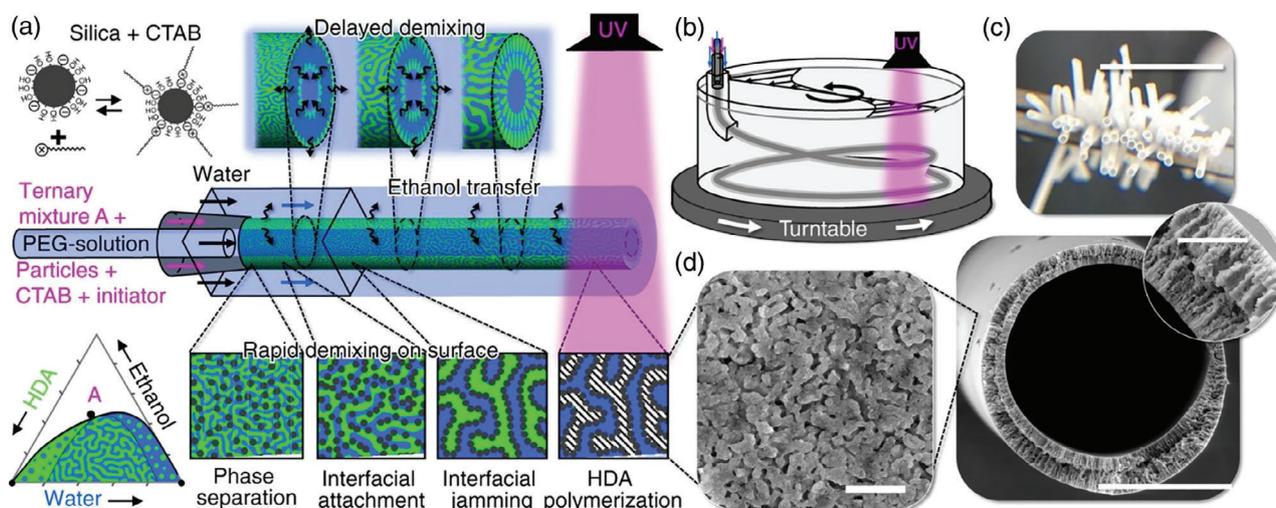


Figure 3. Preparation of a hollow fibre membrane embedded with silicon dioxide nanoparticles (SiO_2 NPs).²⁴

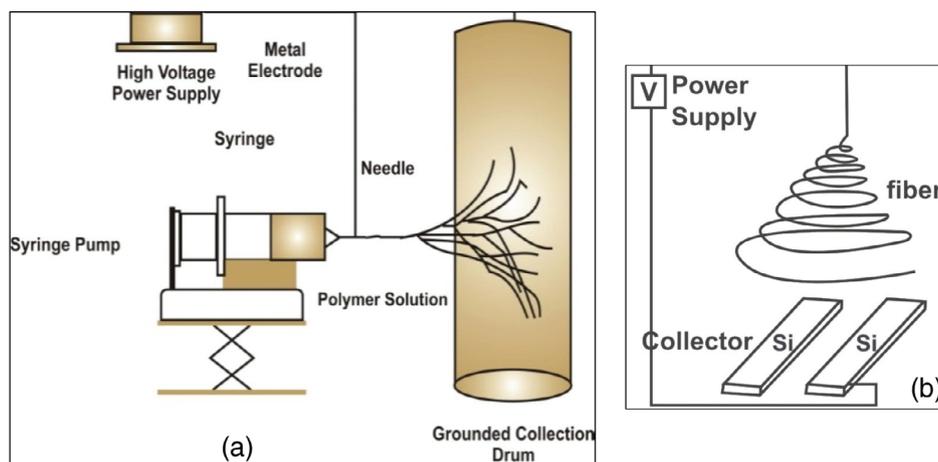


Figure 4. Schematic representation of an electrospinning process of nanofibre mats.²⁵

nanofibres as a result of stream break-down.²⁹ Electrospinning has been successfully used for the preparation of nanofibre membranes suitable for MD. The synthesis of super-hydrophobic PVDF nanofibre membranes has been achieved by the incorporation of multi-walled carbon nanotubes (MWCNTs), SiO₂NPs, and TiO₂NPs onto polymeric membranes (e.g. PVDF membranes) resulting in contact angles higher than 150°.^{30–32} Not only do these modified nanofibre membranes display high contact angles, they are also characterized by a mechanical strength high enough to sustain low pressures in MD.^{30–32} These nanofibre membranes have been successfully used in the production of potable water at fluxes between 28 and 42 L m⁻² h⁻¹ and removal efficiencies of ~99.9%.

MD MEMBRANE MODIFICATION METHODS

Several methods are currently used for the modification of MD membranes, including graft polymerization, interfacial polymerization, and dip coating. Modification processes offer the possibility of synthesizing membranes with desired characteristics such as embedding of NPs to enhance membrane hydrophobicity.

Graft polymerization

In this method, monomers are chemically attached to the core polymer to enhance the properties and functionalities of the latter. The grafted polymer is thermodynamically stable since the monomer is covalently bonded to the core polymer. Graft polymerization is classified into three types: (i) grafting onto; (ii) grafting from; and (iii) grafting through. In grafting onto, the free radical active sites generated from the two polymers combine covalently to form a grafted polymer. In grafting from, the core polymer is initiated to form radicals, which subsequently react with the monomer to produce the desired graft polymer. In grafting through, the free radical active sites of the low molecular weight monomer reacts with the vinyl groups of the core polymer to form a graft polymer with well-defined side chains.³³

Figure 5 presents a typical graft polymerization process. Briefly, the polycarbonate membrane is treated with an argon plasma atmosphere and exposed to oxygen to promote the formation of hydroperoxide active radicals.³⁴ These radicals enhance the formation of grafted membranes by initiating the graft polymerization of the acrylic acid.³⁴ This technique was adopted by Korolkov *et al.*³⁵ to synthesize triethoxyvinylsilane-grafted polyethylene terephthalate (PET) for enhancing membrane hydrophobicity. Acrylic acid

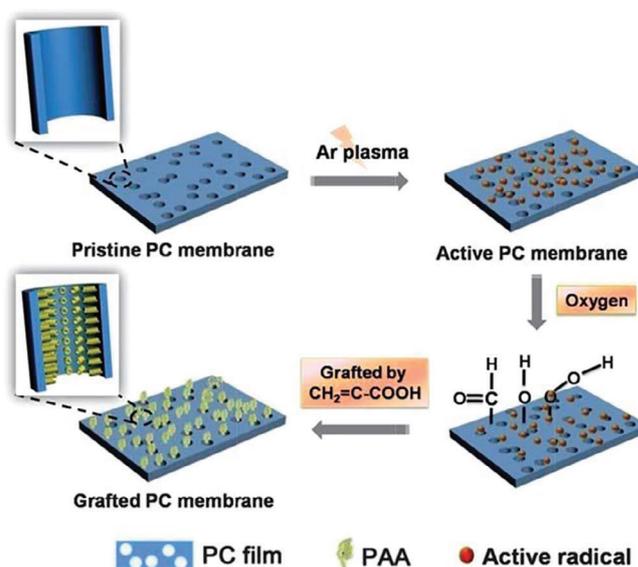


Figure 5. Schematic representation of graft polymerization in membrane modification.³⁴

(6%) is added to initiate the grafting process and the resultant membrane showed high flux with efficient salt removal from water on a direct contact MD mode.³⁵

Plasma polymerization

Plasma polymerization or discharge polymerization is a modification method that activates gaseous or liquid monomers to initiate the polymerization.³⁶ The gas discharges that provide an activation energy are generated from the plasma source. This technique produces highly-branched and crosslinked polymers that react with solid surfaces. The formation of the branched polymers offers a great advantage by reducing several steps which are required in other modifying techniques such as grafting. Another key advantage of plasma polymerization is its environmental friendliness.³⁷ This technique has been used by Song *et al.* to increase the hydrophobicity of MD hollow fibre membranes.³⁸ The coating thickness induced by plasma polymerization is in the range of 1 to 2 μm. This strongly bound modifying layer has shown a low impact on membrane porosity compared to other techniques.^{38,39}

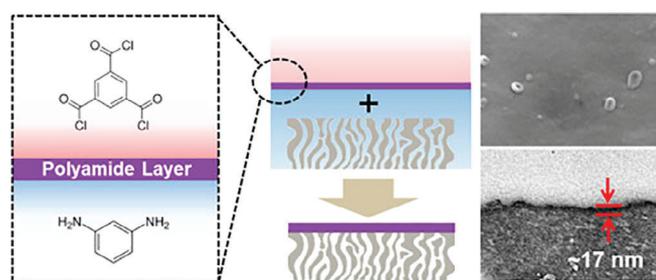


Figure 6. Schematic representation of interfacial polymerization during membrane modification.⁴⁰

Interfacial polymerization

Interfacial polymerization is a type of a step-growth reaction process in which polymerization takes place at the boundary of the different polymers containing one monomer (Fig. 6). Interfacial polymerization reactions are mainly described by the reaction mechanisms proposed by Schotten-Baumann.⁴¹ In this process, diacid chloride in the organic phase reacts with a monomer containing hydrogen atoms, which function as reaction centres or sites.⁴¹ This polymerization is not commonly reported on MD membranes. However, a range of interfacial polymerization-modified polyamine membranes using a wide array of amines and acid chloride monomers were reviewed by Gohil and Ray.⁴² Examples of such membranes include the thin film nano-enhanced membranes for application in water purification. Interfacial polymerization is affected by humidity, temperature, and purity of the reactants.⁴³

Dip coating

In dip coating, a thin film is deposited on the surface of the membrane using the polymer-solution of interest. Dip-coating processes are classified as: (i) immersion; (ii) start-up; (iii) deposition; (vi) evaporation; and (v) drainage (Fig. 7). The coating material thickness, membrane pore size, and membrane structural integrity are determined by the concentration of the dipping polymer, dipping time, and concentration of the crosslinking agent.⁴⁵ Chen *et al.*⁴⁴ explored graft polymerization of poly(*N*-(3-sulfopropyl)-*N*-(methacryloyloxyethyl)-*N,N*-dimethylammonium betaine) (poly(SBMA)) on polystyrene (PS) membrane using casting and dip coating. The

poly(SBMA) solution was introduced to the PS membrane through dipping and casting. The polymerization reaction was then exposed to UV-irradiation to ensure the formation of covalent bond between the PS membrane and the poly(SBMA).⁴⁴

THE USE OF NANOPARTICLES IN MEMBRANE MODIFICATION

Extensive research involving the modification of MD membranes with NPs has been conducted to overcome the challenges associated with membrane flux, fouling, wetting, and porosity.^{46–50} NPs are particulate materials with at least one dimension smaller than 100 nm but larger than atoms and molecules.⁵¹ NPs include particulate metals such as silver (Ag), silica (SiO₂), and titania (TiO₂). Silver nanoparticles (AgNPs) are able to penetrate through the cell walls of microorganisms, interact with their thiol groups and nucleic acids and bind to their enzymes, which leads to the destruction of their cell envelopes and eventual growth inhibition.^{52–54} Due to their toxicity towards several microorganisms (e.g. bacteria, viruses, and fungi), AgNPs have been used in many applications including water treatment, biomedicine, clothing, and textiles.⁵⁵

In water filtration systems, AgNPs act as a preventive measure to reduce the formation of biofilms on the surface or inside the pores of the membrane, thus making the membrane less susceptible to fouling.^{56,57} However, when the AgNPs are deposited onto the membranes at high concentrations, they block the pores of the membranes, hence reducing the water fluxes.⁵⁸ MD membrane fouling studies in the literature are dominated by organic fouling and inorganic fouling (also referred to as scaling).^{18,59} Although few studies on biofouling of MD membranes have been reported in the literature, biofilm formation has been recorded to significantly decrease the efficiency of MD systems.⁶⁰ Zodrow *et al.*⁶⁰ have demonstrated that the growth of bacteria in MD is hindered by high operation temperatures (≥ 60 °C) and high water salinity.⁶⁰ Nevertheless, wastewater systems (i.e. mostly discharging to water bodies) are characterized by high concentrations of thermophilic bacteria used for the removal of biological oxygen demand (BOD).⁶¹ These thermophilic bacteria, mainly found in marine environments, hot springs, hydrothermal vents, and open surface waters, thrive in saline waters, high temperatures (≥ 80 °C) and would potentially induce membrane fouling in MD.⁶² There is no single study reporting the use of NPs for membrane modification in MD to hinder the growth of thermophilic bacteria.

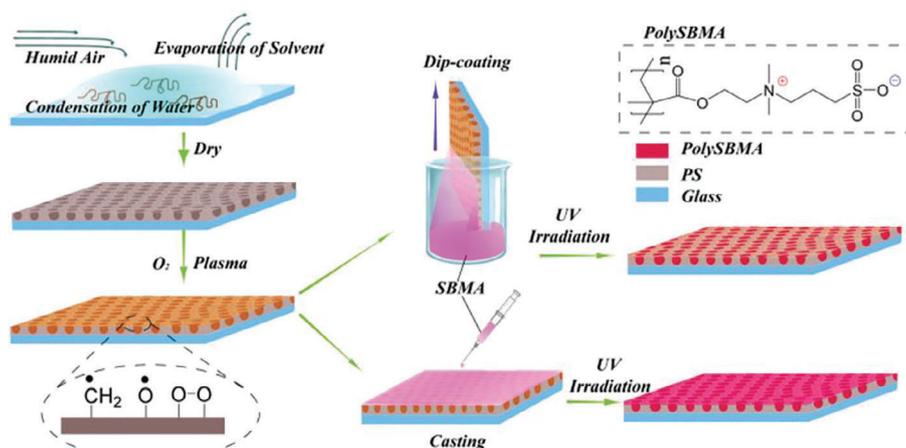


Figure 7. Dip coating in membrane modification.⁴⁴

At different sizes and degree of crystallinity, TiO₂NPs exhibit different affinities towards water molecules.⁶³ Small-sized TiO₂NPs have also shown high hydrophilic properties as anatase.⁶³ Therefore, these properties can be used to render hydrophilicity to the hydrophobic surface of MD membranes for decreasing the surface adsorption of hydrophobic organic foulants. Briefly, unfavourable polar interactions would occur between hydrophilic TiO₂NPs and hydrophobic moieties on foulants. Also, a tightly-bound layer of water molecules on TiO₂NPs would prevent interactions with foulants.⁶⁴

To mitigate wetting challenges associated with MD membranes, SiO₂NPs have been extensively used to enhance the hydrophobicity of PVDF membranes by rendering their surfaces super-hydrophobic with contact angles higher than 160°. ^{47,65} Khumalo *et al.* tested organic modification of SiO₂NPs using hexamethyldisilazane (HDMS) and subsequent embedment in PVDF flat sheet membranes.^{66,67} The resulting membranes were characterized by hydrophobic properties (contact angle ≈ 115°) which enhanced MD performance for the recovery of hydrolysed urine. Silane reagents such as octadecyltrimethoxysilane (OTMS), *N*-octadecyltrichlorosilane (ODTS), chlorodimethyl-octadecyl silane (Cl-DMOS) could be used to further enhance membrane super-hydrophobicity. The OTMS molecule is characterized by a long aliphatic carbon chain (CH₃(CH₂)₁₇-) where the anchor group is (-Si-OCH₃)₃. Furthermore, the anchor groups on ODTS and Cl-DMOS are (-Si-ClCH₂)₃ and (-Si-Cl₃)₃, respectively.^{68–74} The anchor groups on OTMS are more hydrophobic due to the presence of bulky non-polar CH₃ groups. The presence of strong electron withdrawing atoms such as chlorine and oxygen in Cl-DMOS and ODTS cause an uneven distribution of electrons, which could subsequently induce a minimal polarity on one end of the molecule, and slightly reduce its hydrophobicity. This differences in the hydrophobic nature of the SiO₂NPs give rise to different performances in MD membranes.^{75,76}

Membranes prepared in alcohol as a non-solvent during the inversion phase also display intrinsic properties, which result in the formation of super-hydrophobic membranes.⁴⁷ These membranes are characterized by improved water fluxes as well as high separation efficiencies.^{46,47} Wang *et al.*⁷⁷ synthesized hydrophobic membranes using SiO₂NPs, chitosan hydrogel, and fluoro-polymer, i.e. the latter was added to confer amphiphilic properties to these MD membranes for the selective separation of oil from water.⁷⁷ This membrane exhibited high oil–water separation efficiencies compared to commercial hydrophobic PVDF membranes.⁷⁷

Not only do super-hydrophobic characteristics improve the anti-wetting capabilities of membranes, they also enhance self-cleaning properties by a process called lotus effect.⁷⁸ However, for membranes to attain this lotus effect (i.e. lotus leaf), they should be characterized by high contact angles close to 180° and significantly low sliding angle, i.e. the smallest angle that would allow an easy roll-off of water droplets and sufficient removal of dirt from materials.^{79,80} This lotus effect assists in the generation of a slip flow as well as in the reduction of drag forces, and thus would be useful in membrane purification of seawater.⁸¹ Rezaei *et al.* grafted super-hydrophobic SiO₂NPs on the surface of PVDF membranes to mimic the effect of a lotus leaf on liquid repellent.⁸² SiO₂NPs were characterized by water-hating methyl functional groups which subsequently improved the contact angles of the membranes from 139° to 154°. The water-membrane contact angle and roughness observed in this study was similar to those shown by many other previous studies reporting a

decrease in membrane wetting and an improvement on membrane fouling resistance.^{30,46,47,65,82} In addition to several studies reporting the use of SiO₂NPs and TiO₂NPs for enhancing membrane hydrophobicity,^{30,65,82–84} graphene and carbon nanotubes (CNTs) have also been observed to render MD membranes super-hydrophobic.^{31,85} Graphene and CNTs are characterized by benzene rings and sp² carbon atoms arranged hexagonally. This arrangement gives rise to an aromatic ring that is composed of relatively non-polar C–C and C–H bonds which are not solvated by water molecules.⁸⁶ Therefore, graphene and CNTs are hydrophobic in nature unless they are functionalized with hydrophilic moieties such as carboxylic functional groups and thus enhance membrane resistance to wetting.⁸⁷ Not only do graphene and CNTs considerably enhance the anti-wetting membrane properties, they also improve their mechanical strengths, which is essential in MD operations.^{31,85} The incorporation of oxidized graphene and CNTs revert the membrane hydrophobicity to hydrophilicity; thus, assisting in the prevention of membrane fouling.^{88,89} A summary of NP-enhanced membranes for MD processes is presented in Table 1.

The low rate of water production is another setback associated with MD, which could be mitigated by the use of nanofibre membranes. Remarkably, high fluxes have been recorded due to the high porosities of nanofibre membranes;¹⁰² which are also characterized by high surface roughness that allows air entrapment in the membrane surface roughness.⁸⁵ This entrapped air promotes the repulsion of water droplets, thus further improving membrane hydrophobicity.¹⁰³

CONFIGURATIONS COMMONLY USED IN MD

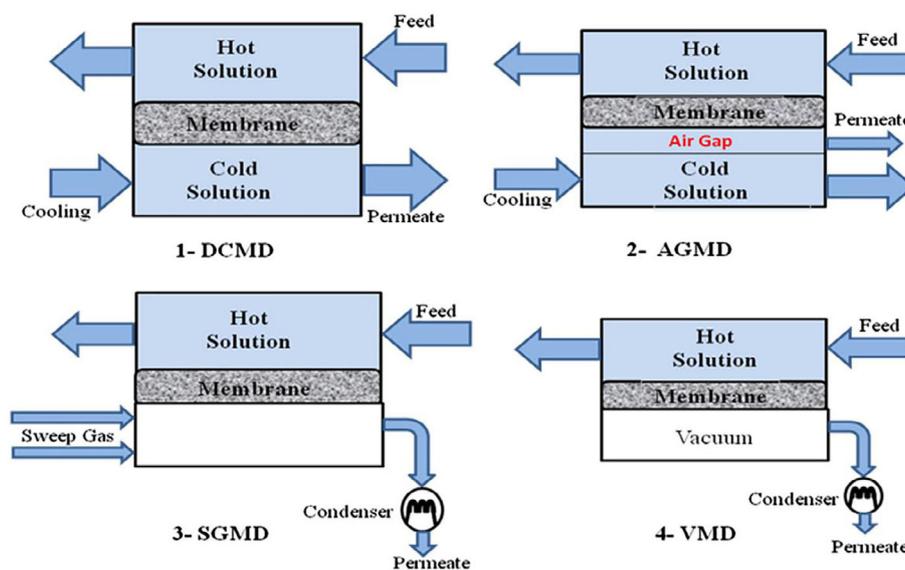
MD under different configurations has been tested for the desalination and production of high-quality water from saline water, where high rejection rates at high permeate fluxes have been achieved.^{30,46,47,76,94,96} Several configurations have also been investigated for the recovery of underground waters contaminated by heavy metals¹⁰⁴ and for the purification of pharmaceutical wastes and textiles wastewater (i.e. commonly achieving high separation percentages).^{105,106} As shown in Fig. 8, MD processes are classified into four configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD).⁷⁶

Direct contact membrane distillation (DCMD)

In DCMD, the hot solution (feed) is in direct contact with the surface of the hot membrane side. Water vapour is then transferred from the hot feed side to the cold permeate side where it condenses. The water vapour is transferred by the vapour gradient across the membrane as a result of the vapour pressure difference (Fig. 8). Unless otherwise stated, the default MD configuration is referred to as DCMD.¹⁰⁸ This configuration has been extensively reviewed where several NPs types (e.g. SiO₂NPs) have been incorporated onto MD membranes for its application in the purification of different types of waters (e.g. oilfield and saline) as well as juice concentration and the removal of metals and ammonia.¹⁰⁹ Although this configuration is known to be susceptible to heat loss as shown in Table 2, Lee *et al.* were able to achieve the thermal efficiency of 0.73 to 0.87 by a countercurrent cascade which is a significant improvement in MD.¹¹⁶

Table 1. Summary of nanoparticle-embedded membranes prepared using different methods and their potential impact on membrane distillation (MD)

Method	Polymer	Nanoparticle	Impact	Reference
Electrospinning	PVDF	CNTs	Improved flux (24–29 L m ⁻² h ⁻¹) and salt rejection (99.9%)	31
Electrospinning	PVA	SiO ₂ NPs	Improved amphiphilic properties leading to high fluxes (45 L m ⁻² h ⁻¹) in the presence of surfactants in solution	90
Electrospinning	PVDF	TiO ₂ NPs	Stabilized high water flux (40 L m ⁻² h ⁻¹)	32
Electrospinning	PVDF	SiO ₂ NPs	High water flux in oil–water separations (24 L m ⁻² h ⁻¹)	91
Coating	PVDF	TiO ₂ NPs	High fouling resistance	83
Electrospinning	PVDF	Al ₂ O ₃ NPs	High metal rejection (95%)	92
Electrospinning	PVDF	SiO ₂ NPs	High stable flux (31 L m ⁻² h ⁻¹)	30
Casting and coating	PVDF	SiO ₂ NPs	High oil-fouling resistance	77
Electrospinning	PVDF	SiO ₂ NPs	High stable flux (48 L m ⁻² h ⁻¹)	93
Electrospinning	PVDF	TiO ₂ NPs	High flux (38 L m ⁻² h ⁻¹)	84
Electrospinning	PVDF	CNTs	Flux enhancement (45 L m ⁻² h ⁻¹)	94
Casting	PVDF	SiO ₂ NPs	High salt rejection (99.9%)	95
Hollowfiber	PVDF/PAN	Clay	High flux (55 L m ⁻² h ⁻¹) and fouling resistance	96
Electrospinning	PVDF	Clay	Wetting resistance	97
Electrospinning and coating	PVDF	SiO ₂ NPs	Fouling and wetting resistance	98
Electrospinning	PVDF-HFP	fluorosilane-coated TiO ₂ NPs	Stable wetting resistance	99
Electrospinning	PVDF-HFP	Graphene	Stable flux (23 L m ⁻² h ⁻¹)	100
Phase inversion	PVDF	SiO ₂ NPs	High salt rejection (99.8%)	101


Figure 8. Graphical representation of the four different configurations commonly used in membrane distillation (MD).¹⁰⁷

Air gap membrane distillation (AGMD)

In this configuration, the feed solution is in direct contact with the hot side of the membrane surface. The total length of vapour diffusion is the sum of membrane thickness and air gap distance. The stagnant air is introduced between the hot surface of the membrane and the condensation side (Fig. 8). The water vapour passes through the air gap to the condensation compartment of the membrane.¹¹⁷ This configuration has been applied in several studies including the removal of toxic metals from water using alumina-modified electrospun PVDF nanofibre membrane characterized by a contact angle close to 150°.^{104,118}

Sweeping gas membrane distillation (SGMD)

In SGMD process, an unreactive gas is used to sweep the vapour from the permeate compartment of the membrane to the condensation compartment outside the membrane area (Fig. 8). Also, there is a mobile gas barrier that prevents the heat loss and assists in mass transfer.¹¹⁹ Onsekizoglu¹¹¹ has summarized the principles, advances, and limitations of membrane configurations within SGMD, including process fundamentals, membrane characteristics, membrane materials, membrane modules, process parameters, flux enhancement, transport mechanisms, and polarization phenomena.¹¹¹

Table 2. Advantages and disadvantages of membrane distillation (MD) configurations

Membrane configuration	Advantages	Disadvantages	References
DCMD	<ul style="list-style-type: none"> • Simple • Efficient 	<ul style="list-style-type: none"> • Susceptible to heat loss 	11,110
AGMD	<ul style="list-style-type: none"> • Minimal heat loss 	<ul style="list-style-type: none"> • Mass transfer barrier • Reduced permeate output 	111,112
SGMD	<ul style="list-style-type: none"> • Reduction of the barrier to the mass transport 	<ul style="list-style-type: none"> • Necessity of a higher condenser capacity 	113,114
VMD	<ul style="list-style-type: none"> • Vacuum air unblocks membrane pores • High fluxes 	<ul style="list-style-type: none"> • Highly complex 	11,115

Vacuum membrane distillation (VMD)

In VMD configuration, vacuum is created on the permeate side of the membrane. The water vapour is driven outside the membrane and condensed (Fig. 8). In this configuration, the loss of heat is significantly minimized.¹²⁰ Tijing *et al.*³¹ have explored the use of a mechanically stable and super-hydrophobic CNT-modified PVDF nanofibre membrane in VMD for studying membrane wetting resistance and flux enhancement. VMD has also been used in solar energy driven systems for the recovery of water from polluted solutions.^{115,121}

Although MD is a promising technology for water recovery, its configurations are characterized by different advantages and disadvantages, which are highlighted in Table 2.

APPLICATIONS OF MD PROCESSES

Several studies have reported the possible use of MD in a variety of separation processes. MD has been applied in the recovery and concentration of nutrients, removal of organics, bacteria, and toxic metal contaminants from water,^{122–124} purification of oil spills,¹²⁵ and desalination of seawater, brackish water, and industrial brines.^{121,126} All these applications involved the use of commercial and laboratory-scale synthesized nano-enhanced membranes.^{30,95,96,127} For instance, a TiO₂-modified PVDF membrane was tested towards organic fouling resistance in a DCMD system and the results were compared to those of pristine PVDF membranes.⁸³ Although both pristine and modified membranes showed similar fouling behaviours, the flux recovery was significantly higher in the modified membranes.⁸³ Applications for the recovery of water from different types of solutions in MD are summarized in Table 3.

Remarkably, MD has a distinct transport mechanism that allows the recovery of precious minerals. This process is induced by the pre-concentration of the product to be recovered on either side of the membrane as a function of the mineral vaporization energy. The non-volatile compounds are concentrated at the feed side of the membrane while volatile compounds are concentrated at the permeate side.^{134,135} This is achieved at a temperature below the critical temperatures of the material being separated to avoid the formation of supercritical fluids in cases where the liquid and vapour state of the compounds are indistinguishable from each other.¹³⁶ The production of ammonia is mostly performed in a solvay process. However, in a recent study,¹³⁷ 1 M of free ammonia was recovered from a feed concentration of 0.2 M in a vacuum membrane distillation process. The recovered

and concentrated ammonia can be precipitated for a further production of struvite. This is a cost-effective method for the production of fertilizer,¹³⁸ and thus contributes to the concept of water-food nexus. Several studies have also shown the separation and concentration of minerals such as hydrochloric acid (HCl) in an HCl/H₂SO₄ (sulphuric acid) mixed system, ionic liquids L-lysine-HCl syrup, extracts, and juices as well as the removal of other contaminants in the presence of organic foulants using commercial and nano-enhanced membranes in MD.^{139–141} Whereas toxic metals (e.g. boron) and organic dyes are removed from water at a 50% efficiency in microfiltration (MF) and forward osmosis (FO), 99% removal efficiencies have been achieved in nano-enhanced MD.^{142–146}

Nevertheless, MD is highly affected by flux decline in recovery processes that include volatile hydrophobic organics as they cause membrane fouling due to hydrophobic–hydrophobic interactions between the organics and the surface of the membrane.^{147,148} In order to understand the membrane and foulant interactions, the following model theories are applied: Zisman theory, Owens/Wendt theory, Fowkens theory and van Oss theory.^{149–152} The Zisman theory generally works best for non-polar surfaces. In order to account for polar type interactions, Owens and Wendt developed the harmonic mean method. Although the Owens/Wendt theory works best for polar surfaces, it requires numerous probe liquids to be tested for contact angles against the membrane–solute interactions being evaluated, leading to a lot of work. Therefore, van Oss modified the Owens/Wendt theory to cater for non-specific (van de Waals) interactions. Thus, the van Oss theory is currently the most studied theory for determination of the membrane–solute interactions for evaluation of membrane fouling.^{66,153,154}

In the van Oss theory, three probe liquids are used to determine the surface free energy of the membrane and the interfacial free energy between the membrane and the foulant (solute). The most commonly used probe liquids are de-ionized water, glycerol and diiodomethane. Diiodomethane is used as the dispersive (non-polar) liquid while de-ionized water and glycerol as polar liquids. The surface tension components of the probe liquids are given in Table 4.

Additionally, the total polar (σ_i^p) and the total surface energy (σ_i^{TOT}) components are also provided. The total surface tension is therefore expressed as:

$$\sigma_i^{TOT} = \sigma_i^D + \sigma_i^p \quad (1)$$

Table 3. Membrane distillation (MD) processes used for purification of different types of water

Feed solution	MD configuration	Membrane type	Thickness (μm)	Contact Angle (deg)	Flux (LMH)	Removal efficiency (%)	References
Oily water	DCMD	PVDF flat sheet	190	82.0	7.50	99.9	127
Sea water, brackish water	DCMD	PP flat sheet	25.0	120	3.00	–	110
Waste water	DCMD	PVDF-Cloisite 15A hollow fibre	252	–	1.50	98.7	128
NaCl solution	DCMD	PE flat sheets	65.0	108	123	–	129
Mine water	VMD	PTFE flat sheet	–	–	5.00	99.9	123
Humic acid solution	VMD	PP hollow fibre	100	–	2.90	98.0	130
Toxic metal wastewater	VMD	PTFE hollow fibre	440	101	5.00	–	131
Trace organic contaminants	DCMD	PTFE flat sheet	175	–	4.00	99.0	132
Lead-contaminated water	AGMD	PVDF nanofibre	100	150	20.0	99.3	92
Ammonia recovery	DCMD	PP hollow fibre	–	142	3.00	–	133

Table 4. The surface tension properties of the probe liquids at 20 °C¹⁵⁵

Probe liquids	σ_l^D (mJ m^{-2})	σ_l^+ (mJ m^{-2})	σ_l^- (mJ m^{-2})	σ_l^P (mJ m^{-2})	σ_l^{TOT} (mJ m^{-2})
Water	21.8	25.5	25.5	51.0	72.8
Glycerol	34.0	3.9	57.4	30.0	64.0
Diiodomethane	50.8	0.0	0.0	0.0	50.8

where

$$\sigma_l^P = 2\sqrt{\sigma_l^+ \sigma_l^-} \quad (2)$$

The surface tension parameters of the solid surface (σ_s^D , σ_s^- , σ_s^+) could be determined through the measured contact angles of the probe liquids characterized by the tension parameters given in Table 4 using the Young–Dupre equation.

$$\sigma_L^{\text{TOT}} (1 + \cos \theta) = 2 \left(\sqrt{\sigma_s^D \sigma_l^D} + \sqrt{\sigma_s^+ \sigma_l^-} \sqrt{\sigma_s^- \sigma_l^+} \right) \quad (3)$$

wherein: σ_l^D is the dispersive component of the surface tension of the liquid, σ_l^+ is the acid component of the surface tension of the liquid, σ_l^- is the base component of the surface tension of the liquid, σ_s^D is the dispersive component of the surface energy of the solid, σ_s^+ is the acid component of the surface energy of the solid, and σ_s^- is the base component of the surface energy of the solid.

In order to determine each surface tension parameter of the solid surface, Eqn (3) could be broken down into the following:

$$\sigma_L^{\text{TOT}} (1 + \cos \theta) = 2 \left(\sqrt{\sigma_s^D \sigma_l^D} \right) \quad (4)$$

where the contact angle of the dispersive liquid is used to calculate the dispersive component of the surface.

$$\sigma_L^{\text{TOT}} (1 + \cos \theta) = 2 \left(\sqrt{\sigma_s^D \sigma_l^D} + \sqrt{\sigma_s^+ \sigma_l^-} \right) \quad (5)$$

where the contact angle of the liquid that has the base component is used to calculate the acid component of the surface.

$$\sigma_L^{\text{TOT}} (1 + \cos \theta) = 2 \left(\sqrt{\sigma_s^D \sigma_l^D} + \sqrt{\sigma_s^+ \sigma_l^-} \sqrt{\sigma_s^- \sigma_l^+} \right) \quad (6)$$

where the contact angle of the liquid that has the acid component is used to calculate the base component of the surface.

The interfacial free energy for interaction between the membrane (m) and the solute or foulant (s) in water (w) is therefore estimated using the following equations.

$$\Delta G_{swm}^D = 2 \left(\sqrt{\sigma_w^D} - \sqrt{\sigma_s^D} \right) \left(\sqrt{\sigma_m^D} - \sqrt{\sigma_w^D} \right) \quad (7)$$

$$\begin{aligned} \Delta G_{swm}^P &= 2\sqrt{\sigma_w^+} \left(\sqrt{\sigma_s^-} + \sqrt{\sigma_m^-} - \sqrt{\sigma_w^-} \right) \\ &+ 2\sqrt{\sigma_w^-} \left(\sqrt{\sigma_s^+} + \sqrt{\sigma_m^+} - \sqrt{\sigma_w^+} \right) - 2\sqrt{\sigma_s^+ \sigma_m^-} - 2\sqrt{\sigma_s^- \sigma_m^+} \end{aligned} \quad (8)$$

$$\Delta G_{swm}^{\text{TOT}} = \Delta G_{swm}^D + \Delta G_{swm}^P \quad (9)$$

where $\Delta G_{swm}^{\text{TOT}}$ is the total free energy of cohesion.

While MD remains as one of the most promising processes in membrane technology, MD research has drifted towards the development of cost-effective methods for the treatment of saline water. Recent studies have focused towards flux enhancement, fouling mitigations, optimization of membrane properties, improvement of membrane wetting resistance using nano-enhanced membranes, optimization of operational parameters, and configurations.^{49,156} Remarkably, the separation of salts from brine, seawater, and brackish water by MD is efficient at a level that allows the permeate to be used for almost any domestic application (i.e. purification efficiency > 99%).^{46,47} However, DCMD or VMD remain susceptible to fouling at high water recoveries due to the presence of salt precipitates (e.g. scaling). He *et al.* demonstrated the capacity of hollow fibre membranes to sustain flux decline in the presence of supersaturated precipitating salts close to the membrane surface.¹⁵⁷ Furthermore, Song *et al.* indicated that the hollow fibre membrane surface design, module design, and cross-flow conditions are key parameters for attaining stable water fluxes and high rejection efficiencies even when the

desalination process is subjected to precipitating salts close to the membranes.³⁹

SUSTAINABILITY AND COST VIABILITY

The concept of desalination has long been investigated to mitigate the water scarcity challenges brought about by inadequate freshwater sources that fail to meet the current water demand. This involves the application of efficient processes such as RO and NF. These processes operate under high pressures, and thus consume a lot of energy resulting in high operational costs. In order to counteract the high operational costs in pressure-driven membrane technology, MD (i.e. which is a highly efficient desalination process) has long been investigated at laboratory scale. Regardless of the advantages in MD, piloting of this process has been relatively slow.

The rate at which researchers have devoted their efforts to MD has exponentially increased over the years. Such efforts involved the application of commercially available nano-enhanced membranes in water desalination at laboratory-scale. An analysis of the research and development trends in the area of MD, previously documented by Thomas *et al.*,¹⁵⁸ clearly shows the occurrence of three phases: initiation, emergence, and growth. As shown in Fig. 9, an escalation in the number of publications for these three phases depicts a generally positive outlook in the development of MD. While MD research was virtually non-existent in the 1980s, most of the research efforts were directed towards further development of MD process during the early to mid-2000s. The current research boom being experienced in MD processes is gearing towards commercialization,¹⁵⁸ with a specific focus in material improvements involving the use of nanomaterials.^{30,46,47,83,94} Ali *et al.*¹⁵⁹ conducted a study that linked publications, patents, and project pilot plants trends to work related to MD development (Fig. 10). To this end, several companies that are focusing on the application of MD technology in water desalination have been identified. These companies include Aquastill and Aquaver in the Netherlands, Memsys in Germany, and Gold Technologies in the United States. Other companies involved in pilot projects in Singapore are also emerging.¹¹

Despite MD research work advancing to pilot-scale level, a cost-benefit analysis of the technology is rarely reported. Khayet¹⁶⁰ has suggested a lack of cost-benefit analysis and energy consumption studies as the main hindering parameter for the development of large-scale MD. Currently, no studies related to the cost-analysis of NP-incorporated MD membranes have been reported, even though several studies have reported the use of NPs in the enhancement of membrane performances.^{30,95} Albeit, some studies have provided general information related to the MD operational cost without necessarily considering the cost implications associated with the incorporation of NPs onto MD membranes. Table 5 provides a summary of cost estimations for MD water purification systems. The figures outlined in Table 5 were calculated using information obtained from the literature. The rate of water production for some MD systems could not be determined due to a lack of information related to the estimated cost of water production.

The cost of water recovery in MD depends on a number of factors, including the cost of operational materials, the tax associated with the production of carbon dioxide from the energy required in MD processes, and many others.^{169–171} In the case of the low cost of heat that is free from taxes (e.g. the use of solar energy), MD becomes cheaper than highly energy demanding processes such

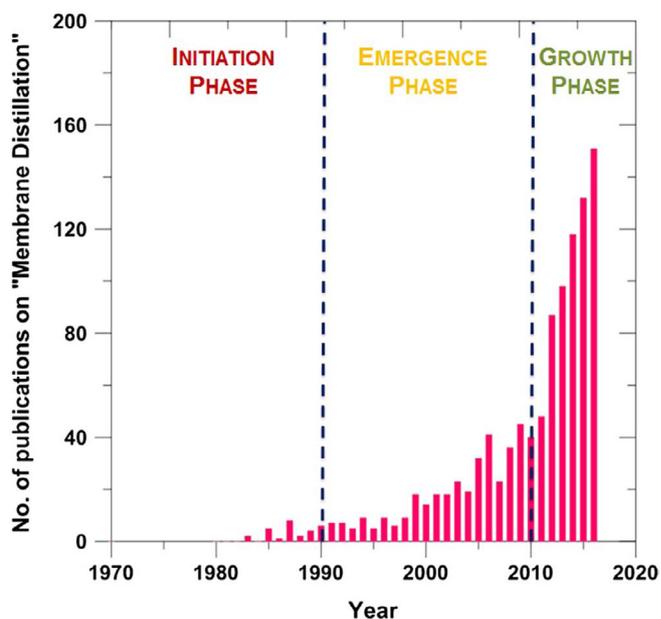


Figure 9. The growth of publications in membrane distillation.¹⁵⁸

as RO and NF.¹⁷³ It was estimated that the cost of water production of $17 \text{ m}^3 \text{ d}^{-1}$ in MD using geothermal energy is approximately $\$13 \text{ m}^{-3}$.¹⁶⁴ In the case where the heat supply in MD was sourced from electricity or fuel-fired plant, Meindersma *et al.*¹⁶⁵ have calculated that the total cost of water was $\$0.16\text{--}0.17 \text{ m}^{-3}$, relative to $\$0.25\text{--}0.35 \text{ m}^{-3}$ required for a RO process.¹⁶⁵ The cost estimated at the Memtill's water recovery systems demonstrated that MD can reduce the cost of water desalination to $\$0.26\text{--}0.54 \text{ m}^{-3}$. This considerable reduction was ascribed to the use of sustainable and cost-effective plant materials to build the operational modules as well as the use of low-cost heat supplies.¹⁶⁵ When determining the cost implications associated with water production in MD, the general parameters that were taken into consideration include the plant availability and capacity, interest rate (%), amortization, modules and membrane assembly ($\$ \text{ m}^{-2}$), installation ($\$$), supporting equipment, ($\$$) electrical cost ($\$ \text{ kW}^{-1} \text{ h}^{-1}$), steam cost ($\$ \text{ kg}^{-1}$), labour cost ($\$ \text{ m}^{-3}$), brine disposal ($\$ \text{ m}^{-3}$), maintenance cost (%), pre-treatment cost ($\$ \text{ m}^{-3}$), thermal energy requirement (kW h m^{-3}), emission factor for natural gas ($\text{kg CO}_2\text{-e kW}^{-1} \text{ h}^{-1}$), emission factor for electricity, ($\text{kg CO}_2\text{-e kW}^{-1} \text{ h}^{-1}$), electrical energy requirement (kW h m^{-3}), and carbon tax ($\$ \text{ t}^{-1} \text{ carbon}$).^{167,169–172}

CONCLUSION AND FUTURE PROSPECTS

Research directed towards MD is currently increasing at a remarkable rate. Various innovative fabrication and modification procedures for MD membranes have been reported in the literature and were summarized in this review. It has been found that NPs-modified membranes provide essential properties that mitigate the challenges associated with MD processes. It has been reported in several studies that these modified membranes attain high water-repellent characteristics, i.e. super-hydrophobic properties, which subsequently assist in the prevention of wetting inside the membrane pores. These super-hydrophobic properties allow the passage of water vapour through the membrane and prevent the passage of water in liquid state, thus enabling the recovery of high-quality water for domestic use. Although bio-fouling of thermophilic bacteria origin has been observed in MD

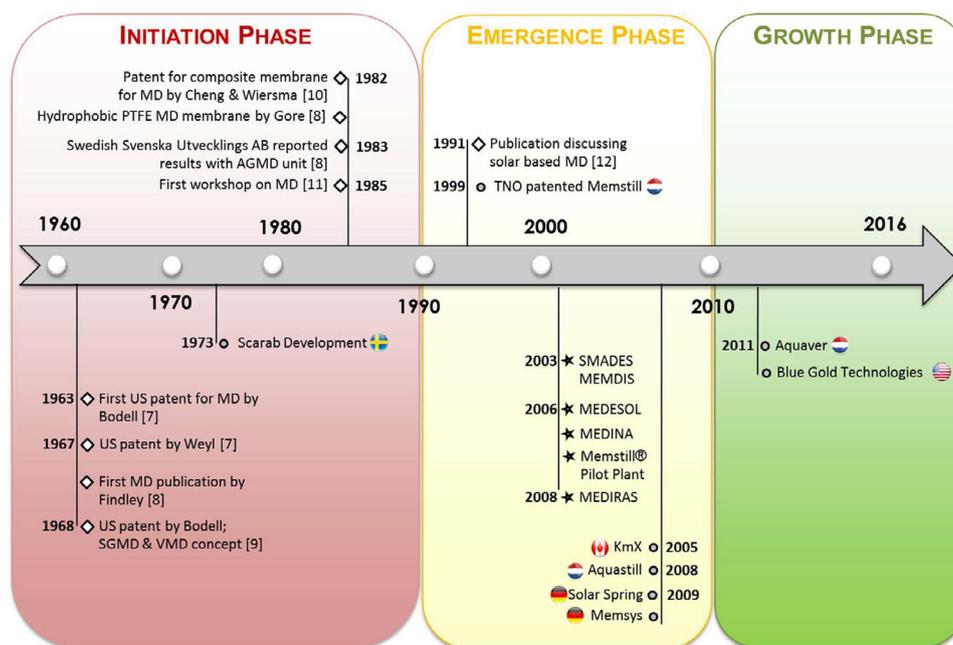


Figure 10. Current developments towards application of membrane distillation in water desalination.¹⁵⁹

Table 5. Estimated water production rate (WPR) and water production cost (WPC) of membrane distillation applications

MD membranes applications	WPR (L d ⁻¹)	WPC (\$ m ⁻³)	Year	Reference
DCMD plant powered by solar energy	500	15.0	1987	161
RO-integrated MD	–	1.32	1999	162
VMD	–	1.20	2003	163
Small scale AGMD powered by geothermal energy	171	130	2005	164
RO-integrated MD with UF/MF pretreatment	–	0.54	2006	165
AGMD pilot plant	0.09	1.00	2007	166
NF/RO-integrated VMD	76.2	0.92	2007	167
Low-grade heat MD	100	15.0	2008	168
Solar powered small scale AGMD	5.88	1.17	2008	169
Laboratory scale DCMD	7.50	1.72	2013	170
Small scale solar AGMD	21.7	5.16	2014	171
Laboratory scale AGMD	996	4.73	2017	172

processes, no study involving the use of well-known antibacterial NPs such as AgNPs have been reported. The rationale behind the use of AgNPs is to incorporate them in the preparation of biofouling-resistant membranes to hinder the growth of bacterial thermophiles.

Several applications of MD processes have been tested at laboratory-scale using different configurations. A review of results from studies involving the use of NP-modified MD membranes for the treatment of seawater, wastewater, brackish water, and surface water provide cost implications associated with this separation process. However, sustainable development towards commercialization has been moving at a slower rate with indications of some water treatment plants based in a few developed countries. It is imperative to systematically develop even more cost-effective purification systems that are integrated with emerging membranes to produce high quality water at large industrial throughput. Nanofibre membranes are less reported in MD applications compared to flat sheet membranes. However, the rate of water recovery of the former supersedes that of flat

sheets. Nanofibre membranes suffer critical challenges of low industrial throughput, and their synthetic procedures involve the use of complicated techniques requiring specialized skills. The equipment used in nanofibre production are high-voltage driven (≥ 10 kV). They also require conducting material collectors and mostly fail to produce uniformly aligned nanofibre membranes. Therefore, high throughput low cost nanofibre production requires future consideration.

Therefore, it can be concluded that the NP-modified membranes are a one-step solution to address many problems associated with MD. NP-incorporated membranes also create a path for achieving super-hydrophobic membranes with contact angles above 150° , which are capable of self-cleaning through the lotus effect process. Carefully designed methods for the incorporation of NPs into these membranes offers the possibility of developing cost-effective and high-performance water recovery technologies. In this regard, breakthroughs in the sustainable and commercial viability and implementation of MD processes in the industrial-scale recovery of water are anticipated.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the National Research Foundation (South Africa), the University of South Africa and Ghent University for providing financial support to conduct this study.

REFERENCES

- Aulenbach DB, Water our second most important natural resource. *Boston College Law Review* **9**:535–552 (1968).
- Muller M, Schreiner B, Smith L, Koppen B Van, Sally H, Aliber M, Cousins B, Tapela B, Merwe-botha, Marlene Van Der Karar E, Pietersen K. Water security in South Africa. Development Planning Division Working Paper Series Number 12, Midrand: DBSA, 2009;1–40.
- Lemieux PM, Lutes CC and Santoianni DA, Emissions of organic air toxics from open burning: a comprehensive review. *Prog Energy Combust* **30**:1–32 (2004).
- Marie A and Vengosh A, Sources of salinity in underground water from Jericho area, Jordan Valley. *Ground Water* **39**:240–248 (2001).
- Mclin SG, Evaluation of aquifer contamination from salt water disposal wells. *Proc Okla Acad Sci* **61**:53–61 (1986).
- Edokpolo B, Yu QJ and Connell D, Health risk assessment of ambient air concentrations of benzene, toluene and xylene (BTX) in service station environments. *Int J Environ Res Public Health* **11**:6354–6374 (2014).
- Haque SA, Salinity problems and crop production in coastal regions of Bangladesh. *Pak J Bot* **38**:1359–1365 (2006).
- Manjula S and Subramanian R, Membrane technology in degumming, dewaxing, deacidifying, and decolorizing edible oils. *Crit Rev Food Sci Nutr* **46**:569–592 (2006).
- Geise GM, Lee HS, Miller DJ, Freeman BD, Mcgrath JE and Paul DR, Water purification by membranes: the role of polymer science. *J Polym Sci Part B Polym Phys* **45**:1390–1398 (2007).
- Singh B, Kochkodan V, Hashaikeh R and Hilal N, A review on membrane fabrication: structure, properties and performance relationship. *Desalination* **326**:77–95 (2013).
- Camacho LM, Dumée L, Zhang J, de Li J, Duke M, Gomez J et al., Advances in membrane distillation for water desalination and purification applications. *Water* **5**:94–196 (2013).
- Gilron J, Song L and Sirkar KK, Design for cascade of crossflow direct contact membrane distillation. *Ind Eng Chem Res* **46**:2324–2334 (2007).
- Drioli E, Ali A and Macedonio F, Membrane distillation: recent developments and perspectives. *Desalination* **356**:56–84 (2015).
- Bourouni K and Chaibi MT, Application of geothermal energy for brackish water desalination in the South of Tunisia, in *Proceedings World Geothermal Congress 2005*. International Geothermal Association, Turkey (2005).
- Khayet M, Membranes and theoretical modeling of membrane distillation: a review. *Adv Colloid Interf Sci* **164**:56–88 (2011).
- Zhang M, Liao B q, Zhou X, He Y, Hong H, Lin H et al., Effects of hydrophilicity/hydrophobicity of membrane on membrane fouling in a submerged membrane bioreactor. *Bioresour Technol* **175**:59–67 (2015).
- Lim JW, Lee JM, Yun SM, Park BJ and Lee YS, Hydrophilic modification of polyacrylonitrile membranes by oxyfluorination. *J Ind Eng Chem* **15**:876–882 (2009).
- Tijing LD, Woo YC, Choi JS, Lee S, Kim SH and Shon HK, Fouling and its control in membrane distillation – a review. *J Membr Sci* **475**:215–244 (2015).
- Ebewele RO, *Polymer Science and Technology*. Chapman & Hall/CRC Press, Boca Raton, FL, pp. 295–315 (2000).
- Xiong Z, Lin H, Liu F, Xiao P, Wu Z, Li T et al., Flexible PVDF membranes with exceptional robust superwetting surface for continuous separation of oil/water emulsions. *Sci Rep* **7**:1–12 (2017).
- Bao JJ, Zou BK, Cheng Q, Huang YP, Wu F, Xu GW et al., Flexible and free-standing LiFePO₄/TPU/SP cathode membrane prepared via phase separation process for lithium ion batteries. *J Membr Sci* **541**:633–640 (2017).
- Tomaszewska M, Preparation and properties of flat-sheet membranes from poly(vinylidene fluoride) for membrane distillation. *Desalination* **104**:1–11 (1996).
- Feng CY, Khulbe KC, Matsuura T and Ismail AF, Recent progresses in polymeric hollow fiber membrane preparation, characterization and applications. *Sep Purif Technol* **111**:43–71 (2013).
- Haase MF, Jeon H, Hough N, Kim JH, Stebe KJ and Lee D, Multifunctional nanocomposite hollow fiber membranes by solvent transfer induced phase separation. *Nat Commun* **8**:1–7 (2017).
- Zafar M, Najeeb S, Khurshid Z, Vazirzadeh M, Zohaib S, Najeeb B et al., Potential of electrospun nanofibers for biomedical and dental applications. *Materials* **9**:1–21 (2016).
- Vonch J, Yarin A and Megaridis CM, Electrospinning: a study in the formation of nanofibers. *J Undergrad Res* **1**:1–5 (2007).
- Jaworek A, Electrospray droplet sources for thin film deposition. *J Mater Sci* **42**:266–297 (2007).
- Nthunya LN, Masheane ML, Malinga SP, Nxumalo EN, Barnard TG, Kao M et al., Greener approach to prepare electrospun antibacterial cyclodextrin/cellulose acetate nanofibres for removal of bacteria from water. *ACS Sustain Chem Eng* **5**:153–160 (2016).
- Fong H, Chun I and Reneker DH, Beaded nanofibers formed during electrospinning. *Polymer* **40**:4585–4592 (1999).
- Dong Z-Q, Ma X-H, Xu Z-L and Gu Z-Y, Superhydrophobic modification of PVDF–SiO₂ electrospun nanofiber membranes for vacuum membrane distillation. *RSC Adv* **5**:67962–67970 (2015).
- Tijing LD, Chul Y, Shim W, He T, Choi J, Kim S et al., Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation. *J Membr Sci* **502**:158–170 (2016).
- Lee E, Kyoungjin A, Hadi P, Lee S and Chul Y, Advanced multi-nozzle electrospun functionalized titanium dioxide/composite membranes for direct contact membrane distillation. *J Membr Sci* **524**:712–720 (2017).
- Bhattacharya A and Misra BN, Grafting: a versatile means to modify polymers techniques, factors and applications. *Prog Polym Sci* **29**:767–814 (2004).
- Wu J, Wang N, Zhang HC, Wang L, Dong H, Zhao Y et al., Acrylic acid grafted porous polycarbonate membrane with smart hydrostatic pressure response to pH. *J Mater Chem A* **1**:4642–4646 (2013).
- Korolkov IV, Gorin YG, Yeszhanov AB, Kozlovskiy AL and Zdorovets MV, Preparation of PET track-etched membranes for membrane distillation by photo-induced graft polymerization. *Mater Chem Phys* **205**:55–63 (2018).
- Puppulo MM, Hughey JR, Weber B, Dillon T, Storey D, Cerkez E et al., Plasma modification of microporous polymer membranes for application in biomimetic dissolution studies. *AAPS Open* **3**:1–13 (2017).
- Akhavan B, Jarvis K and Majewski P, Plasma polymer-functionalized silica particles for heavy metals removal. *ACS Appl Mater Interfaces* **7**:4265–4274 (2015).
- Song L, Li B, Sirkar KK and Gilron JL, Direct contact membrane distillation-based desalination: novel membranes, devices, larger-scale studies, and a model. *Ind Eng Chem Res* **46**:2307–2323 (2007).
- Song L, Ma Z, Liao X, Kosaraju PB, Irish JR and Sirkar KK, Pilot plant studies of novel membranes and devices for direct contact membrane distillation-based desalination. *J Membr Sci* **323**:257–270 (2008).
- Park SJ, Choi W, Nam SE, Hong S, Lee JS and Lee JH, Fabrication of polyamide thin film composite reverse osmosis membranes via support-free interfacial polymerization. *J Membr Sci* **526**:52–59 (2017).
- Morgan PW, Interfacial polymerization, in *Encyclopedia of Polymer Science and Technology – Wiley Online Library*. John Wiley & Sons, New York, NY, pp. 1–125 (2011).
- Gohil JM and Ray P, A review on semi-aromatic polyamide TFC membranes prepared by interfacial polymerization: potential for water treatment and desalination. *Sep Purif Technol* **181**:159–182 (2017).
- Petersen RJ, Composite reverse osmosis and nanofiltration membranes. *J Membr Sci* **83**:81–150 (1993).
- Chen S, Lu X, Hu Y and Lu Q, Biomimetic honeycomb-patterned surface as the tunable cell adhesion scaffold. *Biomater Sci* **3**:85–93 (2015).
- Yimsiri P and MacKley MR, Spin and dip coating of light-emitting polymer solutions: matching experiment with modelling. *Chem Eng Sci* **61**:3496–3505 (2006).
- Chen Y, Tian M, Li X, Wang Y, An AK, Fang J et al., Anti-wetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact membrane distillation of emulsified wastewaters. *J Membr Sci* **535**:230–238 (2017).

- 47 Munirasu S, Banat F, Ahmed A and Abu M, Intrinsically superhydrophobic PVDF membrane by phase inversion for membrane distillation. *Desalination* **417**:77–86 (2017).
- 48 Zhang Y, Wang X, Cui Z, Dioli E and Wang Z, Enhancing wetting resistance of poly(vinylidene fluoride) membranes for vacuum membrane distillation. *Desalination* **415**:58–66 (2017).
- 49 Sun J, Hu C, Zhao K, Li M, Qu J and Liu H, Enhanced membrane fouling mitigation by modulating cake layer porosity and hydrophilicity in an electro-coagulation/oxidation membrane reactor (ECOMR). *J Membr Sci* **550**:72–79 (2018).
- 50 Soyekwo F, Zhang Q, Gao R, Qu Y, Lin C, Huang X *et al.*, Cellulose nanofiber intermediary to fabricate highly-permeable ultrathin nano filtration membranes for fast water purification. *J Membr Sci* **524**:174–185 (2017).
- 51 Buzea C, Blandino IP and Robbie K, Nanomaterials and nanoparticles: sources and toxicity. *Biointerphases* **2**:1–103 (2007).
- 52 Li WR, Xie XB, Shi QS, Zeng HY, Ou-Yang YS and Chen YB, Antibacterial activity and mechanism of silver nanoparticles on *Escherichia coli*. *Appl Microbiol Biotechnol* **85**:1115–1122 (2010).
- 53 Schreurs WJA and Hosenberg H, Effect of silver ions on transport and retention of phosphate by *Escherichia coli*. *J Bacteriol* **152**:7–13 (1982).
- 54 Prabhu S and Poulouse EK, Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *Int Nano Lett* **2**:1–10 (2012).
- 55 Son WK, Youk JH and Park WH, Antimicrobial cellulose acetate nanofibers containing silver nanoparticles. *Carbohydr Polym* **65**:430–434 (2006).
- 56 Huang L, Zhao S, Wang Z, Wu J, Wang J and Wang S, In situ immobilization of silver nanoparticles for improving permeability, antifouling and anti-bacterial properties of ultrafiltration membrane. *J Membr Sci* **499**:269–281 (2016).
- 57 Dong C, Wang Z, Wu J, Wang Y, Wang J and Wang S, A green strategy to immobilize silver nanoparticles onto reverse osmosis membrane for enhanced anti-biofouling property. *Desalination* **401**:32–41 (2017).
- 58 Biswas P and Bandyopadhyaya R, Biofouling prevention using silver nanoparticle impregnated polyethersulfone (PES) membrane: *E. coli* cell-killing in a continuous cross-flow membrane module. *J Colloid Interface Sci* **491**:13–26 (2017).
- 59 Ahmad NA, Leo CP, Ahmad AL and Ramli WKW, Membranes with great hydrophobicity: a review on preparation and characterization. *Sep Purif Rev* **44**:109–134 (2015).
- 60 Zdrov K, Bar-Zeev E, Giannetto MJ and Elimelech M, Biofouling and microbial communities in membrane distillation and reverse osmosis. *Environ Sci Technol* **48**:13155–13164 (2014).
- 61 Phattaranawik J, Fane AG, Pasquier ACS and Bing W, A novel membrane bioreactor based on membrane distillation. *Desalination* **223**:386–395 (2008).
- 62 Frock AD and Kelly RM, Extreme thermophiles: moving beyond single-enzyme biocatalysis. *Curr Opin Chem Eng* **1**:363–372 (2012).
- 63 Hao YQ, Wang YF and Weng YX, Particle-size-dependent hydrophilicity of TiO₂ nanoparticles characterized by Marcus reorganization energy of interfacial charge recombination. *J Phys Chem C* **112**:8995–9000 (2008).
- 64 Koparde VN and Cummings PT, Molecular dynamics study of water adsorption on TiO₂ nanoparticles. *J Phys Chem C* **111**:6920–6926 (2007).
- 65 Wu X, Zhao B, Wang L, Zhang Z, Li J, He X *et al.*, Superhydrophobic PVDF membrane induced by hydrophobic SiO₂ nanoparticles and its use for CO₂ absorption. *Sep Purif Technol* **190**:108–116 (2018).
- 66 Khumalo N, Nthunya L, Derese S, Motsa M, Verliefe A, Kuvarega A *et al.*, Water recovery from hydrolysed human urine samples via direct contact membrane distillation using PVDF/PTFE membrane. *Sep Purif Technol* **211**:610–617 (2019).
- 67 Khumalo NP, Nthunya LN, De Canck E, Derese S, Verliefe AR, Kuvarega AT *et al.*, Congo red dye removal by direct membrane distillation using PVDF/PTFE membrane. *Sep Purif Technol* **211**:578–586 (2019).
- 68 Wang Y and Lieberman M, Growth of ultrasoft octadecyltrichlorosilane self-assembled monolayers on SiO₂. *Langmuir* **19**:1159–1167 (2003).
- 69 Iwasa J, Kumazawa K, Aoyama K, Suzuki H, Norimoto S, Shimoaka T *et al.*, In-situ observation of a self-assembled monolayer formation of octadecyltrimethoxysilane on a silicon oxide surface using a high-speed atomic force microscope. *J Phys Chem C* **120**:2807–2813 (2016).
- 70 Koga Y, Westh P, Nishikawa K and Subramanian S, Is a methyl group always hydrophobic? Hydrophilicity of trimethylamine-*N*-oxide, tetramethyl urea and tetramethylammonium ion. *J Phys Chem B* **115**:2995–3002 (2011).
- 71 Menger FM and Chlebowski ME, Is the ether group hydrophilic or hydrophobic? *Langmuir* **21**:2689–2695 (2005).
- 72 Escorihuela J, Pujari SP and Zuilhof H, Organic monolayers by B(C₆F₅)₃-catalyzed silylation of oxidized silicon surfaces. *Langmuir* **33**:2185–2193 (2017).
- 73 Sugimura H, Saito N, Ishida Y, Ikeda I, Hayashi K and Takai O, Photochemical reaction of organosilane self-assembled monolayer as studied by scanning probe microscopy. *J Vac Sci Technol A Vacuum, Surfaces, Film* **22**:1428–1432 (2004).
- 74 Kumar V, Puri P, Nain S, Bhat KN, Sharma NN, Self assembled monolayers of octadecyltrichlorosilane for dielectric materials. In: *AIP Conference Proceedings* 2016. pp. 2–7.
- 75 Eykens L, De Sitter K, Dotremont C, Pinoy L and Van der Bruggen B, Membrane synthesis for membrane distillation: a review. *Sep Purif Technol* **182**:36–51 (2017).
- 76 Alkudhri A, Darwish N and Hilal N, Membrane distillation: a comprehensive review. *Desalination* **287**:2–18 (2012).
- 77 Wang Z, Hou D and Lin S, Composite membrane with underwater-oleophobic surface for anti-oil-fouling membrane distillation. *Environ Sci Technol* **50**:3866–3874 (2016).
- 78 Zhang M, Feng S, Wang L and Zheng Y, Lotus effect in wetting and self-cleaning. *Biotribology* **5**:31–43 (2016).
- 79 Gould P, Smart, clean surfaces. *Mater Today* **6**:44–48 (2003).
- 80 Latthe SS, Terashima C, Nakata K and Fujishima A, Superhydrophobic surfaces developed by mimicking hierarchical surface morphology of lotus leaf. *Molecules* **19**:4256–4283 (2014).
- 81 Samaha MA, Tafreshi HV and Gad-el-Hak M, Superhydrophobic surfaces: from the lotus leaf to the submarine. *Comptes Rendus Mecanique* **340**:18–34 (2012).
- 82 Rezaei M and Samhaber W, Wetting behaviour of superhydrophobic membranes coated with nanoparticles in membrane distillation. *Chem Eng Trans* **47**:373–378 (2016).
- 83 Razmjou A, Arifin E, Dong G, Mansouri J and Chen V, Superhydrophobic modification of TiO₂ nanocomposite PVDF membranes for applications in membrane distillation. *J Membr Sci* **415–416**:850–863 (2012).
- 84 Mahdi S, Shahabadi S, Rabiee H, Mojtaba S, Mokhtare A, Brant JA, Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO₂/PH) nano fibrous membrane for high flux membrane distillation. *J Membr Sci* 2017;**537**:140–50.
- 85 Moradi R, Karimi-Sabet J, Shariaty-Niassar M and Koochaki MA, Preparation and characterization of polyvinylidene fluoride/graphene superhydrophobic fibrous films. *Polymers* **7**:1444–1463 (2015).
- 86 Aihara J, Yamabe T and Hosoya H, Aromatic character of graphite and carbon nanotubes. *Synth Met* **64**:309–313 (1994).
- 87 Schravendijk P and van der Vegt NFA, From hydrophobic to hydrophilic solvation: an application to hydration of benzene. *J Chem Theory Comput* **1**:643–652 (2005).
- 88 Vatanpour V, Ghadimi A, Karimi A, Khataee A and Yekavalangi ME, Antifouling polyvinylidene fluoride ultrafiltration membrane fabricated from embedding polypyrrole coated multiwalled carbon nanotubes. *Mater Sci Eng C* **89**:41–51 (2018).
- 89 Safarpour M, Khataee A and Vatanpour V, Preparation of a novel polyvinylidene fluoride (PVDF) ultrafiltration membrane modified with reduced graphene oxide/titanium dioxide (TiO₂) nanocomposite with enhanced hydrophilicity and antifouling properties. *Ind Eng Chem Res* **53**:13370–13382 (2014).
- 90 Huang Y, Wang Z, Hou D and Lin S, Coaxially electrospun superamphiphobic silica-based membrane for anti-surfactant-wetting membrane distillation. *J Membr Sci* **531**:122–128 (2017).
- 91 Liao Y, Loh C, Wang R and Fane AG, Electrospun Superhydrophobic membranes with unique structures for membrane distillation. *ACS Appl Mater Interfaces* **6**:16035–16048 (2014).
- 92 Attia H, Alexander S, Wright CJ and Hilal N, Superhydrophobic electrospun membrane for heavy metals removal by air gap membrane distillation (AGMD). *Desalination* **420**:318–329 (2017).
- 93 Hou D, Lin D, Ding C, Wang D and Wang J, Separation and purification technology fabrication and characterization of electrospun

- superhydrophobic PVDF-HFP/SiNPs hybrid membrane for membrane distillation. *Sep Purif Technol* **189**:82–89 (2017).
- 94 An AK, Lee EJ, Guo J, Jeong S, Lee JG and Ghaffour N, Enhanced vapor transport in membrane distillation via functionalized carbon nanotubes anchored into electrospun nanofibres. *Sci Rep* **7**:1–11 (2017).
- 95 Zhang J, Song Z, Li B, Wang Q and Wang S, Fabrication and characterization of superhydrophobic poly(vinylidene fluoride) membrane for direct contact membrane distillation. *Desalination* **324**:1–9 (2013).
- 96 Bonyadi S and Chung TS, Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic–hydrophobic hollow fiber membranes. *J Membr Sci* **306**:134–146 (2007).
- 97 Prince JA, Singh G, Rana D, Matsuura T, Anbharasi V and Shanmugasundaram TS, Preparation and characterization of highly hydrophobic poly(vinylidene fluoride)–clay nanocomposite nanofiber membranes (PVDF–clay NNMs) for desalination using direct contact membrane distillation. *J Membr Sci* **397–398**:80–86 (2012).
- 98 Huang Y, Wang Z, Jin J and Lin S, Novel Janus membrane for membrane distillation with simultaneous fouling and wetting resistance. *Environ Sci Technol* **51**:13304–13310 (2017).
- 99 Lee E, Kyoungjin A, He T, Chul Y and Kyong H, Electrospun nanofiber membranes incorporating fluorosilane-coated TiO₂ nanocomposite for direct contact membrane distillation. *J Membrane Sci* **520**:145–154 (2016).
- 100 Chul Y, Tijing LD, Shim W, Choi J, Kim S, He T et al., Water desalination using graphene-enhanced electrospun nano fiber membrane via air gap membrane distillation. *J Membr Sci* **520**:99–110 (2016).
- 101 Efome JE, Rana D, Matsuura T and Lan CQ, Enhanced performance of PVDF nanocomposite membrane by nano fiber coating: a membrane for sustainable desalination through. *Water Res* **89**:39–49 (2016).
- 102 Jiricek T, Komárek M, Chaloupek J and Lederer T, Flux enhancement in membrane distillation using nanofiber membranes. *J Nanomater* **2016**:1–7 (2016).
- 103 Fang J, Wang H, Wang X and Lin T, Superhydrophobic nanofiber membranes: effects of particulate coating on hydrophobicity and surface properties. *J Text Inst* **103**:937–944 (2012).
- 104 Zolotarev PP, Ugrozov VV, Volkina IB and Nikulin VM, Treatment of waste water for removing heavy metals by membrane distillation. *J Hazard Mater* **37**:77–82 (1994).
- 105 Criscuoli A, Zhong J, Figoli A, Carnevale MC, Huang R and Drioli E, Treatment of dye solutions by vacuum membrane distillation. *Water Res* **42**:5031–5037 (2008).
- 106 Ding Z, Liu L, Liu Z and Ma R, The use of intermittent gas bubbling to control membrane fouling in concentrating TCM extract by membrane distillation. *J Membr Sci* **372**:172–181 (2011).
- 107 Alkhudhiri A, Darwish N and Hilal N, Treatment of saline solutions using air-gap membrane distillation: experimental study. *Desalination* **323**:2–7 (2013).
- 108 Tomaszewska M, Membrane distillation-examples of applications in technology and environmental protection. *Pol J Environ Stud* **9**:27–36 (2000).
- 109 Ashoor BB, Mansour S, Giwa A, Dufour V and Hasan SW, Principles and applications of direct contact membrane distillation (DCMD): a comprehensive review. *Desalination* **398**:222–246 (2016).
- 110 Boubakri A, Hafiane A and Bouguecha SAT, Direct contact membrane distillation: capability to desalt raw water. *Arab J Chem* **10**:S3475–S3481 (2017).
- 111 Onsekizoglu P, Membrane distillation: principle, advances, limitations and future prospects in food industry, in *Distillation – Advances from Modeling to Applications*. INTECH, London, pp. 233–267 (2012).
- 112 Rochd S, Zerradi H, Mizani S, Dezairi A and Ouaskit S, Modélisation de membrane distillation: mass and heat transfer in air-gap membrane distillation. *J Membr Sci Technol* **6**:1–9 (2016).
- 113 Salehi MA and Rostamani R, Review of membrane distillation for the production of fresh water from saline water. *J Nov Appl Sci* **2**:1072–1075 (2013).
- 114 Drioli E, Criscuoli A and Molero LP, Membrane distillation. *Water Wastewater Treatment Technol* **3**:1–14 (2009).
- 115 Khaled F, Chaouachi B, Hidouri K. Study of vacuum membrane distillation coupled with solar energy. In: *International Conference on Green Energy and Conversion Systems, GECS 2017*. 2017. pp. 1–5.
- 116 Lee H, He F, Song L, Gilron J and Sirkar KK, Desalination with a cascade of cross-flow hollow fiber membrane distillation devices integrated with a heat exchanger. *AIChE J* **57**:1780–1795 (2011).
- 117 Alsaadi AS, Ghaffour N, Li JD, Gray S, Francis L, Maab H et al., Modeling of air-gap membrane distillation process: a theoretical and experimental study. *J Membr Sci* **445**:53–65 (2013).
- 118 Bajáková J, Chaloupek J, Lukáš D and Lacarin M, “Drawing” – the production of individual nanofibers by experimental method. *Int Conf Nanomater Res Appl* **9**:21–23 (2011).
- 119 Khayet M, Gordino MP and Mengual JI, Theoretical and experimental studies on desalination using membrane distillation. *Desalination* **157**:297–305 (2003).
- 120 Boukhriss M, Zhani K and Bacha HB, State-of-the-art of various configurations of the membrane distillation unit for distilling seawater. *Int J Emerg Technol Adv Eng* **4**:340–357 (2014).
- 121 Mericq J, Laborie S and Cabassud C, Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination. *Chem Eng J* **166**:596–606 (2011).
- 122 Boonyaraj V, Chiemchaisri C, Chiemchaisri W and Theeparaksapan S, Toxic organic micro-pollutants removal mechanisms in long-term operated membrane bioreactor treating municipal solid waste leachate. *Bioresour Technol* **113**:174–180 (2012).
- 123 Sivakumar M and Ramezani-pour M, Mine water treatment using a vacuum membrane distillation system. *APCBEE Procedia* **5**:157–162 (2013).
- 124 Moradi R, Monfared SM, Amini Y and Dastbaz A, Vacuum enhanced membrane distillation for trace contaminant removal of heavy metals from water by electrospun PVDF/TiO₂ hybrid membranes. *Korean J Chem Eng* **33**:2160–2168 (2016).
- 125 Oitoju TA, Ahmad AL and Ooi BS, Polyvinylidene fluoride (PVDF) membrane for oil rejection from oily wastewater: a performance review. *J Water Process Eng* **14**:41–59 (2016).
- 126 Chiam C and Sarbatly R, Vacuum membrane distillation processes for aqueous solution treatment – a review. *Chem Eng Process Process Intensif* **74**:27–54 (2013).
- 127 Macedonio F, Ali A, Poerio T, El-Sayed E, Drioli E and Abdel-Jawad M, Direct contact membrane distillation for treatment of oilfield produced water. *Sep Purif Technol* **126**:69–81 (2014).
- 128 Mokhtar NM, Lau WJ, Ismail AF and Veerasamy D, Membrane distillation technology for treatment of wastewater from rubber industry in Malaysia. *Procedia CIRP* **26**:792–796 (2015).
- 129 Zuo J, Bonyadi S and Chung T, Exploring the potential of commercial polyethylene membranes for desalination by membrane distillation. *J Membr Sci* **497**:239–247 (2016).
- 130 Wang J, Sun X, Yuan Y, Chen H, Wang H and Hou D, A novel microwave-assisted photo-catalytic membrane distillation process for treating the organic wastewater containing inorganic ions. *J Water Process Eng* **9**:1–8 (2016).
- 131 Ji Z. Treatment of heavy-metal wastewater by vacuum membrane distillation: effect of wastewater properties treatment of heavy-metal wastewater by vacuum membrane distillation: effect of wastewater properties. In: *IOP Conference Series: Earth and Environmental Science Paper*. Bristol: IOP Publishing; 2017. pp. 2–6.
- 132 Asif MB, Hai FI, Kang J, Van De Merwe JP, Leusch FDL, Yamamoto K et al., Degradation of trace organic contaminants by a membrane distillation – enzymatic bioreactor. *Appl Sci* **7**:1–15 (2017).
- 133 Zarebska A, Nieto DR, Christensen KV and Norddahl B, Ammonia recovery from agricultural wastes by membrane distillation: fouling characterization and mechanism. *Water Res* **56**:1–10 (2014).
- 134 Subramani A and Jacangelo JG, Emerging desalination technologies for water treatment: a critical review. *Water Res* **75**:164–187 (2015).
- 135 Kang G and Cao Y, Application and modification of poly(vinylidene fluoride) (PVDF) membranes – a review. *J Membr Sci* **463**:145–165 (2014).
- 136 Hrnčić MK, Cör D, Verboten MT and Knez Ž, Application of supercritical and subcritical fluids in food processing. *Food Qual Saf* **2**:59–67 (2018).
- 137 He Q, Tu T, Yan S, Yang X, Duke M, Zhang Y et al., Relating water vapor transfer to ammonia recovery from biogas slurry by vacuum membrane distillation. *Sep Purif Technol* **191**:182–191 (2018).
- 138 Li Z, Ren X, Zuo J, Liu Y, Duan E, Yang J et al., Struvite precipitation for ammonia nitrogen removal in 7-aminocephalosporanic acid wastewater. *Molecules* **17**:2126–2139 (2012).
- 139 Khayet M, Velázquez A and Mengual JI, Direct contact membrane distillation of humic acid solutions. *J Membr Sci* **240**:123–128 (2004).

- 140 Mohammadi T and Bakhteyari O, Concentration of L-lysine monohydrochloride (L-lysine-HCl) syrup using vacuum membrane distillation. *Desalination* **200**:591–594 (2006).
- 141 Chen TH and Huang YH, Dehydration of diethylene glycol using a vacuum membrane distillation process. *J Taiwan Inst Chem Eng* **74**:233–237 (2017).
- 142 Carnevale MC, Gnisci E, Hilal J and Criscuoli A, Direct contact and vacuum membrane distillation application for the olive mill wastewater treatment. *Sep Purif Technol* **169**:121–127 (2016).
- 143 Tu KL, Nghiem LD and Chivas AR, Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes. *Chem Eng J* **168**:700–706 (2011).
- 144 Hu J, Pu Y, Ueda M, Zhang X and Wang L, Charge-aggregate induced (CAI) reverse osmosis membrane for seawater desalination and boron removal. *J Membr Sci* **520**:1–7 (2016).
- 145 Güler E, Kaya C, Kabay N and Arda M, Boron removal from seawater: state-of-the-art review. *Desalination* **356**:85–93 (2015).
- 146 Criscuoli A, Rossi E, Cofone F and Drioli E, Erratum to boron removal by membrane contactors: the water that purifies water (clean techn environ policy). *Clean Technol Environ Foreign Policy* **12**:63–63 (2010).
- 147 Barancewicz M and Gryta M, Ethanol production in a bioreactor with an integrated membrane distillation module. *Chem Pap* **66**:85–91 (2012).
- 148 García-Payo MC, Izquierdo-Gil MA and Fernández-Pineda C, Air gap membrane distillation of aqueous alcohol solutions. *J Membr Sci* **169**:61–80 (2000).
- 149 Zhu R, Cui S and Wang X, Theoretical foundation of Zisman's empirical equation for wetting of liquids on solid surfaces. *Eur J Phys* **31**:251–256 (2010).
- 150 Rieke PC, Application of Van Oss-Chaudhury-good theory of wettability to interpretation of interfacial free energies of heterogeneous nucleation. *J Cryst Growth* **182**:472–484 (1997).
- 151 Onishchenko DA, Analytical approach to the calculation of the design values of the loads associated with discrete ice features. *Poac'09* **24**:137–145 (2009).
- 152 Spelt JK and Neumann AW, Solid surface tension: the equation of state approach and the theory of surface tension components: theoretical and conceptual considerations. *Langmuir* **3**:588–591 (1987).
- 153 Mahlangu TO, Thwala JM, Mamba BB, D'Haese A and Verliefe ARD, Factors governing combined fouling by organic and colloidal foulants in cross-flow nanofiltration. *J Membr Sci* **491**:53–62 (2015).
- 154 Motsa MM, Mamba BB and Verliefe ARD, Forward osmosis membrane performance during simulated wastewater reclamation: fouling mechanisms and fouling layer properties. *J Water Process Eng* **23**:109–118 (2018).
- 155 Janczuk B, Wojcik W and Zdziennicka A, Determination of the components of the surface tension of some liquids from interfacial liquid–liquid tension measurements. *J Colloid Interface Sci* **157**:384–393 (1993).
- 156 Wang P and Chung TS, Recent advances in membrane distillation processes: membrane development, configuration design and application exploring. *J Membr Sci* **474**:39–56 (2015).
- 157 He F, Gilron J, Lee H, Song L and Sirkar KK, Potential for scaling by sparingly soluble salts in crossflow DCMD. *J Membr Sci* **311**:68–80 (2008).
- 158 Thomas N, Mavukkandy MO, Loutatidou S and Arafat HA, Membrane distillation research & implementation: lessons from the past five decades. *Sep Purif Technol* **189**:108–127 (2017).
- 159 Ali A, Drioli E and Macedonio F, Membrane engineering for sustainable development: a perspective. *Appl Sci* **7**:1026 (2017).
- 160 Khayet M, Solar desalination by membrane distillation: dispersion in energy consumption analysis and water production costs (a review). *Desalination* **308**:89–101 (2013).
- 161 Fane AG, Schofield RW and Fell CJD, The efficient use of energy in membrane distillation. *Desalination* **64**:231–243 (1987).
- 162 Drioli E, Laganh F, Criscuoli A and Barbieri G, Integrated membrane operations in desalination processes. *Desalination* **122**:141–145 (1999).
- 163 Cabassud C and Wirth D, Membrane distillation for water desalination: how to choose an appropriate membrane? *Desalination* **157**:307–314 (2003).
- 164 Bouguecha S, Hamrouni B and Dhahbi M, Small scale desalination pilots powered by renewable energy sources: case studies. *Desalination* **183**:151–165 (2005).
- 165 Meindersma GW, Guijt CM and de Haan AB, Desalination and water recycling by air gap membrane distillation. *Desalination* **187**:291–301 (2006).
- 166 Gazagnes L, Cerneaux S, Persin M, Prouzet E and Larbot A, Desalination of sodium chloride solutions and seawater with hydrophobic ceramic membranes. *Desalination* **217**:260–266 (2007).
- 167 El-Zanati E and El-Khatib KM, Integrated membrane – based desalination system. *Desalination* **205**:15–25 (2007).
- 168 Al-obaidani S, Curcio E, Macedonio F, Di G, Al-hinai H and Drioli E, Potential of membrane distillation in seawater desalination: thermal efficiency, sensitivity study and cost estimation. *J Membr Sci* **323**:85–98 (2008).
- 169 Banat F and Jwaied N, Economic evaluation of desalination by small-scale autonomous solar-powered membrane distillation units. *Desalination* **220**:566–573 (2008).
- 170 Kesieme UK, Milne N, Aral H, Yong C and Duke M, Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation. *Desalination* **323**:66–74 (2013).
- 171 Chang H, Chang C, Hung C, Cheng T and Ho C, Optimization study of small-scale solar membrane distillation desalination systems (s-SMDDS). *Int J Environ Res Public Health* **11**:12064–12087 (2014).
- 172 Pangarkar BL, Deshmukh SK and Guddad MV, Economic assessment of multi-effect membrane distillation (MEMD) for water treatment. *Int J Eng Res Technol* **10**:253–257 (2017).
- 173 van der Bruggen B, Desalination by distillation and by reverse osmosis – trends towards the future. *Membr Technol* **2003**:6–9 (2003).