Desalination, 2020, https://doi.org/10.1016/j.desal.2020.114844

Can emerging membrane-based desalination technologies replace reverse osmosis?

Clara Skuse[1], Alejandro Gallego-Schmid[2,*] Adisa Azapagic[1,*], Patricia Gorgojo[1,*]

[1] Department of Chemical Engineering and Analytical Science, The University of Manchester, M13 9PL, UK

[2] Tyndall Centre for Climate Change Research, School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, M13 9PL, UK

Abstract

Growing uncertainty in the future availability of freshwater sources has led to an increase in installations for desalination of seawater. Reverse osmosis (RO), currently the most widely adopted desalination technique, has caused environmental concerns over the high associated greenhouse gas emissions and generation of large amounts of chemicals-containing brine. Significant consumption of electricity for RO desalination is an additional challenge, particularly in remote locations. In this review, forward osmosis (FO), membrane distillation (MD) and capacitive deionisation (CDI) are assessed as potential substitute technologies and the major recent advancements in each field are discussed. These emerging technologies offer significant advantages over RO, such as higher salt rejection (CDI, MD), higher recovery of water (MD), fewer pre-treatment stages (MD, FO) and the ability to use low-grade energy (MD, FO). In their current state, stand-alone technologies cannot compete with RO until certain challenges are addressed, including pore-wetting (MD) and high energy consumption (MD, CDI, FO). Hybrid systems that combine RO and emerging technologies may be useful for feed waters that cannot be treated by RO alone and their benefits may be able to offset the increase in capital costs. These and other aspects, such as operational stability of hybrid systems, should be considered further in larger-scale, long-term studies.

Keywords: Seawater desalination; Reverse osmosis; Forward osmosis; Membrane distillation; Capacitive deionisation; Hybrid systems

1 Introduction

Only 3% of all global water reserves is available as freshwater. Much of this is in the form of glaciers and ice caps with the remaining 97% being seawater [1]. Factors such as climate change and population growth are expected to affect severely the future availability of water from freshwater sources. For example, the American Geophysical Union predicts that, due to climate change, some glaciers in the Canadian Rockies will disappear altogether by 2100, while others will decrease to 30% (±10%) of their current size relative to 2005 [2]. It is also worth noting that almost two billion people benefit from the Himalayan glacial water; their access to clean water for drinking and agriculture is threatened by the foreseen glacier reduction [3]. Melting glaciers and thermal expansion due to global warming are causing sea levels to rise by 3.3 mm per year [4]. This leads to saltwater intrusion into groundwater drinking supplies, with damaging health consequences on the dependent population. In Bangladesh alone, 20 million people are at high risk of hypertension due to intrusion of untreated saltwater [5,6]. Furthermore, climate change-related droughts are another threat to the availability of freshwater sources [7].

The combination of severe droughts, shrinking glaciers, saltwater intrusion into groundwater and increased water demand has led to predictions of a 40% global water deficit by 2030 [8]. Improvements in the conservation, distribution and management of water are important but additional availability of freshwater is essential in ensuring that the growing demand can be met. Given its abundance, this can be achieved through desalination of seawater, which is becoming one of the key technologies for increasing the availability of clean, drinking water for the global population. Desalination can also help meet the UN's 6th sustainable development goal (SDG6) "to ensure availability and sustainable management of water and sanitation for all" [8]. It also plays a role in other SDGs, including the sustainable use of marine resources (SDG14), promoting sustainable agriculture (SDG2) and development of safe cities (SDG11) [9].

The increase in the desalination market size reflects this growing demand for water. In 2017, the global water desalination market was valued at US $15.43 billion; by 2025, this is expected to increase to US $27 billion. Owing to the relatively high cost of desalination, 67% of plants are located in high-income countries, such as Saudi Arabia (15.5%), USA (11.2%) and UAE (10.1%) [10]. Over the last few decades, there has been a significant market change from thermal- to membrane-based desalination methods, most notably to seawater reverse osmosis (RO). The latter now accounts for 84% of the total number of operating desalination plants, contributing 69% to the desalinated water produced globally [10]. The main driver for this change has been the need to reduce the operating costs associated with high energy consumption of thermal desalination [11].

The specific energy consumption (SEC) for medium to large seawater RO plants has reduced significantly over the last few decades and is currently between 2.5 and 7 kWh/m^3 [12–14]. However, RO requires high-grade energy (electricity), meaning that even low SEC values lead to high energy destruction [15]. Despite the reduced SEC, RO desalination still has high greenhouse gas (GHG) emissions related to the energy use [16], which range from 0.835 to 6.1 kg CO_2 eq. per m^3 of potable water [13,14,17–25]. This is due to the vast majority of desalination plants still relying on energy from fossil fuels. For example, the Middle East, the largest producer of water from seawater desalination, produced only 0.7% of the total water using renewable energy [26].

The global production of 141.5 million m^3/day of brine is another environmental concern [10]. Marine ecosystems with sandy seafloors, high wave action and those already impacted by human activity may not be affected greatly by the release of RO brine [27,28]. However, areas with low ocean currents and sensitive marine life are at high risk. Changes in the salinity of seawater can affect the development and growth rate of larvae and the saline brine reduces the amount of dissolved oxygen in seawater, which can cause hypoxia in marine organisms [29,30]. Chemicals within the brine, such as iron chloride, sodium hypochlorite and sodium bisulphite [31], can also have lethal toxic effects on marine life through acidification and anoxia [32]. The brine itself also contains valuable resources, including magnesium sulphate, calcium carbonate and lithium, which cannot be recovered using current RO technology [31].

Emerging technologies, such as forward osmosis (FO), membrane distillation (MD) and membrane capacitive deionisation (MCDI) are being explored to reduce the energy consumption, fouling and brine issues associated with desalination; successful breakthroughs in their development have led to a rapidly growing research interest [10]. This review aims to inform about the ongoing questions regarding the use of RO and the above-mentioned emerging technologies for seawater desalination. While many of the latter are suitable for brackish water, brine and wastewater treatment, the focus here is on their suitability for seawater desalination. The emphasis is placed on seawater due to its sheer abundance, making it potentially a far more reliable source of water than the diminishing freshwater reserves. The review starts with RO in the next section, covering the process description, current limitations and recent advances. This is followed in section 3 by a review of FO, MD and MCDI, discussing their concepts, advantages over RO, as well as their limitations and state-of-the-art developments. This section also considers if these emerging technologies have the potential to replace RO. Finally, the integration of multiple technologies to form hybrid systems is discussed in section 4, followed by the conclusions and recommendations for further research in section 5.

2 Reverse osmosis

2.1 Process description

The purpose of RO is to remove all colloidal matter and dissolved solids larger than 0.1-1.0 nm in size from a liquid solution [33,34]. The overall desalination process consists of three major stages: pre-treatment, RO operation and post-treatment (Figure 1). Conventional pre-treatment consists of seawater conditioning by coagulation and flocculation (using ferric chloride), granular media filtration to remove coarse solids (algae) and cartridge filters to remove smaller solid particles (fine sand) [35]. The order of the process steps can differ among installations and may include additional units, such as UV radiation, ozonation, chlorination, dechlorination and lime treatment [36].

New plants tend to use membrane filtration pre-treatment methods which have significant benefits compared to the conventional pre-treatment, including lower chemical requirements and higher removal of smaller suspended solids. These pre-treatment systems involve passing the water through a series of filters (Figure 1), starting with coarse strainers with pore sizes >5 µm. The next in series, microfiltration (MF), has pore sizes between 0.1-5 µm and, lastly, ultrafiltration (UF) has pore sizes between 10 and 100 nm [36]. Inline addition of sodium bisulphite, sulphuric acid and antiscalants (such as polyacrylates) is necessary in both conventional and membrane pre-treatment systems.

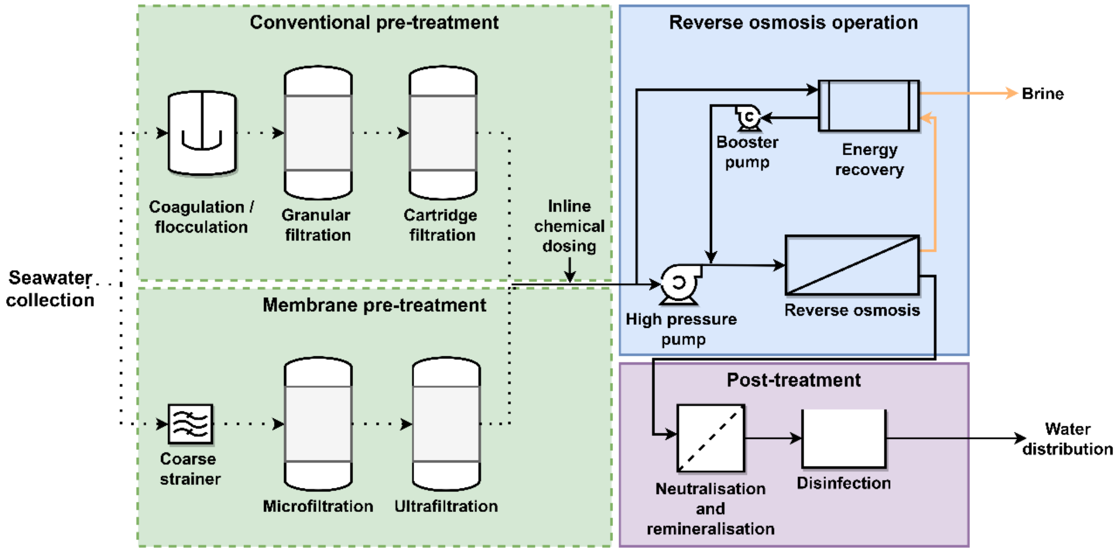

Figure 1. The reverse osmosis process utilising either conventional or membrane pre-treatment, as indicated by the dotted lines (adapted from Voutchkov [35]).

The pre-treated seawater then flows through the feed channel at high pressure (55-70 bar [37,38]) where the water passes through the pores of the semi-permeable membrane contained in a membrane module (Figure 2). The construction materials must have a high pressure tolerance and be corrosion resistant; typically, stainless steels that contain chromium, nickel and molybdenum are used [39]. The water then follows the spiral pathway (in a typical spiral-wound configuration) before being collected in the permeate-collection tube. The impurities are unable to pass and the initial solution concentrates at the point where the applied pressure is not significant enough to overcome the osmotic pressure [40]. This typically leads to brine that is 50% more concentrated than the original feed. Further concentration is not possible without significantly increasing the hydraulic pressure. The brine is passed through an energy-recovery device, typically a pressure exchanger, which transfers up to 97% of the pressure from the brine stream to approximately 65% of the incoming RO feed. Using energy-recovery devices in RO can reduce the energy consumption by as much as 60%, relative to systems without energy recovery [41]. A booster pump ensures that the pressure of the stream leaving the energy-recovery device is equal to the pressure of the feed leaving the high-pressure pump. Isobaric pressure exchangers are used almost exclusively in small- to large-scale RO plants because they achieve far higher conversion efficiencies than centrifugal or Francis turbines. However, only very small-scale RO plants (<3 m^3/d) achieve cost savings by using these energy-recovery devices [42].

Finally, the RO post-treatment typically contains a minerals-enrichment unit whereby ions, such as magnesium and calcium, are added to the permeate water. Lastly, a disinfection unit adds chlorine to the water to suppress the growth of microorganisms during water distribution [35]. The brine (containing the pre-treatment chemicals) and membrane-cleaning agents are mixed and released as an effluent back into the ocean. Recovery of chemicals is economically unfavourable as the ratio of brine to chemicals is so large, and some argue the chemicals are neutralised and diluted sufficiently to avoid harm to marine life [43]. More information on this can be found in section 2.2.3.

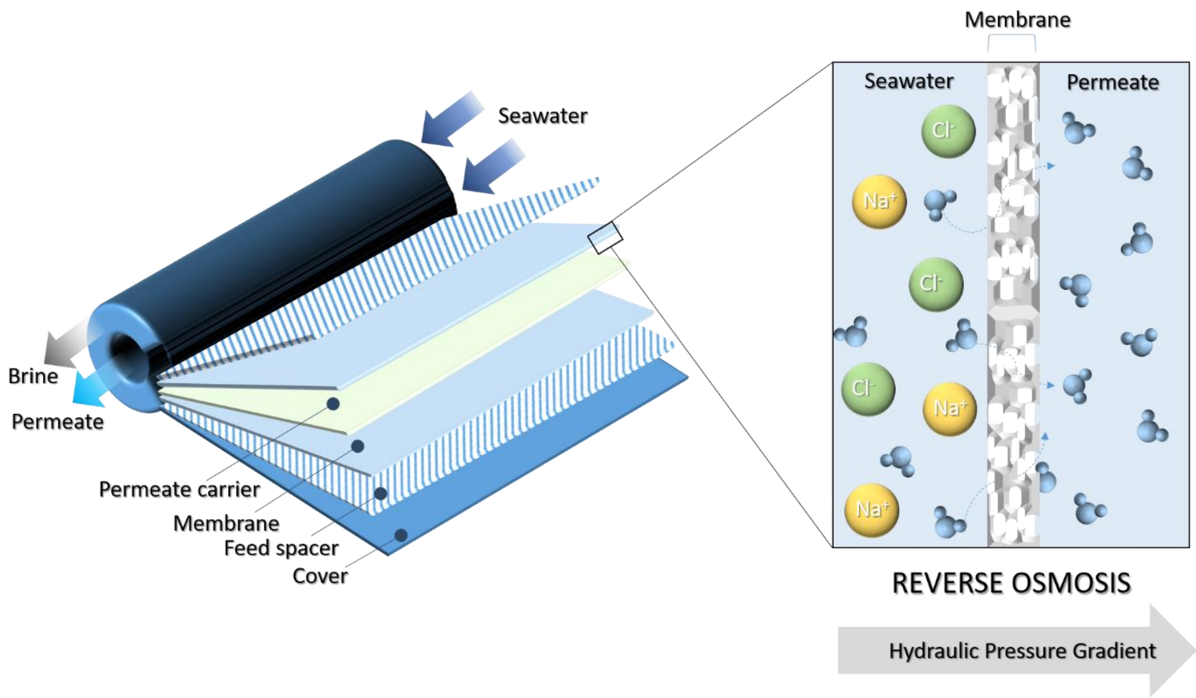

Figure 2. Spiral wound membrane and driving force principles (inset) of reverse osmosis.

2.2 Limitations and recent advances

RO offers significant advantages over previous desalination technologies, including lower energy consumption, lower operating costs and smaller internals, resulting in more compact equipment. It is providing reliably clean, potable water for millions of people whose lives depend on it. However, it is a very energy-demanding process, leading to high GHG emissions [16]. The use of electrical energy also means that RO is inaccessible or too expensive in many regions with high water demand. Other key limitations include membrane fouling and limited water recovery, leading to large amounts of waste brine. These limitations are discussed in turn below, together with recent developments aimed at addressing some of these limitations.

2.2.1 Fouling

Solute build-up at the surface of the membrane, known as concentration polarisation, reduces the pressure gradient across the membrane, reducing the flux and increasing fouling and scaling [44,45]. Fouling is the deposition of organics, inorganics or biological material on the membrane, and scaling is the precipitation of inorganic material onto the membrane surface [46]. Biofouling is controlled by the addition of chlorine during pre-treatment, which mitigates the growth of microorganisms. The residual chlorine is removed by adding sodium bisulphite to prevent chemical oxidation fouling, and scaling is minimised by using polycarboxylate [21]. Even with the addition of these chemicals to the feed water, the membranes must be cleaned routinely, typically using sodium hypochlorite. Furthermore, exposure to chlorine reduces the lifespan of the membranes significantly [47]. Consequently, fouling and scaling are generally regarded as one of the major challenges associated with RO operation [46].

Microplastics, increasingly found in the oceans [48], act as membrane foulants during RO and UF pre-treatment if the particle size is above 100 nm [49]. Smaller-size microplastics (<100 nm) penetrate the membrane and contaminate the drinking water [50]. Microplastics can contain unreacted monomers, many of which are known to be mutagenic and/or carcinogenic [51]. Potential risks to human health include damage to DNA from exposure to the harmful materials, as well as the formation of lesions and inflammations [49]. As the microplastics pollution and our understanding of its impact on marine life and human health increase [52], so will the need for alternative desalination methods capable of removing microplastics from water.

It is worth noting that, while reducing fouling would extend the lifetime of RO membranes, the environmental impacts related to the manufacturing, transportation and incineration of membranes are insignificant relative to the impacts from the RO process associated with electricity consumption and brine production [53]. Nevertheless, RO membranes can be recycled to produce ultra/nanofiltration membranes, further reducing their environmental impacts [54,55].

2.2.2 Electricity consumption

Approximately 71% of the total desalination electricity is consumed by the RO process, 11% by pre-treatment and the rest is used for seawater collection, distribution and ancillary facilities [12]. The electricity consumption for RO operation has decreased significantly in the past decade owing to process improvements [56,57]. However, in an attempt to reduce the impacts of the chemically-intensive conventional pre-treatment stages, the industry is moving towards using MF/UF, which have a higher energy consumption [58]. The elimination of pre-treatment would reduce the electricity consumption and, thus, overall environmental impacts of desalination. This could be achieved by the development of fouling-resistant membranes, or by developing new, energy-efficient desalination technologies with a lower susceptibility for fouling [53]. Other operational changes can also lead to a reduction in electricity consumption. A study by Al-Kaabi et al. [13] found that by changing the seawater intake from open to subsurface would reduce the annual GHG emissions by 58,000 t CO_2 eq. in plant producing 275,000 m^3/day. This is due to the lower turbidity of subsurface water, resulting in higher-quality feed water with fewer solids [13,59], which would in turn reduce pre-treatment requirements. This finding is in agreement with the work by Shahabi et al. [60], who found that subsurface intake reduced the environmental impacts by 31%. Further options for reducing electricity consumption include incorporating new energy-recovery devices, high-efficiency high-pressure pumps and low-pressure multistage RO systems [61].

A growing number of studies show that using renewable electricity for RO can reduce the associated GHG emissions [13,18,19,21,24,53] without a significant impact on the total cost of water production [62,63]. For example, wind-powered RO has achieved low fresh-water production costs (<1 $/m^3$) for pilot-scale systems; however, the specific electricity consumption is still high (>2 kWh/m^3), as booster pumps and additional baseload electricity is required [64,65]. The latter is a particular issue for wind and solar-based technologies due to the intermittency of supply, which can lead to frequent shut-downs. This in turn increases fouling due to the foulants drying on the membrane during the stoppage times, although this could be minimised by appropriate rinsing and shut-down procedures [66].

To ensure continuous operation of the plant, complex forecasting algorithms are required to adjust the power load based on short-term variability [67] as well as additional power supply from the grid [68] or from an onsite diesel generator [69]. To operate a stand-alone RO system with no grid back-up, a variable power-load design is recommended [70]. These configurations are more versatile and able to operate depending on the amount of energy available.

Using batteries for electricity storage can help overcome the intermittency issues but this increases the operating costs [71] as well as environmental and social impacts, such as depletion of metals and generation of hazardous waste [72]. The full life cycle environmental impacts and end-of-life options for batteries need to be understood better to determine whether they are an appropriate alternative for RO plants [73].

A study by Leijon et al. [74] investigated wave energy as a method to ensure continuous RO operation. The authors found that wave power had the potential to increase and stabilise power and freshwater production while preventing excess power generation, especially when a hybrid system of wave power and solar photovoltaic (PV) was used. Hybrid fuel cell-solar PV systems could also overcome intermittency and energy storage issues. A recent study by Rezk et al. [75] compared this hybrid with a diesel generation system for a simulated brackish-water RO plant of 150 m^3/d. The simulation predicted that the hybrid system could produce water at a 76% lower energy cost while avoiding over 70,974 kg/y of CO_2 emissions. Hybrid renewable systems and their cost should be explored further in real RO plants to determine their stability.

Supplying 100% of the energy from renewables can be difficult to achieve in practice, unless the plant is located where the national grid supply is fully based on renewable energy [67]. There are currently only ten countries which generate over 95% of their electricity from renewable sources and these are all in countries where hydropower contributes the majority share [76]. This suggests that they already have freshwater in abundance and do not required desalination to meet their water needs. On the other hand, areas that lack natural freshwater sources and where desalination is critically needed, cannot rely on hydropower but on solar and wind energy. As they lead to the above-mentioned intermittency and operational issues, it is currently unrealistic to expect a grid with 100% renewables in areas with a high desalination water demand.

Heihsel et al. [77] simulated the optimisation of a 100% renewable energy grid for seawater desalination in Australia. The study suggested that this can be achieved using a GIS-based load-shifting model over a large area. The proposed system operates 29 RO plants with flexible capacity that changes based on the water demand and the available renewable energy in the area. This configuration should be investigated further to determine its social and economic feasibility, especially considering the vast pipeline network (35 pipelines with 2.1 m diameter) and the scale of the proposed system (5.5 billion m^3 of water per year).

Improving the water permeability of RO membranes may intuitively suggest that the water flux would be higher, resulting in a lower energy usage. Thus, to enhance the permeability of water, RO membranes have been developed using novel nanomaterials, such as graphene and carbon nanotubes (CNTs), as well as aquaporin-based biomimetic membranes (ABM) [78–83]. However, for RO and forward osmosis (FO), a study by Werber [84] found that the advances in permeability through the use of nanomaterials have a relatively small effect on the process efficiency. These findings are supported by Elimelech [85] and Okamoto [86] who reported that the SEC is largely unaffected by increased permeability as RO is already approaching the minimum theoretical energy for separation, which is a thermodynamic limitation. A simulation study by Mazlan et al. [87] also came to this conclusion, finding that there is an optimal permeance for RO membranes near the thermodynamic limit (10 L/m^2 h bar). Going beyond this value can be unfavourable, as increased permeate flux can increase the effects of concentration polarisation. This in turn reduces the permeance due to an increase in the osmotic pressure, and so the overall effect of increasing membrane permeance is insignificant. Increasing the permeance in this way may also exacerbate the fouling rate.

Instead, the anti-fouling and highly selective properties of nanomaterials and ABM membranes should be explored. Qi et al. [88] used real seawater feed over a 100-day RO operation and found that the ABM membrane could achieve the same water flux as a commercial membrane but at half of the pressure. The study revealed issues related to fouling, but periodic cleaning of the membrane resulted in a 90% recovery of water permeability with chemical stability over a range of pH values (3-10). Thin-film nanocomposite (TFN) membranes with graphene oxide nanosheets can reduce fouling through anti-adhesive and anti-bacterial properties [89]. However, the large-scale manufacturing, costing and long-term stability of these novel membranes need to be understood better before wide-scale commercialisation is possible [90].

2.2.3 Waste brine

Elimination of RO brine is one of the key challenges in preventing water contamination from desalination. The water recovery in most seawater RO plants is limited to between 30 and 50% of the feed water; beyond this range, the required energy for separation increases exponentially [91]. This dependency between water recovery and energy means that zero liquid discharge systems, which recover 100% of pure water, are hard to achieve with RO alone and thus waste brine is produced.

A study by Jones et al. [10] in 2019 estimated that the actual global brine production was about 50% higher than previous estimates. This means that the water recovery of RO plants sits at the lower range of the above-mentioned 30-50% recovery. Thus, RO plants produce around 2 m^3 of concentrated brine for every 1 m^3 of treated water. Globally, over 90% of seawater plants discharge brine directly into open water bodies [92,93]. However, there is increased public awareness and a growing number of studies demonstrating the adverse impacts of brine on marine life due to increased salinity [94–96]. These studies have led to further restrictions on the disposal and treatment of brine, which is expected to motivate development of alternative methods [97]. The brine also contains dissolved chemical products from pre-treatment, including iron chloride, sodium hypochlorite and sodium bisulphite [31]. Even at low concentrations, these chemicals impact the marine environment [94] and their reduction or replacement would improve the environmental performance of RO plants [18]. Recommendations for responsible management of the brine impacts include modelling the brine plume to understand the diffusion rates, longer term monitoring of population and distribution of nearby marine ecosystems and frequent water sampling checks in the brine discharge area [28]. While these are important, generally, direct disposal should only be used as a last resort [98]. Instead, brine treatment methods that minimise the environmental impacts and treat the brine to recover minerals should be prioritised. Current treatment methods include wind-aided intensified evaporation, brine evaporative cooler/concentrators, brine crystallizers and hybrid RO-multiple-effect distillation/RO-MD systems [98,99]. However, it should be noted that these brine treatment methods require additional energy and capital costs [100].

3 Emerging membrane desalination techniques

This section discusses the principles, limitations and recent advances in FO, MD and MCDI, followed by a comparison of these emerging technologies with RO.

3.1 Forward osmosis

3.1.1 Process description

Forward osmosis is a new membrane desalination technology that uses the osmotic pressure difference between seawater and a highly concentrated draw solution (DS). As shown in Figure 3, driven by the osmotic pressure gradient, water moves from the seawater across a semi-permeable membrane into the DS, while the salts and other dissolved solids cannot pass through the membrane and are retained on their respective sides. Currently, only asymmetric membranes (containing a thin 'active' layer and a thicker support layer) are used to retain the solutes [101]. Once the DS is diluted with the fresh water, it is sent to the recovery process where the DS is reconcentrated. The recovered water is then collected for distribution, while the regenerated DS is sent back to the FO module.

The choice of DS is critical; it needs to have a high osmotic pressure, be easily separated from water, non-toxic and cheap [102]. There are not many DSs that fulfil these criteria. Ammonia-based solutions have been used since the early 2000s as the DS can be recovered by moderate heating (60 °C) [103]. Nevertheless, challenges with ensuring the complete removal of ammonia have led to investigations into other DS. Kim et al. [104] used ammonium bicarbonate as the DS in a pilot-scale FO seawater desalination plant which required 265–300 kWh/m^3 of thermal energy; heat recovery was not included in the system. The plant achieved up to 21% water recovery; however, the water contained 17–29 mg/L of ammonium ions. This is below the taste threshold concentration of ammonia in water (35 mg/L) but above the odour threshold (1.5 mg/l) as recognised by the World Health Organisation (WHO) [105].

Many organic and inorganic DS require RO/ultra/nanofiltration during the regeneration process, but this is energetically unfavourable [106]. To address this issue, research is moving towards materials that can be regenerated using solar energy, waste heat and magnetic separators [107], as covered in Section 3.1.3.

Like RO, FO membranes suffer from concentration polarisation (a build-up of material at the surface of the membrane). Because of the spontaneous nature of FO and the asymmetry of the membranes, solutes can also build up at the boundary layer within the membrane. This is named internal concentration polarisation (ICP) which is distinguished from regular or external concentration polarisation (ECP) as indicated in Figure 3. ICP reduces the actual osmotic pressure difference and thus dramatically reduces the driving force. ECP is minimised in FO (and RO) systems by increasing the cross-flow velocity across the membrane surface. ICP cannot be alleviated by process conditions; rather, it can be minimised by using thin membranes with low tortuosity. Recent advancements in FO membranes focus on improving these conditions, as covered in more detail in the next section.

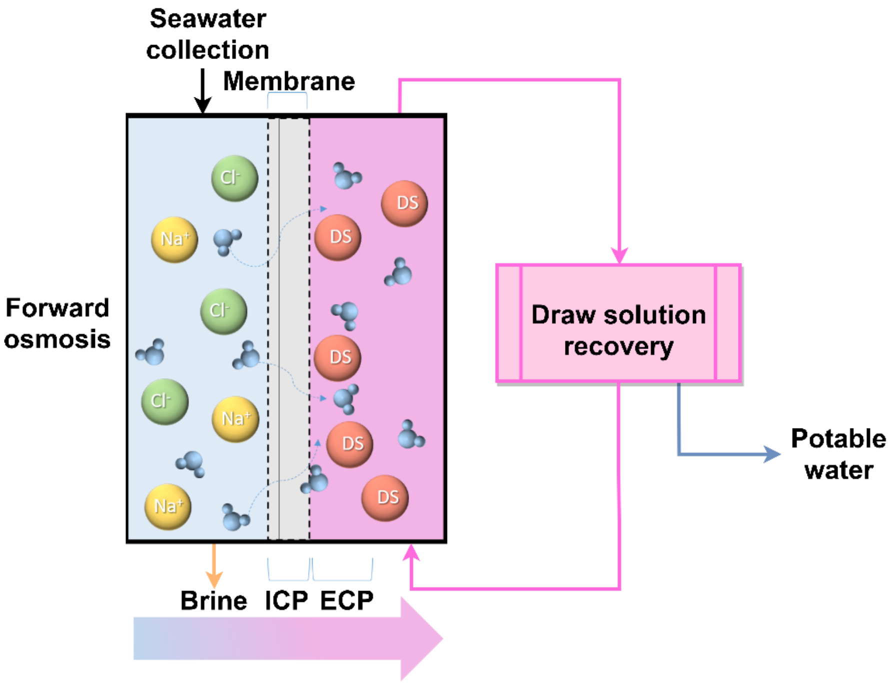

Figure 3. A schematic of forward osmosis indicating areas where internal concentration polarisation (ICP) and external concentration polarisation (ECP) take place. (Adapted from McGinnis and Elimelech [103]*).*

3.1.2 Advantages over reverse osmosis

Due to the absence of pressure, the fouling layer on the FO membrane is compacted loosely and can be removed easily using mechanical cleaning methods rather than chemical treatment [108]. As the FO process occurs spontaneously, hydraulic pressure or high temperatures are not required. This is a key FO advantage, as the actual desalination stage only requires a small amount of energy (0.84 kWh/m^3 [103]). However, the energy consumption is pushed further downstream, to the DS recovery stage. Depending on the type, DS can be recovered using either low-grade energy (such as heat) or even by low energy magnetic separators, as discussed below.

3.1.3 Limitations and recent advances

One of the most substantial FO limitations is the energy consumed during the recovery of the DS [106,109]. A study by McGovern et al. [110] compared FO with RO based on theoretical energy requirements. They found that even with an optimal DS recovery, the overall desalination energy would not be significantly lower than for RO, despite the much lower energy requirements for the desalination step. These findings are in agreement with Awad et al. [111], who investigated 15 pilot FO studies and found that a 40-50% decrease in energy consumption for recovering the DS is required before it can compete with RO. A way to minimise the energy consumption of DS regeneration is to use a solution that does not need to be recovered, effectively eliminating the recovery process [112]. However, this would lead to generation of additional waste through discarded DS. Other approaches include investigating new materials, such as magnetic nanoparticles (MNPs) and ionic liquids (ILs).

MNPs have shown key benefits over previous DSs: they can generate very high osmotic pressures and can be recovered using low energy magnetic separators [106]. Previous studies had indicated that MNPs cannot operate under high enough flux to be commercially viable [113]. More recent studies suggest this is being overcome but long-term stability is still an issue. Tayel et al. [114] investigated magnetic Fe_3O_4 and pectin-coated magnetic Fe_3O_4 as a DS for a range of saline solutions. A maximum flux of 35.7 L/m^2 h was achieved with uncoated Fe_3O_4 and deionised water as the feed solution, but this value fell by 76% with a 1 g/L NaCl feed solution. Coating the MNPs with pectin reduced the flux decline, such that a water flux of 2.6 $L/m^2 h$ was obtained with a 55 g/L solution of NaCl. Organic coatings for MNPs were also investigated in a recent study by Guizani et al. [115], which coated Fe_3O_4 with polyethylene glycol (PEG). They obtained unstable results, with lower molecular-weight PEG showing a flux of 0.33 $L/m^2 h$ and higher molecular-weight PEG achieving 2.52-14.95 $L/m^2 h$. The study suggests that higher flux values may be achieved early on in the experiment but then membrane clogging could have occurred. To test their potential, large-scale manufacturing methods for the MNPs need to be developed [116].

Thermally-responsive ionic liquids (IL) are also being investigated as a DS for FO desalination because they can be recovered using solar energy or waste heat [106]. Recent studies [117,118] investigating ILs have shown improvements in flux and osmotic pressure, but incomplete recovery of the DS means that further separation (RO, MD) is needed. Deep eutectic solvents are a new category of ILs that have low toxicity and high atom-efficiency synthesis, but they need to be regenerated using low-pressure RO or NF [119,120]. A recent study by Bide et al. [119] decorated MNPs with a polymeric deep eutectic solvent in order to combine the positives of both ILs and MNPs. The resulting DS had a high osmotic pressure (68 atm), was easily regenerated using a magnetic separator, had low toxicity, used inexpensive precursors and achieved a stable flux of 8.5 $L/m^2 h$ when tested with a ∼17.5 g/L saline solution. Future research should determine whether these new combined ILs-MNPs can achieve such promising results when dealing with seawater.

To minimise ICP, FO membranes must be thin, with low tortuosity to promote high water permeability [116,121]. Improvements in FO membranes to achieve these characteristics are being conducted through the use of nanomaterials, such as zeolites, CNTs, graphene and aquaporin [116,122]. A study by Ma et al. [123] introduced 0.1 w/v% zeolite into thin-film nanocomposite (TFC) membranes for FO applications. This reduced the ICP effect and resulted in up to 76% higher fluxes against the TFC control membrane. A more recent study by Lim et al. [124] incorporated GO nanosheets into dual-layered TFC FO membranes and achieved higher fluxes (30.3-33.8 $L/m^2 h$) against the commercial cellulose tri-acetate control (8.8 $L/m^2 h$).

Overall, significant advances in the design of the membranes and DS are necessary before FO can compete with RO and be commercialised as a stand-alone technology.

3.2 Membrane distillation

3.2.1 Process description

MD is driven by an induced temperature difference between the hot seawater and the cold permeate water. As such, the seawater is heated to 30-80 ℃ before being passed to the MD module and the permeate is cooled using the cold incoming seawater (< 20 ℃), as shown in Figure 4. The higher operating temperatures promote scaling on the membrane surface and thus an antiscalant is added to the stream prior to heating. Pre-treatment techniques (beyond the addition of an antiscalant) are being investigated, although sources estimate that MD would require less chemically and energy intensive methods than RO [21,125].

Depending on the MD configuration, the permeate can be diluted and directly cooled using the coolant stream (direct contact (DCMD)) or indirectly cooled by a condenser plate which separates the permeate stream from the coolant stream (air gap (AGMD), or liquid/permeate gap (L/PGMD)) [125]. Other MD configurations include vacuum and sweep gas. AGMD and L/PGMD configurations achieve high thermal efficiencies and are more popular in commercial applications (see Table 1). The membrane itself is micro-porous (100 nm-1 μm pore size) and hydrophobic, creating a gas-liquid interface at the surface of the membrane due to surface-tension forces [125,126]. Water evaporates and moves through the pores via diffusion and convection to the low-vapour pressure side where the vapour is condensed. The hydrophobicity of the membrane ensures that the water cannot penetrate the membrane unless it is in vapour form. The non-volatile salts in seawater (such as NaCl and $MgSO_4$) cannot pass through the membrane and high rejection of salts can be achieved (99-100%) [125]. Commercially available membranes for MD systems are generally made from either polypropylene, polytetrafluoroethylene, polyvinylidene fluoride or polyethylene because of the hydrophobic nature and mechanical durability of these materials [127]. There is little information on the required post-treatment processes; however, remineralisation and sterilisation can be expected.

3.2.2 Advantages over reverse osmosis

MD is currently being investigated at lab- and pilot-scales as either an alternative to RO and thermal-based desalination techniques or a complementary technology. The recent rise in interest can be attributed to the advancement of membrane-module configurations which have led to improvements in the flux, pore wetting resistance, energy efficiency and overall cost of the process [125,126,128,129].

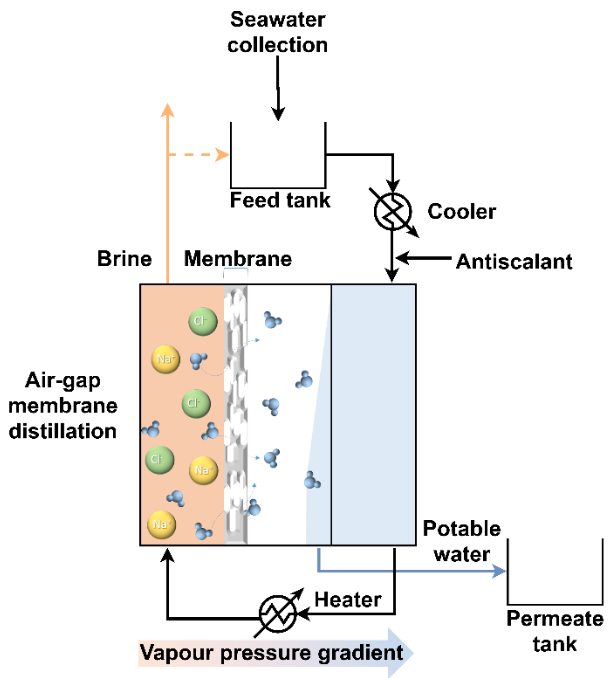

Figure 4. A schematic of the membrane distillation process with an air-gap configuration

In RO, separation occurs due to size exclusion; thus, the size of the membrane pores must be between 0.1 and 1 nm to prevent the passage of the dissolved solids. As MD is not governed by size exclusion, the pore sizes can be up to two orders of magnitude higher (0.1-1 μm) [130]. With larger pores, the MD process is able to mitigate some of the fouling problems which are prevalent in RO, including a lower sensitivity to concentration polarisation [130]. MD operates at atmospheric pressure, resulting in less demanding mechanical properties of the membrane and reduced fouling [131]. Unlike RO, the driving force for MD does not dependent significantly on the concentration of the feed solution. Therefore, MD can treat highly concentrated saline solutions and has the potential for far greater recovery of water, with figures of up to 90% reported in the literature [125].

Table 1. Performance characteristics of pilot/small scale membrane distillation plants developed over the past decade

Reference	**Year**	**Running period**	**Module type[a]**	**Manufacturer**	**Material[b]**	**Membrane area, m^2**	**Feed water type, amount**	**Water flux, $L/m^2\,h$**	**Distillate quality, μS/cm**	**Feed flowrate, L/h**	**Recovery ratio, %**	**Feed temp., °C**	**STEC [c], kWh/m^3**	**GOR [d]**
Raluy [132]	2009	1 year	PGMD spiral wound	-	PTFE	10	Seawater, 43.6 ± 9.9 g/L	0.32±0.1[e]	20-200	100±22	18±14	60-80	140-350	3.4 ± 0.5
Schwantes [133]	2010	-	PGMD	Mediras	PTFE	120	Seawater brine, 47-49 g/kg	1.28 [e]	29	4800	3.20 [e]	65-80	300	2.4
Schwantes [133]	2010	-	PGMD	Cuve-Waters	PTFE	168	Ground water, 28,000 ppm	0.516 [e]	850	4800	1.81[e]	65-80	171	4.4
Schwantes [133]	2011	-	AGMD	Mediras	PTFE	120	Seawater, 35 g/L	0.486 [e]	78	4800	1.22 [e]	80	271	3.1
Winter [134]	2011	1.5 h	PGMD spiral wound	Fraunhofer ISE	PTFE	5-14	Salt solution, 0-105 g/L	0.714-5 [e]	<3.5	200-500	2-12.5	80	130-207	-
Guillén-Burrieza [135]	2011	4 months	AGMD, flat sheet	Scarab	PTFE	2.8	Salt solution, 35 g/L	~5	40-60	1200	1.8	80	2100	-
Winter [136]	2012	-	PGMD	Fraunhofer ISE	PTFE	10	Salt solution, 35 g/L	2.99-3.77 [e]	-	200-500	-	80	91	5.3-7.2
Lee Ong [137]	2012	-	V-MEMD	IBM Research	PTFE	15.2	Salt solution, 35 g/L	4.28-4.87	<15 ppm	180	36.1-45.6	39.8-46.3	-	3.4-3.82
Zhao [138]	2013	-	V-MEMD, flat sheet	Memsys	PTFE	1.88-5	Seawater	3-8.7	8-10	90	20-40	45-60	-	1.52-2.70
Wang [139]	2014	5 months	VMD, hollow fibre		PP	2.16	Salt solution, 35 g/L	4-14.4	< 30	1000-1260	<5	55-75	750	-
Zaragoza [140]	2014	Several months	AGMD, flat sheet	Scarab	PTFE	2.8	Salt solution, 35 g/L	5.5	40-60	1200	1	65	930	-
		Several months	LGMD, flat sheet	Keppel Seghers	-	9	Salt solution, 35 g/L	3.1	2-5	1560	2	50	2150	-
		Several months	LGMD, flat sheet (3 in series)	Keppel Seghers	-	9	Salt solution, 35 g/L	5	>5	1020	4	50	440	-
		Several months	LGMD, spiral wound	Solar Spring	PTFE	10	Salt solution, 35 g/L	3.2	2-5	600	5	55	295	-
Nakoa [141]	2014	-	DCMD	Membrane Solution	PTFE	0.11	Brackish water, 13 g/L	2-6	-	240-600	-	30-45	1667-3611 [e]	0.1
Ruiz-Aguirre [142]	2014	-	LGMD, spiral wound	Solar Spring	PTFE	10	Salt solution, 35 g/L	0.84-3.18	50-200	400-600	1.3-5.1	16.3-56.4	-	2.26-2.76

Reference	Year	Running period	Module type[a]	Manufacturer	Material[b]	Membrane area, m^2	Feed water type, amount	Water flux, L/m^2 h	Distillate quality, μS/cm	Feed flowrate, L/h	Recovery ratio, %	Feed temp., °C	STEC [c], kWh/m^3	GOR [d]
		-	AGMD, spiral wound	Aquastill	PE	24	Salt solution, 35 g/L	0.75-1	50-200	550	2.8-4.7	38-52	-	4.2-6.6
Duong [143]	2016	9 h	AGMD, spiral wound	Aquastill	LDPE	7.2	Seawater and salt solution, 35 g/L	1	<100	150	5	70	90-95	6-7
Mohamed [144]	2017	6 months	V-MEMD	Memsys	PTFE	6.4	Salt solution, 30 mS/cm	2.58-7.71	-	40-120	7.7-76.4	50-85	300-700	1-2.2
Ruiz-Aguirre [145]	2017	1 h	PGMD, spiral wound	Solar Spring	PTFE	10	Salt solution, 35 g/L	1-3	2-50	400-600	2-6	60-80	180-325	3.5-2
		1 h	AGMD, spiral wound	Aquastill	PE	7.2	Salt solution, 35 g/L	1.5-4	8-700	400-600	2-6	60-80	250-425	>1.5
		1 h	AGMD, spiral wound	Aquastill	PE	24	Salt solution, 35 g/L	0.6-2	100-200	400-600	2-6	60-80	100-150	6.5-4.3
Boukhriss [146]	2018	-	AGMD	-	PTFE	10	Brackish water, 4.2-12.5 g/L	0.5- 7.4	<20	288	1.74-25.7 [a]	25-80	-	-
Andrés-Mañas [147]	2018	4 months	V-MEMD	Memsys	PTFE	6.4	Seawater, 37-40 mS/cm	8.5	50, <5	150	36	75	200	3.19
Zarzoum [148]	2019	10 months	DCMD	-	-	10	-	0.4375	-	-	-	60-80	-	-
Najib [149]	2019	4 h	DCMD, spiral wound	SolarSpring	-	10	Salt solution, 35 g/L	1.74 [e]	368 ppm	50-300	1.1-6.6	80	200-500	0.37-2.73
Lee [150]	2020	50 days	AGMD, spiral wound	Aquastill	PE	156 [a]	Seawater, 35.84 g/L	1.13-1.26	<200	4447-4893	-	75-80	199-232	0.59-0.68
Andrés-Mañas [128]	2020	-	V-AGMD, spiral wound	Aquastill	LDPE	7.2	Salt solution, 35.1 g/L	3.7-8.7	Salt rejection 98.965%	400-1100	-	80	~261	4.6-2.5
		-	AGMD, spiral wound	Aquastill	LDPE	7.2	Salt solution, 35.1 g/L	2.8-6.2	Salt rejection of 99.89%	400-1100	-	80	~458	2.7-1.4
		-	V-AGMD, spiral wound	Aquastill	LDPE	25.9	Salt solution, 35.1 g/L	1.1-2.9	Salt rejection of 98.55%	400-1100	-	80	49	13.5-8.5
		-	AGMD, spiral wound	Aquastill	LDPE	25.9	Salt solution, 35.1 g/L	0.8-2.0	Salt rejection of 99.69%	400-1100	-	80	~152	6.6-4.7

[a] AGMD: air-gap membrane distillation. DCMD: direct contact membrane distillation. LGMD: liquid-gap membrane distillation. PGMD: permeate-gap membrane distillation. V-AGMD: vacuum-enhanced air-gap membrane distillation V-MEMD: vacuum-multi effect membrane distillation. VMD: vacuum membrane distillation.

[b] LDPE: low-density polyethylene. PE: polyethylene. PP: polypropylene. PTFE: polytetrafluoroethylene.

[c] STEC: specific thermal energy consumption.

[d] GOR: gained output ratio.

[e] Value calculated from available data.

Given that MD operates at atmospheric pressure and reasonable temperatures (30-80 ℃), the physical demand on the construction materials is lower. This is likely to reduce significantly the initial capital and maintenance costs [125]. The overall expected cost of drinking water produced by a large-scale MD plant is estimated to be between 0.5 and 1.17 $/m^3 [125,151]. For comparison, medium-to-large scale RO plants have an overall cost of water production of 0.5-3 $/m^3 [12]. A membrane distillation unit also has the potential to be more compact than RO, as it can use lightweight process equipment with fewer process stages [152]. Furthermore, the reduction in membrane pollution mitigates the need for extensive pre-treatment processes or chemical additives [125]. For example, biodegradable antiscalants with lower environmental impacts (e.g. Carboxyline®) have shown to be effective in MD systems [147,153]. Also, less chemically aggressive clean-in-place fluids can be used, such as citric acid, deionised water and sodium hydroxide [154,155]. As the clean-in-place chemicals are used only every few months, the quantities are lower than in RO [21].

One of the significant advantages of MD is that it can be driven by low-grade heat rather than relying on electricity like RO. Many industrial processes generate waste heat that is not used and released into the environment. For example, in the UK alone, industrial processes generate over 40 TWh/y of heat, which could be recovered [156]. While the energy consumption for the MD process is higher than for RO (see next section), using waste heat streams could result in a net decrease in energy consumption [85]. This also means that the process could be driven by 100% renewable heat, which could be sourced from biomass if industrial heat is not readily available.

3.2.3 Limitations and recent advances

Despite having advantages over RO, MD is still not a widely commercialised technology. It is generally agreed that the two largest issues for industrial-scale MD systems are pore wetting [157,158] and low thermal efficiency [159]. Fouling and low water flux also have a considerable effect on the MD performance [152].

3.2.3.1 Pore wetting

Pore wetting can occur when amphiphilic molecules (surfactants) attach to the surface of the membrane pore. Liquids and substances within the water can also act as pore wetting agents if they have low surface tension (alcohols). Contact of the pore-wetting agent on the membrane surface results in a reduction of the pore liquid entry pressure (Figure 5). Once the liquid entry pressure is below the transmembrane hydraulic pressure difference, a channel is created whereby the feed water is able to pass through the membrane [152]. The effects are usually shown by a sharp increase in permeate conductivity, as the salt rejection capability is reduced. More information on the pore wetting mechanisms can be found in the work by Wang et al. [160].

Removing the pore-wetting agents from the feed water would lead to more complex and energy intensive pre-treatment. Instead, research is focused around the development of anti-wetting and anti-fouling membranes. Increasing the hydrophobicity of MD membranes to super-hydrophobic levels improves their wetting resistance [161–163]. Nevertheless, attractive interactions between the hydrophobic membrane and (typically) hydrophobic foulants mean that superhydrophobic membranes may increase the fouling propensity [164]. Attachment of foulants blocks the membrane pores, reducing the available space for vapour transfer and lowering the flux [165–170].

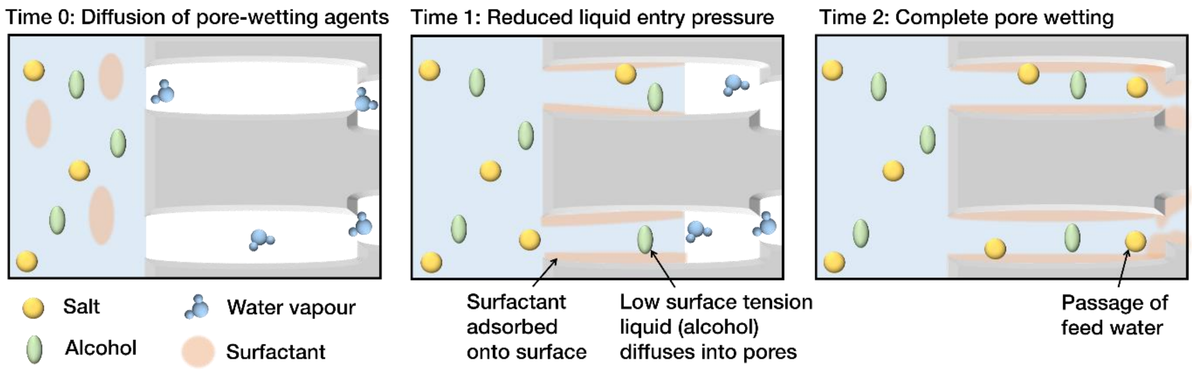

Figure 5. A schematic depicting two routes to pore wetting caused by the adsorption of a material onto the membrane surface (surfactants), or by the presence of a low surface tension material (alcohols) in the feed

Prince et al. [83] chose a different route to overcome the pore wetting issue. They synthesised a triple-layer membrane with a hydrophobic support layer and a top hydrophilic layer, which resulted in a 27% increase in liquid entry pressure and a pore wetting resistance of up to 95 h compared with 15 h with the control membrane. In another study, a double-layer membrane developed by Huang et al. [120] contained an omniphobic substrate and a skin layer that acted hydrophilic in air and superoleophobic underwater. The membrane had both anti-wetting and anti-fouling properties and maintained stable performance during the 10-h experiment with the saline feed containing either a wetting agent (sodium dodecyl sulphate) or a hydrophobic foulant (crude oil). Other authors have also been able to improve the resistance to pore wetting to manageable levels through surface modifications [171,172]. However, these results have only been achieved at lab-scale. Efficient, large-scale manufacturing methods for the fabrication of these membranes should be developed and tested to overcome the pore-wetting issue [157].

3.2.3.2 Water flux and fouling

Another MD limitation is the relatively low flux (~1-4 vs 12-17 L/m^2 h for RO [86]). To alleviate this issue, research into doping polymers with nano-additives, known as mixed matrix membranes, is being conducted with promising results [126,173–176]. In a recent study on AGMD by Leaper et al. [126], the addition to polyvinylidene fluoride (PVDF) of 0.3 wt% of graphene oxide (GO) functionalised with 3-(aminopropyl)triethoxysilane resulted in an 86% increase in the permeate flux when compared with pure PVDF. This enhancement is attributed to the effects of GO on the rate of demixing during phase inversion, which increases the surface and bulk porosity of the membrane. The degree of GO reduction (rGO), referring to the number of oxygen atoms in GO, was found to affect the GO-PVDF membranes in a similar work by Abdel-Karim et al. [177]. The flux was enhanced by 169% compared with pure PVDF when rGO fillers of 0.5 wt% were added to the polymer matrix. A recent study also investigated the effects of GO-mixed matrix membranes and found that a 1 wt% addition of GO into the polysulfone membrane resulted in a four times increase in permeate quality (99.85% salt rejection) [178]. However, the permeate flux of the GO-polysulfone membranes was lower than that of the pure polysulfone membrane (20.8 compared with 26.9 L/m^2 h). Alternatively, a GO layer deposited on the permeate side of a DCMD system can also increase permeate flux as the hydrophilic graphene layer promotes faster condensation. Intrchom et al. [179] demonstrated this enhancement on a commercial polytetrafluoroethylene membrane, achieving a 15% increase in flux compared to the unmodified version.

Metal-organic frameworks (MOFs) mixed into PVDF membranes have also shown higher water flux, as they increase the pore size and porosity [174]. A study by Cheng et al. [173] blended 1 wt%

aluminium fumarate MOF with PVDF to form hollow fibre membranes for desalination of 3.5 wt% NaCl via DCMD. The membranes displayed 50.5% higher flux and 46.2% higher thermal efficiency when compared to pristine PVDF, and yet retained high salt rejection of >99.9% over the 50-hour testing. The thermal efficiency increase was attributed to the reduction of heat loss by thermal conduction. Another study by Tijing et al. [176] reported the synthesis of superhydrophobic nanofibre membranes (PVDF-co-hexafluoropropylene) doped with CNTs for DCMD. The electrospun membranes reached higher contact angles (158.5˚), improved mechanical properties (by 360%) and greater porosities (by 15%) when compared to pristine PVDF. The increase in porosity led to 33-63% higher fluxes compared to commercial PVDF membranes. However, the duration of the experiment was only 300 min. In that time, the 5% CNT membrane (which had the most promising flux and mechanical results) experienced a flux decline of approximately 30%, which suggests fouling issues. More information on the use of carbon nanomaterials in MD can be found in a review by Leaper et al. [180]. Further studies on the immobilisation of carbon nanomaterials on membrane supports are required for their application in MD [181]. Investigating the performance of multiple nanomaterials within one study (with identical process conditions) would allow for more consistent comparisons [180]. Longer-term pilot-scale studies are also required to address the uncertainty surrounding the use of these membranes.

3.2.3.3 Energy consumption

Energy consumption is also one of the key issues targeted for MD improvements. Currently, the thermal energy consumption of MD systems ranges from 49 to 350 kWh/m^3 [127,128] although it can be as high as 1700 kWh/m^3 [127]. The consumption of electricity (for pumping) is much smaller but still notable at 0.6-1.8 kWh/m^3 [127]. These values highlight the importance of selecting an appropriate source of thermal energy, as well as incorporating heat recovery systems in MD, to reduce the environmental impacts associated with the energy use. Without these, MD cannot compete with RO in terms of energy consumption.

In addition, using renewable energy would also improve the environmental performance of MD. This is the reason that many current plants are powered by low-grade and/or renewable energy. As indicated in Table 1, twelve installations combine solar thermal and PV to supply the required energy [128,132–134,138–140,142,145–148]. Other plants use a combination of solar thermal and waste heat [133], electricity from the grid [144,150], geothermal energy [149] or a salinity-gradient solar pond [141].

Another critical variable for MD related to energy is the gained output ratio (GOR). It refers to the ratio of recoverable latent heat of evaporation over the total heat supplied to the system, or rather, it indicates how many times the latent heat of vaporisation can be captured and reused again to evaporate the feed water. Continued optimisation of module configurations and operation conditions over time has helped to increase the energy efficiency of MD plants. Table 1 shows this evolution in the past ten years for all known MD plants for which these data are available. For example, until very recently, the specific thermal energy consumption (STEC) was > 90 kWh/m^3 and GOR < 7. A recent study by Andrés-Mañas reported GOR values of 13.5 [128], which is an improvement on traditional thermal desalination technologies (GOR ~9.5 [182]). This system used a vacuum-enhanced air gap module configuration where the vacuum sucks the air from the gap and increases the mass transfer. The resulting STEC was 49 kWh/m^3 which is the lowest on record for MD. Since all current MD plants are at the pilot/small scale, further energy improvements are to be expected with their anticipated scale-up to commercial size.

3.2.3.4 Water recovery

Although MD can achieve water recoveries of up to 90% [183], the actual values are low (typically ~5% per pass) as can be seen in Table 1 [133,135,139,140,142,149]. This is likely due to the plants operating under single-pass configurations, which is a typical mode for MD testing (in pilot/small-scale plants). Therefore, further tests are necessary to determine the potential to increase the water recovery efficiency and alleviate the brine production issue. One way of achieving this would be to operate MD plants with feed recirculation and multi-pass systems until the desired recovery is achieved [184]. Another possibility is to use a series of cascading MD units, which would allow for continuous operation with high water recovery [183]. This is similar to the memsys vacuum multi-effect membrane distillation (V-MEMD) module, which achieves higher water recovery (~20-40% [138,144,147]). On the other hand, operating at low water recovery rates could be favourable as the brine would have a lower salt content and hence the impact of brine disposal could be lower [21].

3.3 Membrane capacitive deionisation

3.3.1 Process description

Instead of removing the bulk water from the salt (as in RO, FO and MD), MCDI removes the salt from the water. Research on capacitive deionisation (CDI) began without using the membrane. In both CDI and MCDI systems, the feed-water flows between a porous carbon anode and cathode and relies on an electric field between them. The salt ions form electrical double layers at the surface of the electrodes' pores and are held in place by electrostatic attraction. Once the pore surface is saturated with electrosorbed ions, the salt ions are discharged from the electrodes by reducing or reversing the cell voltage. This process regenerates the electrodes while forming a highly saline brine solution. The regeneration step also recovers a portion of the initial charging energy; Długołęcki et al. [185] found that 83% of the initial charging energy can be recovered this way. The addition of an ion-exchange membrane (Figure 6a) to the CDI system prevents the adsorption of ions onto the electrode during regeneration, leading to lower energy requirements and higher salt removal capacities than conventional CDI. A more recent development is flow-electrode capacitive deionisation (FCDI) (Figure 6b), whereby the electrodes are formed of a non-static carbon slurry. These systems can operate continuously as the carbon slurry can be regenerated downstream, while new slurry is added back upstream [186].

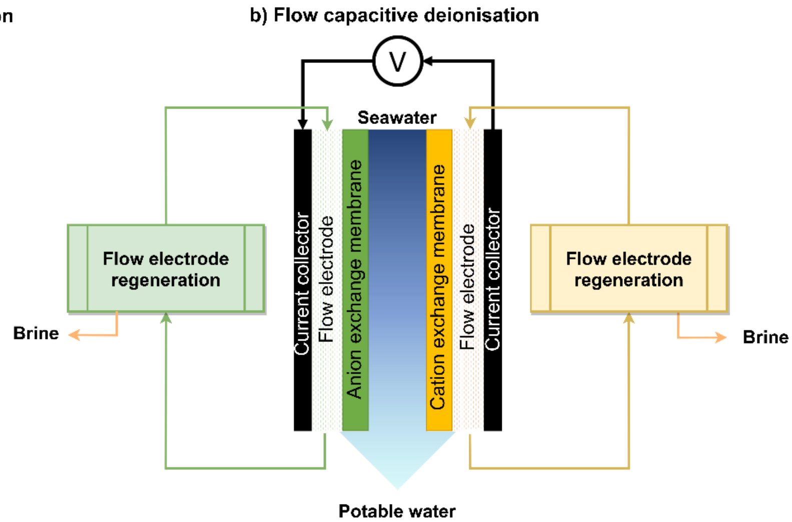

Figure 6. A schematic of a) membrane capacitive deionisation and b) flow capacitive deionisation (adapted from Suss [187] *and Hassanvand* [188]*)*

3.3.2 Advantages over reverse osmosis

The recent rise in MCDI research can be attributed to the low-energy and cost-efficient brackish water desalination, which have led to investigations into using MCDI for seawater applications [186,189–191]. MCDI has the potential for a much higher rejection of solutes than RO because it removes the salt from the water rather than the other way round. This is intuitively a more energy efficient approach, given that there is much less salt than the water in both brackish and seawater. MCDI can be highly selective such that it can be used for the separation of monovalent and divalent ions, which is an important issue in the controlling of hardness in water [192]. Selectively removing monovalent cations is useful within seawater resource recovery and positively impacts the remineralisation process [193]. A further advantage of MCDI over RO is that it operates under ambient pressures and temperatures and, as such, has a lower propensity for fouling [187].

3.3.3 Limitations and recent advances

High energy efficiencies have been reported for MCDI systems treating water with the salinity below 10 g/L, which is ideal for applications in brackish water desalination [187]. As the salinity of seawater is much higher (∼35 g/L), currently MCDI systems are not able to treat seawater without large energy penalties. The main reason for this is that conventional static electrodes are limited by how much salt they can adsorb. For example, Tang et al. [189] investigated ways to increase the salt removal capacity in MCDI using an over-potential MCDI system with reverse polarity. By increasing the voltage from 1 to 2.4 V, the authors found that the electrical conductivity of a seawater sample (37 g/L) was reduced by 99.9%. However, the energy consumption for this system was very high (83.2 kWh/m^3), an order of magnitude greater than that of the RO process (2.5-7 kWh/m^3).

On the other hand, Jeon et al. [186] showed that a flow-electrode MCDI system increased the maximum treatable salt concentration (32.1 g/L) without requiring a large electrical voltage (1.2 V). The flow electrodes allow for continuous operation through the integration of the operational and regeneration stages (Figure 6b), which is an essential contribution to the potential commercialisation of this technology for seawater applications. Furthermore, seawater can be used as the flow-electrode aqueous electrolyte [194,195]. Another recent study by Porada et al. [196] also investigated flow-MCDI for more saline feed waters (~24 g/L) but found that the energy requirements were 2-2.5 times higher than for RO. However, their theoretical predictions suggested that MCDI could achieve high water recoveries (up to 95%) without an energy penalty. Water recovery is a challenging topic in MCDI research, with an ongoing debate on how best to compare MCDI with different technologies [195].

Replacing the porous carbon electrodes could be the key to increasing MCDI charge efficiency. Srimuk et al. [190] compared the conventional carbon MCDI set-up with a new system using molybdenum disulfide/carbon nanotube electrodes for the desalination of 500 mM NaCl solution (~29 g/L). The cell voltage was 0.8 V for both systems and the energy consumption per ion was reduced from over 20,000 to 24.6 kT for the MoS_2/CNT system. Cation intercalation deionisation is another similar technology that is being investigated for seawater desalination. Srimuk et al. [191] treated saline water of 600 mM NaCl (35 g/L) using a silver/silver chloride battery. The applied electrical voltage was only 0.2 V, resulting in desalination at a far lower energy consumption than previously recorded for MCDI (2.5 kT per ion), as well as stable operation over 100 cycles.

Lastly, the cost of the ion exchange membranes can range from \$20-\$100 per m^2 [197], with the top end being one order of magnitude higher than for commercial RO membranes [198]. In addition to the high membrane costs, the electrodes are also expensive and need to be replaced often, which results in high life cycle costs and environmental impacts [198,199]. The latter have been investigated in several life cycle assessment studies, including a recent CDI wastewater study by Shiu et al. [200] which found that the use of materials and chemicals during fabrication contributed 52-89.8% to the total environmental impacts. Related research [200,201] has also recommended the replacement or management of certain materials (N,N-dimethylacetamide, titanium and N-methyl-2-pyrrolidone) before MCDI is fully commercialised for desalination. Other scale-up challenges were highlighted in a recent review by McNair et al. [195], which recommended that future MCDI research should focus on fouling, cleaning, cycling stability and pilot-scale studies.

3.4 Summary comparison of emerging technologies and reverse osmosis

Table 2 summarises the major performance characteristics of the evaluated emerging technologies against RO. As can be seen, FO and MD experience lower fouling rates and need fewer pre-treatment stages, which could reduce the environmental impacts from the release of chemicals into the brine. FO and MCDI operate at ambient pressure and temperature, avoiding the need for high-tolerance construction materials. Nevertheless, the advantages of FO are extremely dependent on the DS recovery stage, which needs to be improved. However, all of the emerging technologies have higher energy consumptions than RO at this stage and require further developments to improve their economic feasibility. It is worth highlighting that MD and FO can operate using low-grade energy, which could enable the development of desalination systems powered by waste heat, thus reducing consumption of fossil-fuel-derived energy and related environmental impacts.

In addition, there are indications that coupling the emerging technologies with RO to form hybrid systems could help overcome some of the limitations of the stand-alone technologies. This is discussed in more detail in the next section.

4 Hybrid systems

With thousands of RO desalination plants currently operating and with no current plans for deployment of large-scale plants utilising alternative methods, it could be a long time before the desalination industry replaces RO. Therefore, hybrid systems could be an excellent opportunity to test, further develop and allow the sector to grow confidence in the new systems. The major hybrid configurations reported in the literature over the past ten years are summarised in Table 3. These were selected for consideration here if studies used seawater as the initial feed water and they reported key information on energy consumption, water recovery and salt rejection. The period is limited to the past decade to reflect the rapid improvements in the efficiencies of the technologies.

4.1 Forward and reverse osmosis

The FO-RO hybrids remove a portion of the salts from the feed, so that the RO can be operated at lower pressures. The latter can lead to reductions in the overall energy consumption as shown by Seo [202] and Yangali-Quintanilla [203]. These studies investigated the use of secondary wastewater effluent and (unspecified) wastewater as the FO draw solution, which is advantageous as it avoids the need for regeneration of the draw solution. A further advantage is that FO dilutes the seawater to reduce the energy consumption of the RO process, as found in these two studies. They reported that using the hybrid system reduced the SEC to 1.37-1.82 kWh/m^3 [202] and 1.5 kWh/m^3 [203], which in turn could reduce the associated GHG emissions. In addition, as FO reduces the severity of fouling in RO, fewer chemicals and less cleaning could be required. FO could replace some of the more energy-intensive pre-treatment stages, leading to an overall reduction in the energy consumption. However, further research should consider capital and operational costs, including potential cost-offset strategies through the generation of valuable products. The latter was explored by Arjmandi et al. [204] who considered the simultaneous generation of potable water and concentrated whey from seawater and cheese whey. The optimisation of process configurations should also be explored further. Seo et al. [202] recommended in their optimisation study that fast feed-flow and slow draw-flow velocities should be adopted for FO to minimise the SEC of RO. They suggested that the FO elements should be configured with a parallel connection to slow the draw-flow velocity.

4.2 Reverse osmosis and membrane distillation

Combining RO with MD can increase water recovery and, consequently, reduce the amount of brine released into the environment. A pilot-scale study by Lee et al. [205] found that MD could recover an additional 30% of the water in the RO brine and estimated that the SEC was lower than for stand-alone RO (2.81 compared to 3.32 kWh/m^3). The study also incorporated a pressure retarded osmosis (PRO) unit for energy recovery and was able to reduce the SEC further to 2.68 kWh/m^3. The authors used theoretical costing models to estimate when the hybrid systems were more cost-effective than stand-alone RO. The operating costs of RO-MD and RO-MD-PRO were found to be lower (1.04 and 1.07 \$/m^3, respectively) than stand-alone RO (1.26 \$/m^3) only when the cost of electricity exceeded 0.20 \$/kWh.

Bindels et al. [153] investigated different RO-AGMD configurations to determine cost of increasing water recovery in RO. The study found that recoveries as high as 84.6% could be achieved when a biodegradable antiscalant was added to the feed. This configuration also achieved a low cost of water (0.63 \$/m^3). However, the study assumed that all of the heat required for MD was provided as waste heat, and thus incurred no additional cost. Therefore, this configuration can only be recommended in regions with neighbouring process plants that generate waste heat.

The cost of using RO-MD needs to be evaluated against using stand-alone RO and conventional zero-liquid discharge methods (e.g. evaporation ponds) to understand better the economic feasibility of this hybrid system, as it produces a more concentrated brine that still needs to be treated. Ideally, no brine would be released to sea, especially in pristine coastal areas with mild ocean currents. A hybrid system incorporating RO, MD and membrane distillation crystalliser (RO-MD-MDC) is being investigated as a zero-liquid discharge method. This involves feeding the concentrated MD brine into a membrane crystalliser to recover valuable minerals from the seawater [206–208]. While additional separations will increase the operating and capital costs, the sale of recovered material could offset the cost. However, using MDC incurs an energy penalty that is not well documented in current studies [206–208]. An older study assessed different RO-MD-MDC sequences and estimated a SEC of approximately 28 kWh/m^3, which could be reduced to 1.61-2.05 kWh/m^3 if appropriate thermal energy was already available in the plant [209]. These figures demonstrates the importance of incorporating freely available low-grade heat sources if this technology is used. Recommendations for future RO-MD-MDC studies include investigating pilot-scale systems over a longer term to understand pore-wetting and stability challenges. Furthermore, the selective recovery of certain valuable seawater elements (e.g. lithium) should be investigated. Further information on this can be found in a review by Naidu et al. [210].

Table 2. Comparison of emerging desalination techniques with reverse osmosis for seawater desalination.

Parameter	Reverse osmosis	Forward osmosis	Membrane distillation	Membrane capacitive deionisation
Thermal energy consumption, kWh/m^3 potable water	-	-	49-350 [57,128,211].	-
Electrical energy consumption, kWh/m^3 potable water	2.5-7 [12–14,127].	3-68 [38,56]. The forward osmosis process has low energy consumption but regeneration of draw solution can be energy intensive. Additional ~0.25 kWh/m^3 required for circulation pumps [103].	0.6-1.8 [127] required for circulation pumps.	83.2 [189]
Type of energy required when integrated with renewable energy	Reliable electricity.	Energy for regeneration dependent on draw solution; can potentially use low-grade energy [212].	Low-grade energy/waste heat [130].	Electricity [187].
Ease of pre-treatment	Extensive pre-treatment steps are required to mitigate membrane fouling [59]; must be chemically cleaned.	Fouling is reversible and can be mechanically removed [108].	Fewer pre-treatment chemicals required [21,125]. Antiscalants required to reduce calcium scaling [165].	Absence of hydraulic pressure reduces fouling.
Operating pressure and temperatures	50-70 bar, ambient temperature [37,38].	Atmospheric pressure but high pressures/temperatures may be required during draw solution regeneration [213].	1 bar; 30-90˚C; higher temperatures maximise flux [125].	1 bar, ambient temperature [187].
Water recovery	35-50% [10].	Up to 50% , although rarely used as stand-alone technology [107,214].	Usually ~5-40% [142,144,147,149], although >90% is possible [183].	Uncertain, potentially significantly higher than 50% [187,196].
Water desalination cost, $\$/m^3$	0.5-3 [12,63].	0.8-2 [214].	0.64-5.2 [125,151,215].	Unknown, however capital costs and membrane costs are higher than RO [198,199].
Current market share in desalination	Most widely used (~65% share) [127].	Emerging (<2%) [127].	Emerging (<2%) [127].	Not commercialised for seawater desalination.

Table 3. Characteristics of hybrid systems for seawater desalination.

Hybrid type[a]	**Energy consumption, kWh/m^3**	**Water recovery, %**	**Salt rejection, %**	**Remarks**	**Reference**
FO-RO[b]	1.37 – 1.82	~35-55	99	Wastewater and seawater used	[202]
FO-RO	1.5	2	98	Water desalination cost: \$0.91/m^3	[203]
FO-Crystallisation-RO	17.4	68	-	Water desalination cost: \$0.64-0.70/m^3	[216]
RO-MD	4.8 [d]	84.6	-	Water desalination cost: \$0.63/m^3 [d]	[153]
RO-CD-UF-MD	4.8 [d]	66.9	-	Water desalination cost: \$1.05/m^3 [d]	[153]
RO-NF-MD	4.8 [d]	73.4	-	Water desalination cost: \$0.70/m^3 [d]	[153]
RO-MD	2.81	30% of RO brine	-	Operational cost: \$1.04/m^3	[205]
RO-MD-PRO	2.68	30% of RO brine	-	Operational cost: \$1.07/m^3	[205]
RO-MD-RED	6.5	90	100	Energy recovered from saline brine	[217]
RO-MD-MDC	-	90	-	Production of 21 kg/m^3 of NaCl crystals	[206]
RO-MD-MDC	3 in addition to RO alone	99.8	-	Equipment and energy costs: €1.09/m^3; recovery of $CaCO_3$, NaCl and KCl	[207]
RO-MD-MDC[b]	-	-	-	Addition of MDC contributes >0.5% of the energy consumption	[208]
RO-CDI	3.17	-	>99.9	Ultrapure water production (TDS[c]< 2 ppm)	[218]
RO-MCDI	0.15-0.21 in addition to RO alone	50% of RO permeate	>99.9	Bromide removal efficiency: 68.7-70.3%	[219]
RO-MCDI	4.24-11	14.6	-	Small-scale plant, 2 m^3/d	[220]
RO-FCDI	1.3 in addition to RO alone	45	95%	Used after one-pass RO module	[194]

[a] CD: Chemical deposition; CDI: Capacitive deionisation; FCDI: flow-electrode capacitive deionisation; FO: Forward osmosis; MCDI: Membrane capacitive deionisation; MD: Membrane distillation; MDC: Membrane crystallisation; NF: nanofiltration; OARO: Osmotically assisted reverse osmosis; PRO: Pressure retarded osmosis; RED: Reverse electrodialysis; RO: Reverse osmosis; UF: ultrafiltration.
[b] Theoretical study.
[c] Total dissolved solids.
[d] Assumes 100% of the thermal energy is provided as free waste heat.

4.3 Reverse osmosis and membrane capacitive deionisation

RO-MCDI is being investigated to replace the 2nd pass in two-pass RO systems to achieve higher salt rejection and reduce the SEC. Jande et al. [218] demonstrated that in this hybrid system, MCDI could produce ultra-pure water from RO permeate using 3.17 kWh/m^3 of water. Thus, this system could be of particular interest for applications that require ultrapure (e.g. pharmaceuticals and electronics) as well as potable water. The high rejection capabilities of RO-MCDI hybrids could also potentially open up desalination opportunities in new locations previously disregarded due to contamination issues. For example, Dorji et al. [219] investigated the removal of bromide from RO permeate using MCDI. The study demonstrated that safe drinking water could be produced from contaminated seawater at no significant cost increase; the use of MCDI only increased the SEC by 0.15-0.21 kWh/m^3.

Chung et al. [194] used flow-electrode MCDI with selective ion exchange membranes. They investigated using a one-pass RO with flow-electrode MCDI system against a two-pass RO system. The 2nd pass in a seawater RO plant has an energy consumption similar to that of brackish water (0.2-0.4 kWh/m^3) [194]. The flow-electrode MCDI separation stage was found to have a greater energy consumption than this (1.3 kWh/m^3) and did not achieve the same permeate quality. The study suggested that pumping efficiency improvements at larger scales would reduce SEC. The flow-electrode MCDI system was able to remove selectively monovalent ions over divalent ions, which means that a lower quantity of divalent ions needs to be reintroduced during remineralisation. While the study argued that this selective behaviour would reduce the energy and financial burden of the remineralisation stage, it is important to note that this stage has a minor contribution (~2% [221]) to the total desalination energy.

Overall, hybrid RO-MCDI has benefits in applications that require high rejection of solutes. Future research needs include optimising the desorption process through automation [219] or exploring different electrolytes (within FCDI research).

4.4 Hybrids without reverse osmosis

Ghaffour et al. [222] carried out an extensive review on MD hybrids for water production, including MD combinations with FO, bioreactors, mechanical vapour compression and conventional thermal desalination technologies (multi-stage flash and multi-effect distillation). The review suggested that MD can provide the largest improvements when included in these conventional distillation systems, where the abundance of waste heat enables cost-effective integration. MD hybrids could be considered for more bespoke applications, as recommended in a study by Luo et al. [223]. They investigated osmotic membrane bioreactor-MD, which uses an FO membrane within a bioreactor and the diluted draw solution is recovered using MD. The study demonstrated that simultaneous wastewater reuse and seawater desalination were achievable with reasonable water flux. A key recommended application included the implementation on cruise ships, where there is both a supply of seawater and a need for wastewater reuse.

4.5 Summary comparison of stand-alone and hybrid systems

Figure 7 provides a qualitative comparison of RO, FO, MD, MCDI and their hybrid counter-parts. Further information on the methodology, including the scoring matrix, can be found in the supplementary information. The following key performance criteria discussed in the paper and summarised in Table 2 are considered:

- energy consumption: the desalination technology must have a low energy consumption to be environmentally and economically feasible;
- renewable energy: it must be easy to integrate renewable energy to power the desalination process in order to reduce the associated GHG emissions; the quality of the required energy is a good indicator of this since high-grade energy (electricity) can be more difficult to generate and store than low grade energy (heat);
- pre-treatment: this stage must not be energy and chemically intensive to reduce water treatment costs and environmental pollution;
- water recovery: this parameter must be maximised to increase process efficiency and reduce the volume of brine; for stand-alone MCDI, water recovery is not considered due to a lack of data and the score has been left blank; and
- water cost: the water production costs must be low to ensure the process is economically feasible and cost-competitive with current technologies.

  The comparison in Figure 7 on the above five criteria is based on a scale from 0 to 1, where values closer to unity are preferred and all the criteria are considered to be of equal importance. On this basis, the RO-FO hybrid could be considered the best option, as the only alternative with two of the criteria equal to unity (the energy consumption and ease of pre-treatment). It also has the second lowest water costs. The next best system is RO-MD (with the highest water recovery), followed by RO (lowest costs). MCDI is overall the worst option among the stand-alone technologies. It is interesting to note that the hybrid systems tend to perform overall better than the single technologies.

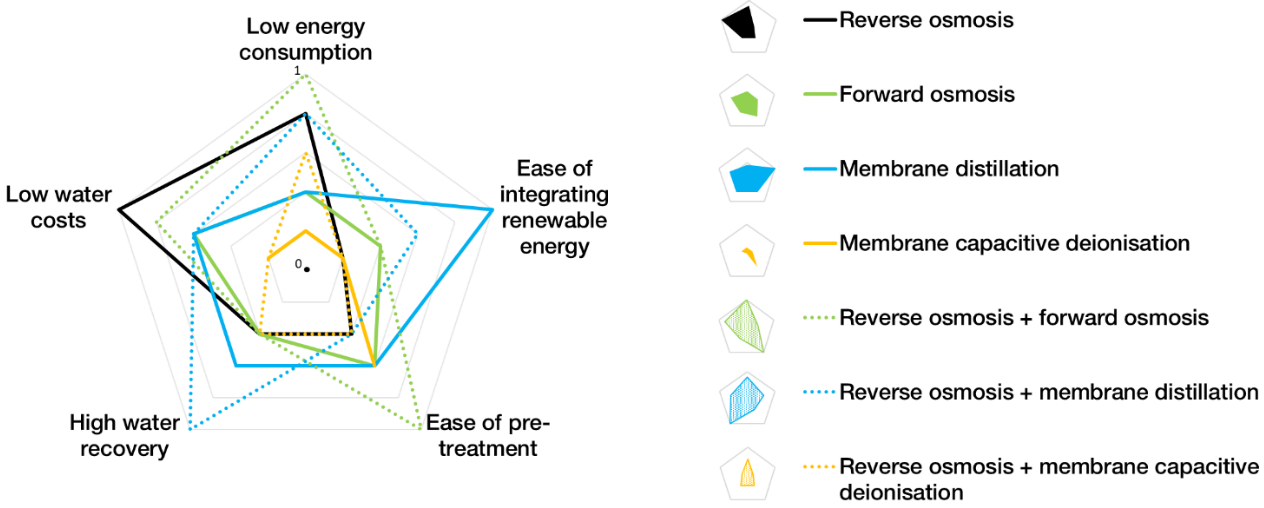

Figure 7 Summary comparison of stand-alone and hybrid systems

However, these comparisons should be treated with caution due to a lack of data related to commercial applications of the emerging technologies. Also, some criteria may be considered more important than others, particularly the energy consumption and costs. Finally, it should be borne in mind that RO is the only option available at scale and hence optimised – if deployed commercially, the emerging technologies would also benefit from the economies of scale and their performance would improve.

5 Conclusions

Desalinated seawater is an increasingly important source of potable water. While reverse osmosis currently has the largest market share, the process has major limitations, including high electrical consumption (and associated GHG emissions) and production of waste brine. The impacts of the brine on local marine life still need to be understood better, but can be potentially damaging. Using renewable energy to power reverse osmosis (RO) can reduce significantly the associated GHG emissions, but further work is needed on incorporating these systems to alleviate the intermittency issues. Desalination via RO is an additional challenge in remote areas and islands due to the unavailability and cost of electricity.

To address some of the above issues, alternative desalination technologies are being developed, including forward osmosis (FO), membrane distillation (MD) and membrane capacitive deionisation (MCDI). However, at present, their widespread adoption is limited by several factors. Although FO can treat seawater at a lower energy consumption and fouling than RO, the energy demand for the recovery of draw solution is still too high to compete energetically with RO. Similarly for MD, the high thermal energy requirements mean that the overall energy consumption is still higher than for RO, although significant improvements in internal heat recovery, through improved membrane module design and process optimisation, have reduced its energy intensity in recent years. Furthermore, the use of nanomaterials has led to major membrane improvements, including increased flux and pore-wetting resistance. However, further studies with these novel membranes are necessary to demonstrate whether MD can compete with RO on a large scale.

Currently, most applications of MCDI focus on brackish water but recent developments in membranes and cell architecture have enabled its use for seawater desalination. However, these studies are at small scale and the associated energy consumption is, at best, 16 times greater than for RO.

Combining FO and RO in a hybrid system can avoid the recovery stage by reusing wastewater as a draw solution, leading to a significant decrease in the energy consumption. However, pilot-scale studies using real seawater and wastewater are required to understand the versatility and stability of the system. Hybrid RO-MD systems can also offer lower energy consumptions, as well as higher water recovery and cost-competitiveness in areas with challenging electricity supply. Zero-liquid discharge systems are achievable using a combination of RO-MD-MDC and could lead to additional resource recovery (e.g. $MgSO_4$). However, the energy consumption of these hybrid systems needs to be understood better. RO-MCDI hybrids can produce ultra-pure water at low energy consumption and achieve greater rejections of contaminants like bromide, opening up new desalination possibilities in polluted areas that may have been disregarded before.

Several overlapping challenges pervade desalination technologies, such as fouling, energy consumption and operational stability. Improvements in membranes and module designs would benefit all techniques. This review confirms that RO is currently the most suitable technology for the desalination of seawater as it has the lowest specific water cost. However, there are opportunities for the emerging technologies. As the need for seawater desalination increases and environmental legislation becomes tighter, the impacts of brine disposal will motivate the industry to consider hybrid systems to treat the brine and recover minerals. There are also opportunities for the integration of these technologies with RO to reduce the environmental impacts of the pre-treatment stages. Hybrid systems are showing promising results at laboratory and pilot scales, but further costing analyses are required. It is recommended that emerging membrane desalination technologies are explored in greater detail for integration into current reverse osmosis plants.

Acknowledgements

The authors are grateful to the EPSRC for funding under the grant number EP/S032258/1. Clara Skuse would like to acknowledge the EPSRC for funding this work through the NOWNANO CDT and Raphael Ricardo Zepon Tarpani for his valuable help at the initial stages of the review.

References

1. Gleick P., Water in Crisis: A Guide to the World's Fresh Warer Resources, Oxford University Press (1993).
2. Clarke, G.K.C.; Jarosch, A.H.; Anslow, F.S.; Radic, V.; Menounos, B. Projected deglaciation of western Canada in the in the 21st century century. *Nat. Geosci.* **2015**, doi:10.1038/NGEO2407.
3. Wester, P.; Mishra, A.; Mukherji, A.; Shrestha, A.B. *The Hindu Kush Himalaya Assessment*; Springer International Publishing, 2019; ISBN 978-3-319-92287-4.
4. NASA Global Climate Change, Vital Signs of the Planet Available online: https://climate.nasa.gov/vital-signs/sea-level/ (accessed on Jul 15, 2020).
5. Shammi, M.; Rahman, M.; Bondad, S.; Bodrud-Doza, M. Impacts of Salinity Intrusion in Community Health: A Review of Experiences on Drinking Water Sodium from Coastal Areas of Bangladesh. *Healthcare* **2019**, *7*, 50, doi:10.3390/healthcare7010050.
6. Khan, A.E.; Ireson, A.; Kovats, S.; Mojumder, S.K.; Khusru, A.; Rahman, A.; Vineis, P. Drinking water salinity and maternal health in coastal Bangladesh. *Environ. Health Perspect.* **2011**, doi:10.1289/ehp.1002804.
7. Gray, E.T. Megadrought Available online: https://svs.gsfc.nasa.gov/11753 (accessed on Jul 15, 2020).
8. United Nations Sustainable Development Goal 6 Synthesis Report on Water and Sanitation.
9. United Nations Transforming our word, the 2030 Agenda for sustainable development.
10. Jones, E.; Qadir, M.; van Vliet, M.T.H.; Smakhtin, V.; Kang, S. The state of desalination and brine production: A global outlook. *Sci. Total Environ.* **2019**, *657*, 1343–1356, doi:10.1016/j.scitotenv.2018.12.076.

11. Van der Bruggen, B.; Vandecasteele, C. Distillation vs. membrane filtration: overview of process evolutions in seawater desalination. *Desalination* **2002**, *143*, 207–218, doi:https://doi.org/10.1016/S0011-9164(02)00259-X.
12. Voutchkov, N. Energy use for membrane seawater desalination – current status and trends. *Desalination* **2018**, *431*, 2–14, doi:10.1016/j.desal.2017.10.033.
13. Al-Kaabi, A.H.; Mackey, H.R. Environmental assessment of intake alternatives for seawater reverse osmosis in the Arabian Gulf. *J. Environ. Manage.* **2019**, *242*, 22–30, doi:10.1016/j.jenvman.2019.04.051.
14. Stokes, J.R.; Horvath, A. Energy and Air Emission Effects of Water Supply. *Environ. Sci. Technol.* **2009**, *43*, 2680–2687, doi:10.1021/es801802h.
15. Shahzad, M.W.; Burhan, M.; Ng, K.C. A standard primary energy approach for comparing desalination processes. *npj Clean Water* **2019**, *2*, 1, doi:10.1038/s41545-018-0028-4.
16. Amy, G.; Ghaffour, N.; Li, Z.; Francis, L.; Linares, R.V.; Missimer, T.; Lattemann, S. Membrane-based seawater desalination: Present and future prospects. *Desalination* **2017**, *401*, 16–21, doi:10.1016/j.desal.2016.10.002.
17. Al-Shayji, K.; Aleisa, E. Characterizing the fossil fuel impacts in water desalination plants in Kuwait: A Life Cycle Assessment approach. *Energy* **2018**, *158*, 681–692, doi:10.1016/j.energy.2018.06.077.
18. Shahabi, M.P.; McHugh, A.; Anda, M.; Ho, G. Environmental life cycle assessment of seawater reverse osmosis desalination plant powered by renewable energy. *Renew. Energy* **2014**, *67*, 53–58, doi:10.1016/j.renene.2013.11.050.
19. Raluy, R.G.; Serra, L.; Uche, J. Life cycle assessment of MSF, MED and RO desalination technologies. *Energy* **2006**, *31*, 2361–2372, doi:10.1016/j.energy.2006.02.005.
20. Meneses, M.; Pasqualino, J.C.; Céspedes-Sánchez, R.; Castells, F. Alternatives for reducing the environmental impact of the main residue from a desalination plant. *J. Ind. Ecol.* **2010**, *14*, 512–527, doi:10.1111/j.1530-9290.2010.00225.x.
21. Tarnacki, K.; Meneses, M.; Melin, T.; van Medevoort, J.; Jansen, A. Environmental assessment of desalination processes: Reverse osmosis and Memstill®. *Desalination* **2012**, *296*, 69–80, doi:10.1016/j.desal.2012.04.009.
22. Biswas, W.K. Life cycle assessment of seawater desalinization in Western Australia. *World Acad. Sci. Eng. Technol.* **2009**, *35*, 369–375.
23. Shahabi, M.P.; McHugh, A.; Anda, M.; Ho, G. Comparative economic and environmental assessments of centralised and decentralised seawater desalination options. *Desalination* **2015**, *376*, 25–34, doi:10.1016/j.desal.2015.08.012.
24. Goga, T.; Friedrich, E.; Buckley, C.A. Environmental life cycle assessment for potable water production – A case study of seawater desalination and mine-water reclamation in South Africa. *Water SA* **2019**, *45*, 700–709, doi:10.17159/wsa/2019.v45.i4.7552.
25. Du, Y.; Liu, Y.; Xie, L.; Zhang, S. Economic, Energy, Exergo-Economic, and Environmental Analyses and Multiobjective Optimization of Seawater Reverse Osmosis Desalination Systems with Boron Removal. *Ind. Eng. Chem. Res.* **2019**, *58*, 14193–14208, doi:10.1021/acs.iecr.9b01933.
26. IEA Desalinated water affects the energy equation in the Middle East Available online: https://www.iea.org/commentaries/desalinated-water-affects-the-energy-equation-in-the-middle-east (accessed on Jul 15, 2020).
27. Petersen, K.L.; Heck, N.; Reguero, B.G.; Potts, D.; Hovagimian, A.; Paytan, A. Biological and Physical Effects of Brine Discharge from the Carlsbad Desalination Plant and Implications for Future Desalination Plant Constructions. *Water* **2019**, *11*, 208, doi:10.3390/w11020208.
28. Danoun, R.; Jones, I.S.F.; Mulhearn, P. Desalination Plants: Potential impacts of brine discharge on marine life, 2007.
29. Dupavillon, J.L.; Gillanders, B.M. Impacts of seawater desalination on the giant Australian cuttlefish Sepia apama in the upper Spencer Gulf, South Australia. *Mar. Environ. Res.* **2009**, *67*, 207–218, doi:10.1016/j.marenvres.2009.02.002.
30. Ahmed, M.; Anwar, R. An Assessment of the Environmental Impact of Brine Disposal in Marine Environment. *Int. J. Mod. Eng. Res. www.ijmer.com* **2012**, *2*.

31. Shahzad, M.W.; Ybyraiymkul, D.; Burhan, M.; Ng, K.C. Renewable Energy-Driven Desalination Hybrids for Sustainability. In *Desalination and Water Treatment*; InTech, 2018.
32. Portillo, E.; Ruiz de la Rosa, M.; Louzara, G.; Ruiz, J.M.; Marín-Guirao, L.; Quesada, J.; González, J.C.; Roque, F.; González, N.; Mendoza, H. Assessment of the abiotic and biotic effects of sodium metabisulphite pulses discharged from desalination plant chemical treatments on seagrass (Cymodocea nodosa) habitats in the Canary Islands. *Mar. Pollut. Bull.* **2014**, *80*, 222–233, doi:10.1016/j.marpolbul.2013.12.048.
33. Youcai, Z. Leachate Treatment Engineering Processes. In *Pollution Control Technology for Leachate from Municipal Solid Waste*; Elsevier, 2018; pp. 361–522.
34. Khulbe, K.C. Pore Size, Pore Size Distribution, and Roughness at the Membrane Surface. In *Synthetic Polymeric Membranes*; Springer Berlin Heidelberg: Berlin, Heidelberg; pp. 101–139.
35. Voutchkov, N. Considerations for selection of seawater filtration pretreatment system. *Desalination* **2010**, *261*, 354–364, doi:https://doi.org/10.1016/j.desal.2010.07.002.
36. Jamaly, S.; Darwish, N.N.; Ahmed, I.; Hasan, S.W. A short review on reverse osmosis pretreatment technologies. *Desalination* 2014, *354*, 30–38.
37. Tularam, G.A.; Ilahee, M. Environmental concerns of desalinating seawater using reverse osmosis. *J. Environ. Monit.* **2007**, *9*, 805–13, doi:10.1039/b708455m.
38. Roy, S.; Ragunath, S. Emerging membrane technologies for water and energy sustainability: Future prospects, constraints and challenges. *Energies* **2018**, *11*, doi:10.3390/en11112997.
39. Al-Odwani, A.; Al-Tabtabaei, M.; Al-Hashim, A.; Carew, J.; Al-Atram, F. Erosion of construction materials in a reverse osmosis plant utilizing seawater in Kuwait. *Desalination* **2000**, *129*, 137–145.
40. Greenlee, L.F.; Lawler, D.F.; Freeman, B.D.; Marrot, B.; Moulin, P. Reverse osmosis desalination: Water sources, technology, and today's challenges. *Water Res.* **2009**, *43*, 2317–2348, doi:10.1016/j.watres.2009.03.010.
41. Stover, R. Energy Recovery Devices for High Pressure Hydraulic Applications. **2009**.
42. Arenas Urrea, S.; Díaz Reyes, F.; Peñate Suárez, B.; de la Fuente Bencomo, J.A. Technical review, evaluation and efficiency of energy recovery devices installed in the Canary Islands desalination plants. *Desalination* **2019**, *450*, 54–63, doi:https://doi.org/10.1016/j.desal.2018.07.013.
43. Gies, E. *Scientific American*. 2019,.
44. Kim, S.; Hoek, E.M.V. Modeling concentration polarization in reverse osmosis processes. *Desalination* **2005**, *186*, 111–128, doi:10.1016/j.desal.2005.05.017.
45. Cavaco Morão, A.I.; Brites Alves, A.M.; Geraldes, V. Concentration polarization in a reverse osmosis/nanofiltration plate-and-frame membrane module. *J. Memb. Sci.* **2008**, *325*, 580–591, doi:10.1016/j.memsci.2008.08.030.
46. Goh, P.S.; Lau, W.J.; Othman, M.H.D.D.; Ismail, A.F. Membrane fouling in desalination and its mitigation strategies. *Desalination* **2018**, *425*, 130–155, doi:10.1016/j.desal.2017.10.018.
47. Al-Abri, M.; Al-Ghafri, B.; Bora, T.; Dobretsov, S.; Dutta, J.; Castelletto, S.; Rosa, L.; Boretti, A. Chlorination disadvantages and alternative routes for biofouling control in reverse osmosis desalination. *npj Clean Water* **2019**, *2*, 2, doi:10.1038/s41545-018-0024-8.
48. Jambeck, J.R.; Geyer, R.; Wilcox, C.; Siegler, T.R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K.L. Plastic waste inputs from land into the ocean. *Science (80-.).* **2015**, *347*, 768–771, doi:10.1126/science.1260352.
49. Schuhen, K.; Toni Sturm, M.; Frank Herbort, A. Technological Approaches for the Reduction of Microplastic Pollution in Seawater Desalination Plants and for Sea Salt Extraction. In *Plastics in the Environment*; IntechOpen, 2019.
50. Poerio; Piacentini; Mazzei Membrane Processes for Microplastic Removal. *Molecules* **2019**, *24*, 4148, doi:10.3390/molecules24224148.
51. Lithner, D.; Larsson, A.; Dave, G. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Sci. Total Environ.* **2011**, *409*, 3309–3324, doi:10.1016/j.scitotenv.2011.04.038.
52. Caruso, G. Microplastics in Marine Environments: Possible Interactions with the Microbial Assemblage. *J. Pollut. Eff. Control* **2015**, *03*, doi:10.4172/2375-4397.1000e111.

53. Vince, F.; Aoustin, E.; Bréant, P.; Marechal, F. LCA tool for the environmental evaluation of potable water production. *Desalination* **2008**, *220*, 37–56, doi:10.1016/j.desal.2007.01.021.
54. García-Pacheco, R.; Lawler, W.; Landaburu-Aguirre, J.; García-Calvo, E.; Le-Clech, P. 4.14 End-of-Life Membranes: Challenges and Opportunities. In *Comprehensive Membrane Science and Engineering*; Elsevier, 2017; pp. 293–310.
55. Moradi, M.R.; Pihlajamäki, A.; Hesampour, M.; Ahlgren, J.; Mänttäri, M. End-of-life RO membranes recycling: Reuse as NF membranes by polyelectrolyte layer-by-layer deposition. *J. Memb. Sci.* **2019**, *584*, 300–308, doi:https://doi.org/10.1016/j.memsci.2019.04.060.
56. Li, Z.; Siddiqi, A.; Anadon, L.D.; Narayanamurti, V. Towards sustainability in water-energy nexus: Ocean energy for seawater desalination. *Renew. Sustain. Energy Rev.* **2018**, *82*, 3833–3847, doi:10.1016/j.rser.2017.10.087.
57. Cherif, H.; Belhadj, J. Environmental Life Cycle Analysis of Water Desalination Processes. In *Sustainable Desalination Handbook: Plant Selection, Design and Implementation*; Elsevier, 2018; pp. 527–559 ISBN 9780128094969.
58. Anis, S.F.; Hashaikeh, R.; Hilal, N. Reverse osmosis pretreatment technologies and future trends: A comprehensive review. *Desalination* 2019, *452*, 159–195.
59. Badruzzaman, M.; Voutchkov, N.; Weinrich, L.; Jacangelo, J.G. Selection of pretreatment technologies for seawater reverse osmosis plants: A review. *Desalination* 2019, *449*, 78–91.
60. Shahabi, M.P.; McHugh, A.; Ho, G. Environmental and economic assessment of beach well intake versus open intake for seawater reverse osmosis desalination. *Desalination* **2015**, *357*, 259–266, doi:10.1016/j.desal.2014.12.003.
61. Kurihara, M.; Takeuchi, H. Earth-Friendly Seawater Desalination System Required in the 21st Century. *Chem. Eng. Technol.* **2018**, *41*, 401–412, doi:10.1002/ceat.201700430.
62. Caldera, U.; Bogdanov, D.; Breyer, C. Desalination Costs Using Renewable Energy Technologies. In *Renewable Energy Powered Desalination Handbook: Application and Thermodynamics*; Elsevier Inc., 2018; pp. 287–329 ISBN 9780128152447.
63. Caldera, U.; Breyer, C. Learning Curve for Seawater Reverse Osmosis Desalination Plants: Capital Cost Trend of the Past, Present, and Future. *Water Resour. Res.* **2017**, *53*, 10523–10538, doi:10.1002/2017WR021402.
64. Gökçek, M. Integration of hybrid power (wind-photovoltaic-diesel-battery) and seawater reverse osmosis systems for small-scale desalination applications. *Desalination* **2018**, *435*, 210–220, doi:10.1016/j.desal.2017.07.006.
65. Gilau, A.M.; Small, M.J. Designing cost-effective seawater reverse osmosis system under optimal energy options. *Renew. Energy* **2008**, *33*, 617–630, doi:10.1016/j.renene.2007.03.019.
66. Freire-Gormaly, M.; Bilton, A.M. Experimental quantification of the effect of intermittent operation on membrane performance of solar powered reverse osmosis desalination systems. *Desalination* **2018**, *435*, 188–197, doi:10.1016/j.desal.2017.09.013.
67. Li, Q.; Loy-Benitez, J.; Nam, K.; Hwangbo, S.; Rashidi, J.; Yoo, C. Sustainable and reliable design of reverse osmosis desalination with hybrid renewable energy systems through supply chain forecasting using recurrent neural networks. *Energy* **2019**, *178*, 277–292, doi:10.1016/j.energy.2019.04.114.
68. Mito, M.T.; Ma, X.; Albuflasa, H.; Davies, P.A. Reverse osmosis (RO) membrane desalination driven by wind and solar photovoltaic (PV) energy: State of the art and challenges for large-scale implementation. **2019**, doi:10.1016/j.rser.2019.06.008.
69. Atallah, M.O.; Farahat, M.A.; Lotfy, M.E.; Senjyu, T. Operation of conventional and unconventional energy sources to drive a reverse osmosis desalination plant in Sinai Peninsula, Egypt. *Renew. Energy* **2020**, *145*, 141–152, doi:https://doi.org/10.1016/j.renene.2019.05.138.
70. Peñate, B.; Castellano, F.; Bello, A.; García-Rodríguez, L. Assessment of a stand-alone gradual capacity reverse osmosis desalination plant to adapt to wind power availability: A case study. *Energy* **2011**, *36*, 4372–4384, doi:https://doi.org/10.1016/j.energy.2011.04.005.
71. Ahmed, F.E.; Hashaikeh, R.; Hilal, N. Solar powered desalination – Technology, energy and future outlook. *Desalination* **2019**, *453*, 54–76, doi:10.1016/j.desal.2018.12.002.
72. Dehghani-Sanij, A.R.; Tharumalingam, E.; Dusseault, M.B.; Fraser, R. Study of energy storage systems and environmental challenges of batteries. *Renew. Sustain. Energy Rev.* **2019**, *104*, 192–

208, doi:10.1016/j.rser.2019.01.023.
73. Pellow, M.A.; Ambrose, H.; Mulvaney, D.; Betita, R.; Shaw, S. Research gaps in environmental life cycle assessments of lithium ion batteries for grid-scale stationary energy storage systems: End-of-life options and other issues. *Sustain. Mater. Technol.* 2020, *23*, e00120.
74. Leijon, J.; Salar, D.; Engström, J.; Leijon, M.; Boström, C. Variable renewable energy sources for powering reverse osmosis desalination, with a case study of wave powered desalination for Kilifi, Kenya. *Desalination* **2020**, *494*, 114669, doi:https://doi.org/10.1016/j.desal.2020.114669.
75. Rezk, H.; Sayed, E.T.; Al-Dhaifallah, M.; Obaid, M.; El-Sayed, A.H.M.; Abdelkareem, M.A.; Olabi, A.G. Fuel cell as an effective energy storage in reverse osmosis desalination plant powered by photovoltaic system. *Energy* **2019**, *175*, 423–433, doi:https://doi.org/10.1016/j.energy.2019.02.167.
76. International Renewable Energy Agency REmap Energy Generation and Capacity Available online: https://www.irena.org/Statistics/View-Data-by-Topic/Energy-Transition/REmap-Energy-Generation-and-Capacity (accessed on Jul 15, 2020).
77. Heihsel, M.; Ali, S.M.H.; Kirchherr, J.; Lenzen, M. Renewable-powered desalination as an optimisation pathway for renewable energy systems: the case of Australia's Murray–Darling Basin. *Environ. Res. Lett.* **2019**, *14*, 124054, doi:10.1088/1748-9326/ab57ab.
78. Bano, S.; Mahmood, A.; Kim, S.J.; Lee, K.H. Graphene oxide modified polyamide nanofiltration membrane with improved flux and antifouling properties. *J. Mater. Chem. A* **2015**, *3*, 2065–2071, doi:10.1039/c4ta03607g.
79. Wang, F.; Wu, Y.; Huang, Y. Novel application of graphene oxide to improve hydrophilicity and mechanical strength of aramid nanofiber hybrid membrane. *Compos. Part A Appl. Sci. Manuf.* **2018**, *110*, 126–132, doi:10.1016/j.compositesa.2018.04.023.
80. Raval, H.D.; Rana, P.S.; Maiti, S. A novel high-flux, thin-film composite reverse osmosis membrane modified by chitosan for advanced water treatment. *RSC Adv.* **2015**, *5*, 6687–6694, doi:10.1039/c4ra12610f.
81. Ghaseminezhad, S.M.; Barikani, M.; Salehirad, M. Development of graphene oxide-cellulose acetate nanocomposite reverse osmosis membrane for seawater desalination. *Compos. Part B Eng.* **2019**, *161*, 320–327, doi:10.1016/j.compositesb.2018.10.079.
82. Ali, M.E.A.; Wang, L.; Wang, X.; Feng, X. Thin film composite membranes embedded with graphene oxide for water desalination. *Desalination* **2016**, *386*, 67–76, doi:10.1016/j.desal.2016.02.034.
83. Li, Y.; Qi, S.; Tian, M.; Widjajanti, W.; Wang, R. Fabrication of aquaporin-based biomimetic membrane for seawater desalination. *Desalination* **2019**, *467*, 103–112, doi:10.1016/j.desal.2019.06.005.
84. Werber, J.R.; Deshmukh, A.; Elimelech, M. The Critical Need for Increased Selectivity, Not Increased Water Permeability, for Desalination Membranes. *Environ. Sci. Technol. Lett* **2016**, *3*, 20, doi:10.1021/acs.estlett.6b00050.
85. Elimelech, M.; Phillip, W.A. The future of seawater desalination: Energy, technology, and the environment. *Science (80-.).* 2011, *333*, 712–717.
86. Okamoto, Y.; Lienhard, J.H. How RO membrane permeability and other performance factors affect process cost and energy use: A review. *Desalination* 2019, *470*.
87. Mazlan, N.M.; Peshev, D.; Livingston, A.G. Energy consumption for desalination — A comparison of forward osmosis with reverse osmosis, and the potential for perfect membranes. *Desalination* **2016**, *377*, 138–151, doi:10.1016/j.desal.2015.08.011.
88. Qi, S.; Wang, R.; Chaitra, G.K.M.; Torres, J.; Hu, X.; Fane, A.G. Aquaporin-based biomimetic reverse osmosis membranes: Stability and long term performance. *J. Memb. Sci.* **2016**, *508*, 94–103, doi:10.1016/j.memsci.2016.02.013.
89. Inurria, A.; Cay-Durgun, P.; Rice, D.; Zhang, H.; Seo, D.-K.; Lind, M.L.; Perreault, F. Polyamide thin-film nanocomposite membranes with graphene oxide nanosheets: Balancing membrane performance and fouling propensity. *Desalination* **2019**, *451*, 139–147, doi:10.1016/j.desal.2018.07.004.
90. Zhao, D.L.; Japip, S.; Zhang, Y.; Weber, M.; Maletzko, C.; Chung, T.S. Emerging thin-film

nanocomposite (TFN) membranes for reverse osmosis: A review. *Water Res.* 2020, *173*, 115557.
91. Cerci, Y.; Cengel, Y.; Wood, B.; Kahraman, N.; Karakas, E.S. *Improving the thermodynamic and economic efficiencies of desalination plants*; 2003;
92. Gude, V.G. Desalination and sustainability - An appraisal and current perspective. *Water Res.* 2016, *89*, 87–106.
93. Panagopoulos, A.; Haralambous, K.J.; Loizidou, M. Desalination brine disposal methods and treatment technologies - A review. *Sci. Total Environ.* 2019, *693*.
94. Miri, R.; Chouikhi, A. Ecotoxicological marine impacts from seawater desalination plants. *Desalination* **2005**, *182*, 403–410, doi:10.1016/j.desal.2005.02.034.
95. Missimer, T.M.; Maliva, R.G. Environmental issues in seawater reverse osmosis desalination: Intakes and outfalls. *Desalination* **2018**, *434*, 198–215, doi:10.1016/j.desal.2017.07.012.
96. Frank, H.; Rahav, E.; Bar-Zeev, E. Short-term effects of SWRO desalination brine on benthic heterotrophic microbial communities. *Desalination* **2017**, *417*, 52–59, doi:10.1016/j.desal.2017.04.031.
97. Panagopoulos, A.; Haralambous, K.-J.; Environmental impacts of desalination and brine treatment - Challenges and mitigation measures, Mar. Pollut. Bull. 161 (Part B) (2020) 111773, doi:10.1016/j.marpolbul.2020.111773.
98. Giwa, A.; Dufour, V.; Al Marzooqi, F.; Al Kaabi, M.; Hasan, S.W. Brine management methods: Recent innovations and current status. *Desalination* 2017, *407*, 1–23.
99. Mavukkandy, M.O.; Chabib, C.M.; Mustafa, I.; Al Ghaferi, A.; AlMarzooqi, F. Brine management in desalination industry: From waste to resources generation. *Desalination* 2019, *472*.
100. Afrasiabi, N.; Shahbazali, E. RO brine treatment and disposal methods. *Desalin. Water Treat.* **2011**, *35*, 39–53, doi:10.5004/dwt.2011.3128.
101. Manickam, S.S.; McCutcheon, J.R. Understanding mass transfer through asymmetric membranes during forward osmosis: A historical perspective and critical review on measuring structural parameter with semi-empirical models and characterization approaches. *Desalination* **2017**, *421*, 110–126, doi:https://doi.org/10.1016/j.desal.2016.12.016.
102. Ibrahim, G.P.S.; Isloor, A.M.; Yuliwati, E. *A Review : Desalination by Forward Osmosis*; Elsevier Inc., 2019; ISBN 9780128135518.
103. McGinnis, R.L.; Elimelech, M. Energy requirements of ammonia-carbon dioxide forward osmosis desalination. *Desalination* **2007**, *207*, 370–382, doi:10.1016/j.desal.2006.08.012.
104. Kim, Y.; Lee, J.H.; Kim, Y.C.; Lee, K.H.; Park, I.S.; Park, S.-J. Operation and simulation of pilot-scale forward osmosis desalination with ammonium bicarbonate. *Chem. Eng. Res. Des.* **2015**, *94*, 390–395, doi:https://doi.org/10.1016/j.cherd.2014.08.015.
105. WHO *Guidelines for Drinking-water Quality*; 2011;
106. Long, Q.; Jia, Y.; Li, J.; Yang, J.; Liu, F.; Zheng, J.; Yu, B. Recent Advance on Draw Solutes Development in Forward Osmosis. *Processes* **2018**, *6*, 165, doi:10.3390/pr6090165.
107. Li, Z.; Linares, R.V.; Sarp, S.; Amy, G. Direct and Indirect Seawater Desalination by Forward Osmosis. In *Membrane-Based Salinity Gradient Processes for Water Treatment and Power Generation*; Elsevier, 2018; pp. 245–272 ISBN 9780444639615.
108. Lee, S.; Boo, C.; Elimelech, M.; Hong, S. Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). *J. Memb. Sci.* **2010**, *365*, 34–39, doi:10.1016/j.memsci.2010.08.036.
109. Subramani, A.; Badruzzaman, M.; Oppenheimer, J.; Jacangelo, J.G. Energy minimization strategies and renewable energy utilization for desalination: A review. *Water Res.* 2011, *45*, 1907–1920.
110. McGovern, R.K.; Lienhard V, J.H. On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *J. Memb. Sci.* 2014, *469*, 245–250.
111. Awad, A.M.; Jalab, R.; Minier-Matar, J.; Adham, S.; Nasser, M.S.; Judd, S.J. The status of forward osmosis technology implementation. *Desalination* 2019, *461*, 10–21.
112. Sant'Anna, V.; Marczak, L.D.F.; Tessaro, I.C. Membrane concentration of liquid foods by forward osmosis: Process and quality view. *J. Food Eng.* 2012, *111*, 483–489.
113. Ling, M.M.; Chung, T.S. Desalination process using super hydrophilic nanoparticles via forward

osmosis integrated with ultrafiltration regeneration. *Desalination* **2011**, *278*, 194–202, doi:10.1016/j.desal.2011.05.019.
114. Tayel, A.; Nasr, P.; Sewilam, H. Forward osmosis desalination using pectin-coated magnetic nanoparticles as a draw solution. *Clean Technol. Environ. Policy* **2019**, *21*, 1617–1628, doi:10.1007/s10098-019-01738-5.
115. Guizani, M.; Maeda, T.; Ito, R.; Funamizu, N. Synthesis and Characterization of Magnetic Nanoparticles as a Candidate Draw Solution for Forward Osmosis. *J. Water Environ. Technol.* **2018**, *16*, 63–71, doi:10.2965/jwet.17-040.
116. Wang, Y.N.; Goh, K.; Li, X.; Setiawan, L.; Wang, R. Membranes and processes for forward osmosis-based desalination: Recent advances and future prospects. *Desalination* **2018**, *434*, 81–99, doi:10.1016/j.desal.2017.10.028.
117. Zeweldi, H.G.; Bendoy, A.P.; Park, M.J.; Shon, H.K.; Kim, H.-S.; Johnson, E.M.; Kim, H.; Lee, S.-P.; Chung, W.-J.; Nisola, G.M. Tetrabutylammonium 2,4,6-trimethylbenzenesulfonate as an effective and regenerable thermo-responsive ionic liquid drawing agent in forward osmosis for seawater desalination. *Desalination* **2020**, *495*, 114635, doi:https://doi.org/10.1016/j.desal.2020.114635.
118. Ju, C.; Park, C.; Kim, T.; Kang, S.; Kang, H. Thermo-responsive draw solute for forward osmosis process; poly(ionic liquid) having lower critical solution temperature characteristics. *RSC Adv.* **2019**, *9*, 29493–29501, doi:10.1039/C9RA04020J.
119. Bide, Y.; Shokrollahzadeh, S. Toward tailoring of a new draw solute for forward osmosis process: Branched poly (deep eutectic solvent)-decorated magnetic nanoparticles. *J. Mol. Liq.* **2020**, *320*, 114409, doi:https://doi.org/10.1016/j.molliq.2020.114409.
120. El Achkar, T.; Fourmentin, S.; Greige-Gerges, H. Deep eutectic solvents: An overview on their interactions with water and biochemical compounds. *J. Mol. Liq.* **2019**, *288*, 111028, doi:https://doi.org/10.1016/j.molliq.2019.111028.
121. Zhao, S.; Zou, L.; Tang, C.Y.; Mulcahy, D. Recent developments in forward osmosis: Opportunities and challenges. *J. Memb. Sci.* **2012**, *396*, 1–21, doi:10.1016/j.memsci.2011.12.023.
122. Chun, Y.; Mulcahy, D.; Zou, L.; Kim, I.S. A short review of membrane fouling in forward osmosis processes. *Membranes (Basel).* 2017, *7*.
123. Ma, N.; Wei, J.; Qi, S.; Zhao, Y.; Gao, Y.; Tang, C.Y. Nanocomposite substrates for controlling internal concentration polarization in forward osmosis membranes. *J. Memb. Sci.* **2013**, *441*, 54–62, doi:10.1016/j.memsci.2013.04.004.
124. Lim, S.; Park, M.J.; Phuntsho, S.; Tijing, L.D.; Nisola, G.M.; Shim, W.G.; Chung, W.J.; Shon, H.K. Dual-layered nanocomposite substrate membrane based on polysulfone/graphene oxide for mitigating internal concentration polarization in forward osmosis. *Polymer (Guildf).* **2017**, *110*, 36–48, doi:10.1016/j.polymer.2016.12.066.
125. Kiss, A.A.; Kattan Readi, O.M. An industrial perspective on membrane distillation processes. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 2047–2055, doi:10.1002/jctb.5674.
126. Leaper, S.; Abdel-Karim, A.; Faki, B.; Luque-Alled, J.M.; Alberto, M.; Vijayaraghavan, A.; Holmes, S.M.; Szekely, G.; Badawy, M.I.; Shokri, N.; et al. Flux-enhanced PVDF mixed matrix membranes incorporating APTS-functionalized graphene oxide for membrane distillation. *J. Memb. Sci.* **2018**, *554*, 309–323, doi:10.1016/J.MEMSCI.2018.03.013.
127. González, D.; Amigo, J.; Suárez, F. Membrane distillation: Perspectives for sustainable and improved desalination. *Renew. Sustain. Energy Rev.* **2017**, *80*, 238–259, doi:10.1016/j.rser.2017.05.078.
128. Andrés-Mañas, J.A.; Ruiz-Aguirre, A.; Acién, F.G.; Zaragoza, G. Performance increase of membrane distillation pilot scale modules operating in vacuum-enhanced air-gap configuration. *Desalination* **2020**, *475*, 114202, doi:10.1016/j.desal.2019.114202.
129. Prince, J.A.; Rana, D.; Matsuura, T.; Ayyanar, N.; Shanmugasundaram, T.S.; Singh, G. Nanofiber based triple layer hydro-philic/-phobic membrane - a solution for pore wetting in membrane distillation. *Sci. Rep.* **2015**, *4*, 6949, doi:10.1038/srep06949.
130. Alkhudhiri, A.; Darwish, N.; Hilal, N. Membrane distillation: A comprehensive review. *Desalination* **2012**, *287*, 2–18, doi:10.1016/j.desal.2011.08.027.

131. Abu-Zeid, M.A.E.R.; Zhang, Y.; Dong, H.; Zhang, L.; Chen, H.L.; Hou, L. A comprehensive review of vacuum membrane distillation technique. *Desalination* 2015, *356*, 1–14.
132. Raluy, R.G.; Schwantes, R.; Subiela, V.J.; Peñate, B.; Melián, G.; Betancort, J.R. Operational experience of a solar membrane distillation demonstration plant in Pozo Izquierdo-Gran Canaria Island. *Desalination* **2012**, *290*, 1–13, doi:10.1016/j.desal.2012.01.003.
133. Schwantes, R.; Cipollina, A.; Gross, F.; Koschikowski, J.; Pfeifle, D.; Rolletschek, M.; Subiela, V. Membrane distillation: Solar and waste heat driven demonstration plants for desalination. *Desalination* **2013**, *323*, 93–106, doi:10.1016/j.desal.2013.04.011.
134. Winter, D.; Koschikowski, J.; Wieghaus, M. Desalination using membrane distillation: Experimental studies on full scale spiral wound modules. *J. Memb. Sci.* **2011**, *375*, 104–112, doi:10.1016/j.memsci.2011.03.030.
135. Guillén-Burrieza, E.; Blanco, J.; Zaragoza, G.; Alarcón, D.-C.; Palenzuela, P.; Ibarra, M.; Gernjak, W. Experimental analysis of an air gap membrane distillation solar desalination pilot system. *J. Memb. Sci.* **2011**, *379*, 386–396, doi:10.1016/j.memsci.2011.06.009.
136. Winter, D.; Koschikowski, J.; Ripperger, S. Desalination using membrane distillation: Flux enhancement by feed water deaeration on spiral-wound modules. *J. Memb. Sci.* **2012**, *423–424*, 215–224, doi:10.1016/j.memsci.2012.08.018.
137. Ong, C.L.; Escher, W.; Paredes, S.; Khalil, A.S.G.; Michel, B. A novel concept of energy reuse from high concentration photovoltaic thermal (HCPVT) system for desalination. **2012**, doi:10.1016/j.desal.2012.04.005.
138. Zhao, K.; Heinzl, W.; Wenzel, M.; Büttner, S.; Bollen, F.; Lange, G.; Heinzl, S.; Sarda, N. Experimental study of the memsys vacuum-multi-effect-membrane-distillation (V-MEMD) module. *Desalination* **2013**, *323*, 150–160, doi:https://doi.org/10.1016/j.desal.2012.12.003.
139. Wang, Y.; Xu, Z.; Lior, N.; Zeng, H. An experimental study of solar thermal vacuum membrane distillation desalination. *Desalin. Water Treat.* **2014**, *53*, 1–11, doi:10.1080/19443994.2014.927187.
140. Zaragoza, G.; Ruiz-Aguirre, A.; Guillén-Burrieza, E. Efficiency in the use of solar thermal energy of small membrane desalination systems for decentralized water production. *Appl. Energy* **2014**, *130*, 491–499, doi:10.1016/j.apenergy.2014.02.024.
141. Nakoa, K.; Rahaoui, K.; Date, A.; Akbarzadeh, A.; Al Jabal Al Gharbi University, A.; Jabal Al Gharbi, A. An experimental review on coupling of solar pond with membrane distillation. **2015**, doi:10.1016/j.solener.2015.06.010.
142. Ruiz-Aguirre, A.; Alarcón-Padilla, D.-C.; Zaragoza, G. Productivity analysis of two spiral-wound membrane distillation prototypes coupled with solar energy. *Desalin. Water Treat.* **2015**, *55*, 2777–2785, doi:10.1080/19443994.2014.946711.
143. Duong, H.C.; Cooper, P.; Nelemans, B.; Cath, T.Y.; Nghiem, L.D. Evaluating energy consumption of air gap membrane distillation for seawater desalination at pilot scale level. *Sep. Purif. Technol.* **2016**, *166*, 55–62, doi:10.1016/j.seppur.2016.04.014.
144. Mohamed, E.S.; Boutikos, P.; Mathioulakis, E.; Belessiotis, V. Experimental evaluation of the performance and energy efficiency of a Vacuum Multi-Effect Membrane Distillation system. *Desalination* **2017**, *408*, 70–80, doi:https://doi.org/10.1016/j.desal.2016.12.020.
145. Ruiz-Aguirre, A.; Andrés-Mañas, J.A.; Fernández-Sevilla, J.M.; Zaragoza, G. Comparative characterization of three commercial spiral-wound membrane distillation modules. *Desalin. WATER Treat.* **2017**, *61*, 152–159, doi:10.5004/dwt.2016.11075.
146. Boukhriss, M.; Khemili, S.; Ben Hamida, M.B.; Ben Bacha, H. Simulation and experimental study of an AGMD membrane distillation pilot for the desalination of seawater or brackish water with zero liquid discharged. *Heat Mass Transf. und Stoffuebertragung* **2018**, *54*, 3521–3531, doi:10.1007/s00231-018-2383-6.
147. Andrés-Mañas, J.A.; Ruiz-Aguirre, A.; Acién, F.G.; Zaragoza, G. Assessment of a pilot system for seawater desalination based on vacuum multi-effect membrane distillation with enhanced heat recovery. *Desalination* **2018**, *443*, 110–121, doi:10.1016/j.desal.2018.05.025.
148. Zarzoum, K.; Zhani, K.; Ben Bacha, H.; Koschikowski, J. Experimental parametric study of membrane distillation unit using solar energy. *Sol. Energy* **2019**, *188*, 1274–1282, doi:10.1016/j.solener.2019.07.025.

149. Najib, A.; Orfi, J.; Ali, E.; Saleh, J. Thermodynamics analysis of a direct contact membrane distillation with/without heat recovery based on experimental data. *Desalination* **2019**, *466*, 52–67, doi:10.1016/j.desal.2019.05.009.
150. Lee, C.K.; Park, C.; Woo, Y.C.; Choi, J.S.; Kim, J.O. A pilot study of spiral-wound air gap membrane distillation process and its energy efficiency analysis. *Chemosphere* **2020**, *239*, 124696, doi:10.1016/j.chemosphere.2019.124696.
151. Al-Obaidani, S.; Curcio, E.; Macedonio, F.; Di Profio, G.; Al-Hinai, H.; Drioli, E. Potential of membrane distillation in seawater desalination: Thermal efficiency, sensitivity study and cost estimation. *J. Memb. Sci.* **2008**, *323*, 85–98, doi:10.1016/j.memsci.2008.06.006.
152. Deshmukh, A.; Boo, C.; Karanikola, V.; Lin, S.; Straub, A.P.; Tong, T.; Warsinger, D.M.; Elimelech, M. Membrane distillation at the water-energy nexus: Limits, opportunities, and challenges. *Energy Environ. Sci.* 2018, *11*, 1177–1196.
153. Bindels, M.; Carvalho, J.; Gonzalez, C.B.; Brand, N.; Nelemans, B. Techno-economic assessment of seawater reverse osmosis (SWRO) brine treatment with air gap membrane distillation (AGMD). *Desalination* **2020**, *489*, 114532, doi:https://doi.org/10.1016/j.desal.2020.114532.
154. Guillen-Burrieza, E.; Ruiz-Aguirre, A.; Zaragoza, G.; Arafat, H.A. Membrane fouling and cleaning in long term plant-scale membrane distillation operations. *J. Memb. Sci.* **2014**, *468*, 360–372, doi:10.1016/j.memsci.2014.05.064.
155. Castillo, E.H.C.; Thomas, N.; Al-Ketan, O.; Rowshan, R.; Abu Al-Rub, R.K.; Nghiem, L.D.; Vigneswaran, S.; Arafat, H.A.; Naidu, G. 3D printed spacers for organic fouling mitigation in membrane distillation. *J. Memb. Sci.* **2019**, *581*, 331–343, doi:10.1016/j.memsci.2019.03.040.
156. Jouhara, H.; Khordehgah, N.; Almahmoud, S.; Delpech, B.; Chauhan, A.; Tassou, S.A. Waste heat recovery technologies and applications. *Therm. Sci. Eng. Prog.* 2018, *6*, 268–289.
157. Rezaei, M.; Warsinger, D.M.; Lienhard V, J.H.; Duke, M.C.; Matsuura, T.; Samhaber, W.M. Wetting phenomena in membrane distillation: Mechanisms, reversal, and prevention. *Water Res.* 2018, *139*, 329–352.
158. Huang, Y.-X.; Wang, Z.; Lin, S. Developing Anti-Wetting and Anti-Fouling Membranes for Membrane Distillation Available online: https://www.usbr.gov/research/dwpr/DWPR_Reports.html (accessed on Nov 9, 2019).
159. Zhang, Y.; Peng, Y.; Ji, S.; Li, Z.; Chen, P. Review of thermal efficiency and heat recycling in membrane distillation processes. *Desalination* **2015**, *367*, 223–239, doi:https://doi.org/10.1016/j.desal.2015.04.013.
160. Wang, Z.; Chen, Y.; Sun, X.; Duddu, R.; Lin, S. Mechanism of pore wetting in membrane distillation with alcohol vs. surfactant. *J. Memb. Sci.* **2018**, *559*, 183–195, doi:10.1016/j.memsci.2018.04.045.
161. Himma, N.F.; Prasetya, N.; Anisah, S.; Wenten, I.G. Superhydrophobic membrane: progress in preparation and its separation properties. *Rev. Chem. Eng.* **2019**, *35*, 211–238, doi:10.1515/revce-2017-0030.
162. Hou, D.; Christie, K.S.S.; Wang, K.; Tang, M.; Wang, D.; Wang, J. Biomimetic superhydrophobic membrane for membrane distillation with robust wetting and fouling resistance. *J. Memb. Sci.* **2020**, *599*, 117708, doi:10.1016/j.memsci.2019.117708.
163. Kharraz, J.A.; An, A.K. Patterned superhydrophobic polyvinylidene fluoride (PVDF) membranes for membrane distillation: Enhanced flux with improved fouling and wetting resistance. *J. Memb. Sci.* **2020**, *595*, 117596, doi:10.1016/j.memsci.2019.117596.
164. Nthunya, L.N.; Gutierrez, L.; Khumalo, N.; Derese, S.; Mamba, B.B.; Verliefde, A.R.; Mhlanga, S.D. Superhydrophobic PVDF nanofibre membranes coated with an organic fouling resistant hydrophilic active layer for direct-contact membrane distillation. *Colloids Surfaces A Physicochem. Eng. Asp.* **2019**, *575*, 363–372, doi:10.1016/j.colsurfa.2019.05.031.
165. Warsinger, D.M.; Swaminathan, J.; Guillen-Burrieza, E.; Arafat, H.A.; Lienhard V, J.H. Scaling and fouling in membrane distillation for desalination applications: A review. **2014**, doi:10.1016/j.desal.2014.06.031.
166. Nguyen, Q.M.; Jeong, S.; Lee, S. Characteristics of membrane foulants at different degrees of SWRO brine concentration by membrane distillation. *Desalination* **2017**, *409*, 7–20,

doi:10.1016/j.desal.2017.01.007.
167. Naidu, G.; Jeong, S.; Vigneswaran, S.; Hwang, T.-M.; Choi, Y.-J.; Kim, S.-H. A review on fouling of membrane distillation. *Desalin. Water Treat.* **2016**, *57*, 10052–10076, doi:10.1080/19443994.2015.1040271.
168. Gryta, M. Calcium sulphate scaling in membrane distillation process ‡. *Chem. Pap.* **2009**, *63*, 146–151, doi:10.2478/s11696-008-0095-y.
169. Curcio, E.; Ji, X.; Di Profio, G.; Sulaiman, A.O.; Fontananova, E.; Drioli, E. Membrane distillation operated at high seawater concentration factors: Role of the membrane on CaCO3 scaling in presence of humic acid. *J. Memb. Sci.* **2010**, *346*, 263–269, doi:10.1016/j.memsci.2009.09.044.
170. He, F.; Sirkar, K.K.; Gilron, J. Studies on scaling of membranes in desalination by direct contact membrane distillation: CaCO3 and mixed CaCO3/CaSO4 systems. *Chem. Eng. Sci.* **2009**, *64*, 1844–1859, doi:10.1016/j.ces.2008.12.036.
171. Lee, J.; Boo, C.; Ryu, W.H.; Taylor, A.D.; Elimelech, M. Development of Omniphobic Desalination Membranes Using a Charged Electrospun Nanofiber Scaffold. *ACS Appl. Mater. Interfaces* **2016**, *8*, 11154–11161, doi:10.1021/acsami.6b02419.
172. Lin, S.; Nejati, S.; Boo, C.; Hu, Y.; Osuji, C.O.; Elimelech, M. Omniphobic Membrane for Robust Membrane Distillation. *Environ. Sci. Technol. Lett.* **2014**, *1*, 443–447, doi:10.1021/ez500267p.
173. Cheng, D.; Zhao, L.; Li, N.; Smith, S.J.D.; Wu, D.; Zhang, J.; Ng, D.; Wu, C.; Martinez, M.R.; Batten, M.P.; et al. Aluminum fumarate MOF/PVDF hollow fiber membrane for enhancement of water flux and thermal efficiency in direct contact membrane distillation. *J. Memb. Sci.* **2019**, *588*, doi:10.1016/j.memsci.2019.117204.
174. Yang, F.; Efome, J.E.; Rana, D.; Matsuura, T.; Lan, C. Metal–Organic Frameworks Supported on Nanofiber for Desalination by Direct Contact Membrane Distillation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 11251–11260, doi:10.1021/acsami.8b01371.
175. Kebria, M.R.S.; Rahimpour, A.; Bakeri, G.; Abedini, R. Experimental and theoretical investigation of thin ZIF-8/chitosan coated layer on air gap membrane distillation performance of PVDF membrane. *Desalination* **2019**, *450*, 21–32, doi:10.1016/j.desal.2018.10.023.
176. Tijing, L.D.; Woo, Y.C.; Shim, W.G.; He, T.; Choi, J.S.; Kim, S.H.; Shon, H.K. Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation. *J. Memb. Sci.* **2016**, *502*, 158–170, doi:10.1016/j.memsci.2015.12.014.
177. Abdel-Karim, A.; Luque-Alled, J.M.; Leaper, S.; Alberto, M.; Fan, X.; Vijayaraghavan, A.; Gad-Allah, T.A.; El-Kalliny, A.S.; Szekely, G.; Ahmed, S.I.A.; et al. PVDF membranes containing reduced graphene oxide: Effect of degree of reduction on membrane distillation performance. *Desalination* **2019**, *452*, 196–207, doi:10.1016/j.desal.2018.11.014.
178. Camacho, L.M.; Pinion, T.A.; Olatunji, S.O. Behavior of mixed-matrix graphene oxide – Polysulfone membranes in the process of direct contact membrane distillation. *Sep. Purif. Technol.* **2020**, *240*, 116645, doi:10.1016/j.seppur.2020.116645.
179. Intrchom, W.; Roy, S.; Humoud, M.; Mitra, S.; Intrchom, W.; Roy, S.; Humoud, M.S.; Mitra, S. Immobilization of Graphene Oxide on the Permeate Side of a Membrane Distillation Membrane to Enhance Flux. *Membranes (Basel).* **2018**, *8*, 63, doi:10.3390/membranes8030063.
180. Leaper, S.; Abdel-Karim, A.; Gorgojo, P. The use of carbon nanomaterials in membrane distillation membranes: A review. *Front. Chem. Sci. Eng.* **2020**, doi:https://doi.org/10.1007/s11705-020-1993-y.
181. Karama Alsebaeai, M.; Latif Ahmad, A. Membrane distillation: Progress in the improvement of dedicated membranes for enhanced hydrophobicity and desalination performance. **2020**, doi:10.1016/j.jiec.2020.03.006.
182. Hamed, O.A.; Al-Sofi, M.A.K.; Imam, M.; Mustafa, G.M.; Ba Mardouf, K.; Al-Washmi, H. Thermal performance of multi-stage flash distillation plants in Saudi Arabia. *Desalination* **2000**, *128*, 281–292, doi:10.1016/S0011-9164(00)00043-6.
183. He, F.; Gilron, J.; Sirkar, K.K. High water recovery in direct contact membrane distillation using a series of cascades. *Desalination* **2013**, *323*, 48–54,

doi:https://doi.org/10.1016/j.desal.2012.08.006.
184. Lokare, O.R.; Tavakkoli, S.; Khanna, V.; Vidic, R.D. Importance of feed recirculation for the overall energy consumption in membrane distillation systems. *Desalination* **2018**, *428*, 250–254, doi:10.1016/j.desal.2017.11.037.
185. Długołęcki, P.; van der Wal, A. Energy Recovery in Membrane Capacitive Deionization. *Environ. Sci. Technol.* **2013**, *47*, 4904–4910, doi:10.1021/es3053202.
186. Jeon, S. Il; Park, H.R.; Yeo, J.G.; Yang, S.; Cho, C.H.; Han, M.H.; Kim, D.K. Desalination via a new membrane capacitive deionization process utilizing flow-electrodes. *Energy Environ. Sci.* **2013**, *6*, 1471–1475, doi:10.1039/c3ee24443a.
187. Suss, M.E.; Porada, S.; Sun, X.; Biesheuvel, P.M.; Yoon, J.; Presser, V. Water desalination via capacitive deionization: what is it and what can we expect from it? *Energy Environ. Sci.* **2015**, *8*, 2296–2319, doi:10.1039/C5EE00519A.
188. Hassanvand, A.; Wei, K.; Talebi, S.; Chen, G.Q.; Kentish, S.E. The role of ion exchange membranes in membrane capacitive deionisation. *Membranes (Basel).* 2017, *7*.
189. Tang, K.; Kim, Y.; Chang, J.; Mayes, R.T.; Gabitto, J.; Yiacoumi, S.; Tsouris, C. Seawater desalination by over-potential membrane capacitive deionization: Opportunities and hurdles. *Chem. Eng. J.* **2019**, *357*, 103–111, doi:10.1016/j.cej.2018.09.121.
190. Srimuk, P.; Lee, J.; Fleischmann, S.; Choudhury, S.; Ackel, N.J.¨; Zeiger, M.; Kim, C.; Aslan, M.; Presser, V. Faradaic deionization of brackish and sea water via pseudocapacitive cation and anion intercalation into few-layered molybdenum disulfide. **2017**, doi:10.1039/c7ta03120c.
191. Srimuk, P.; Husmann, S.; Presser, V. Low voltage operation of a silver/silver chloride battery with high desalination capacity in seawater. *RSC Adv.* **2019**, *9*, 14849–14858, doi:10.1039/C9RA02570G.
192. Nativ, P.; Lahav, O.; Gendel, Y. Separation of divalent and monovalent ions using flow-electrode capacitive deionization with nanofiltration membranes. *Desalination* **2018**, *425*, 123–129, doi:https://doi.org/10.1016/j.desal.2017.10.026.
193. Choi, J.; Lee, H.; Hong, S. Capacitive deionization (CDI) integrated with monovalent cation selective membrane for producing divalent cation-rich solution. *Desalination* **2016**, *400*, 38–46, doi:https://doi.org/10.1016/j.desal.2016.09.016.
194. Chung, H.J.; Kim, J.; Kim, D.I.; Gwak, G.; Hong, S. Feasibility study of reverse osmosis-flow capacitive deionization (RO-FCDI) for energy-efficient desalination using seawater as the flow-electrode aqueous electrolyte. **2020**, doi:10.1016/j.desal.2020.114326.
195. McNair, R.; Szekely, G.; Dryfe, R.A.W. Ion-Exchange Materials for Membrane Capacitive Deionization. *ACS ES&T Water* **2020**, doi:10.1021/acsestwater.0c00123.
196. Porada, S.; Zhang, L.; Dykstra, J.E. Energy consumption in membrane capacitive deionization and comparison with reverse osmosis. *Desalination* **2020**, *488*, 114383, doi:https://doi.org/10.1016/j.desal.2020.114383.
197. Hand, S.; Guest, J.S.; Cusick, R.D. Technoeconomic Analysis of Brackish Water Capacitive Deionization: Navigating Tradeoffs between Performance, Lifetime, and Material Costs. *Environ. Sci. Technol.* **2019**, *53*, 13353–13363, doi:10.1021/acs.est.9b04347.
198. Qin, M.; Deshmukh, A.; Epsztein, R.; Patel, S.K.; Owoseni, O.M.; Walker, W.S.; Elimelech, M. Comparison of energy consumption in desalination by capacitive deionization and reverse osmosis. *Desalination* **2019**, *455*, 100–114, doi:10.1016/j.desal.2019.01.003.
199. Patel, S.K.; Qin, M.; Walker, W.S.; Elimelech, M. Energy Efficiency of Electro-Driven Brackish Water Desalination: Electrodialysis Significantly Outperforms Membrane Capacitive Deionization. *Environ. Sci. Technol.* **2020**, *54*, 3663–3677, doi:10.1021/acs.est.9b07482.
200. Shiu, H.Y.; Lee, M.; Chao, Y.; Chang, K.C.; Hou, C.H.; Chiueh, P. Te Hotspot analysis and improvement schemes for capacitive deionization (CDI) using life cycle assessment. *Desalination* **2019**, *468*, doi:10.1016/j.desal.2019.114087.
201. Yu, T.H.; Shiu, H.Y.; Lee, M.; Chiueh, P. Te; Hou, C.H. Life cycle assessment of environmental impacts and energy demand for capacitive deionization technology. *Desalination* **2016**, *399*, 53–60, doi:10.1016/j.desal.2016.08.007.
202. Seo, J.; Kim, Y.M.; Chae, S.H.; Lim, S.J.; Park, H.; Kim, J.H. An optimization strategy for a forward osmosis-reverse osmosis hybrid process for wastewater reuse and seawater

desalination: A modeling study. *Desalination* **2019**, *463*, 40–49, doi:10.1016/j.desal.2019.03.012.
203. Yangali-Quintanilla, V.; Li, Z.; Valladares, R.; Li, Q.; Amy, G. Indirect desalination of Red Sea water with forward osmosis and low pressure reverse osmosis for water reuse. *Desalination* **2011**, *280*, 160–166, doi:10.1016/j.desal.2011.06.066.
204. Arjmandi, M.; Pourafshari Chenar, M.; Altaee, A.; Arjmandi, A.; Peyravi, M.; Jahanshahi, M.; Binaeian, E. Caspian seawater desalination and whey concentration through forward osmosis (FO)-reverse osmosis (RO) and FO-FO-RO hybrid systems: Experimental and theoretical study. *J. Water Process Eng.* **2020**, *37*, 101492, doi:https://doi.org/10.1016/j.jwpe.2020.101492.
205. Lee, S.; Choi, J.; Park, Y.G.; Shon, H.; Ahn, C.H.; Kim, S.H. Hybrid desalination processes for beneficial use of reverse osmosis brine: Current status and future prospects. *Desalination* 2019, *454*, 104–111.
206. Ji, X.; Curcio, E.; Al Obaidani, S.; Di Profio, G.; Fontananova, E.; Drioli, E. Membrane distillation-crystallization of seawater reverse osmosis brines. *Sep. Purif. Technol.* **2010**, *71*, 76–82, doi:10.1016/j.seppur.2009.11.004.
207. Creusen, R.; van Medevoort, J.; Roelands, M.; van Renesse van Duivenbode, A.; Hanemaaijer, J.H.; van Leerdam, R. Integrated membrane distillation–crystallization: Process design and cost estimations for seawater treatment and fluxes of single salt solutions. *Desalination* **2013**, *323*, 8–16, doi:10.1016/j.desal.2013.02.013.
208. Guan, G.; Wang, R.; Wicaksana, F.; Yang, X.; Fane, A.G. Analysis of membrane distillation crystallization system for high salinity brine treatment with zero discharge using Aspen flowsheet simulation. *Ind. Eng. Chem. Res.* **2012**, *51*, 13405–13413, doi:10.1021/ie3002183.
209. Macedonio, F.; Curcio, E.; Drioli, E. Integrated membrane systems for seawater desalination: energetic and exergetic analysis, economic evaluation, experimental study. *Desalination* **2007**, *203*, 260–276, doi:10.1016/j.desal.2006.02.021.
210. Naidu, G.; Tijing, L.; Johir, M.A.H.; Shon, H.; Vigneswaran, S. Hybrid membrane distillation: Resource, nutrient and energy recovery. *J. Memb. Sci.* 2020, *599*, 117832.
211. Ruiz-Aguirre, A.; Andrés-Mañas, J.A.; Fernández-Sevilla, J.M.; Zaragoza, G. Experimental characterization and optimization of multi-channel spiral wound air gap membrane distillation modules for seawater desalination. *Sep. Purif. Technol.* **2018**, *205*, 212–222, doi:10.1016/j.seppur.2018.05.044.
212. Akther, N.; Sodiq, A.; Giwa, A.; Daer, S.; Arafat, H.A.; Hasan, S.W. Recent advancements in forward osmosis desalination: A review. *Chem. Eng. J.* **2015**, *281*, 502–522, doi:10.1016/j.cej.2015.05.080.
213. Ang, W.L.; Wahab Mohammad, A.; Johnson, D.; Hilal, N. Forward osmosis research trends in desalination and wastewater treatment: A review of research trends over the past decade. *J. Water Process Eng.* 2019, *31*.
214. Osipi, S.R.; Secchi, A.R.; Borges, C.P. Cost analysis of forward osmosis and reverse osmosis in a case study. In; Basile, A., Cassano, A., Rastogi, N.K.B.T.-C.T. and F.D. on (Bio-) M., Eds.; Elsevier, 2020; pp. 305–324 ISBN 978-0-12-816777-9.
215. Zaragoza, G.; Andrés-Mañas, J.A.; Ruiz-Aguirre, A. Commercial scale membrane distillation for solar desalination. *npj Clean Water* **2018**, *1*, doi:10.1038/s41545-018-0020-z.
216. Park, K.; Kim, D.Y.; Jang, Y.H.; Kim, M. gyu; Yang, D.R.; Hong, S. Comprehensive analysis of a hybrid FO/crystallization/RO process for improving its economic feasibility to seawater desalination. *Water Res.* **2020**, *171*, 115426, doi:10.1016/j.watres.2019.115426.
217. Tufa, R.A.; Noviello, Y.; Di Profio, G.; Macedonio, F.; Ali, A.; Drioli, E.; Fontananova, E.; Bouzek, K.; Curcio, E. Integrated membrane distillation-reverse electrodialysis system for energy-efficient seawater desalination. *Appl. Energy* **2019**, *253*, 113551, doi:10.1016/j.apenergy.2019.113551.
218. Jande, Y.A.C.; Minhas, M.B.; Kim, W.S. Ultrapure water from seawater using integrated reverse osmosis-capacitive deionization system. *Desalin. Water Treat.* **2015**, *53*, 3482–3490, doi:10.1080/19443994.2013.873352.
219. Dorji, P.; Kim, D.I.; Hong, S.; Phuntsho, S.; Shon, H.K. Pilot-scale membrane capacitive deionisation for effective bromide removal and high water recovery in seawater desalination.

Desalination **2020**, *479*, 114309, doi:10.1016/j.desal.2020.114309.
220. Yao, S.; Ji, M. A Small RO and MCDI coupled seawater desalination plant and its performance simulation analysis and optimization. *Processes* **2020**, *8*, 944, doi:10.3390/PR8080944.
221. Gude, V.G.; Khandan, N.; Deng, S.; Maganti, A. Energy consumption and recovery in reverse osmosis. *Desalin. Water Treat.* 2013, *36*.
222. Ghaffour, N.; Soukane, S.; Lee, J.G.; Kim, Y.; Alpatova, A. Membrane distillation hybrids for water production and energy efficiency enhancement: A critical review. *Appl. Energy* 2019, *254*, 113698.
223. Luo, W.; Phan, H. V.; Li, G.; Hai, F.I.; Price, W.E.; Elimelech, M.; Nghiem, L.D. An Osmotic Membrane Bioreactor−Membrane Distillation System for Simultaneous Wastewater Reuse and Seawater Desalination: Performance and Implications. *Environ. Sci. Technol.* **2017**, *51*, 14311–14320, doi:10.1021/acs.est.7b02567.

Can emerging membrane-based desalination technologies replace reverse osmosis?

Clara Skuse, Alejandro Gallego-Schmid, Adisa Azapagic, Patricia Gorgojo

Supplementary information

The scoring matrix for Figure 7 in the main article is given below. Each of the five performance criteria is scored on a scale from 0 to 1, with a score of 1 assigned to the technology with the best performance for that criterion and the scores for other technologies expressed relative to 1. Therefore, higher scores are preferred. All the indicators are considered equally important.

'Low energy consumption' scores are based on the specific energy consumption (kWh/m^3) of the technologies (see Tables 2 and 3 in the manuscript). 'Ease of integrating renewable energy' scores are based on the energy grade required to power the process. 'Ease of pre-treatment' scores depend on how chemically- and energy-intensive the pre-treatment stages are, which is closely linked to the fouling propensity. 'High water recovery' scores are based on the achieved water recoveries. For stand-alone MCDI, water recovery is not considered due to a lack of data and the score has been left blank. 'Low water costs' scores are based on current predictions/simulations of the overall cost of water production, including capital and operating costs.

Table S1 *Scoring matrix for Figure 7 in the paper [a].*

Indicator	**Reverse osmosis**	**Forward osmosis**	**Membrane distillation**	**Membrane capacitive deionisation**	**Reverse osmosis + forward osmosis**	**Reverse osmosis + membrane distillation**	**Reverse osmosis + membrane capacitive deionisation**
Low energy consumption / kWh/m^3	0.8 2.5-7	0.4 3-68	0.4 49-350	0.2 83.2	1 ~1.5	0.8 3-6.5	0.6 3-11
Ease of integrating renewable energy	0.2	0.4	1	0.2	0.4	0.6	0.2
Ease of pre-treatment	0.4	0.6	0.6	0.6	1	0.4	0.4
High water recovery / %	0.4 35-50	0.4 20-50	0.6 5-90	- -	0.4 2-55	1 70-99	0.4 15-75
Low water costs / $/m^3	1 0.5-3	0.6 0.8-2	0.6 0.64-5.2	0.2 High	0.8 0.91	0.6 0.63 - 1	0.2 High

[a] For the quantitative criteria (energy consumption, water recovery and water cost) the actual values used to derive the scores are shown in the bottom left-hand corner. For the other two criteria, the scores were derived on a qualitative basis, based on their properties using authors' judgement.