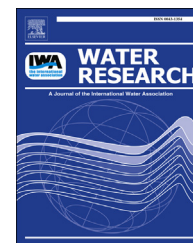


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## Review

# Emerging desalination technologies for water treatment: A critical review



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## ARTICLE INFO

## Article history:

Received 28 November 2014

Received in revised form

12 February 2015

Accepted 16 February 2015

Available online 26 February 2015

## Keywords:

Nanotechnology membranes

Industrial water desalination

Energy minimization

Produced water treatment

Reverse osmosis

## ABSTRACT

In this paper, a review of emerging desalination technologies is presented. Several technologies for desalination of municipal and industrial wastewater have been proposed and evaluated, but only certain technologies have been commercialized or are close to commercialization. This review consists of membrane-based, thermal-based and alternative technologies. Membranes based on incorporation of nanoparticles, carbon nanotubes or graphene-based ones show promise as innovative desalination technologies with superior performance in terms of water permeability and salt rejection. However, only nanocomposite membranes have been commercialized while others are still under fundamental developmental stages. Among the thermal-based technologies, membrane distillation and adsorption desalination show the most promise for enhanced performance with the availability of a waste heat source. Several alternative technologies have also been developed recently; those based on capacitive deionization have shown considerable improvements in their salt removal capacity and feed water recovery. In the same category, microbial desalination cells have been shown to desalinate high salinity water without any external energy source, but to date, scale up of the process has not been methodically evaluated. In this paper, advantages and drawbacks of each technology is discussed along with a comparison of performance, water quality and energy consumption.

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<http://dx.doi.org/10.1016/j.watres.2015.02.032>

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## 1. Introduction

Freshwater is a renewable resource, but increasing population growth and population density has strained the ability of many local supplies to sustain water quantity requirements at suitable levels of water quality. In response to the United Nations prediction that 2–7 billion people will face water scarcity by the middle of the century (Hameeteman, 2013), the water industry has become increasingly reliant upon desalination of ocean and brackish water supplies. Desalination processes are broadly categorized as thermal or membrane-based technologies (Greenlee et al., 2009). Although thermal desalination has remained the primary technology of choice in the Middle East, membrane processes, such as reverse osmosis (RO), have rapidly developed since the 1960s (Loeb and Sourirajan, 1963) and currently surpass thermal processes in new plant installations (Greenlee et al., 2009). The primary drawback with desalination is associated with costs (Subramani et al., 2011); those associated with electricity for seawater desalination using RO are 30% of the total cost of desalinated water. Higher energy consumption also translates to a corresponding increase in greenhouse gas (GHG) emissions (Raluy et al., 2005). Thus, reducing energy consumption is critical for lowering the cost of desalination and addressing environmental concerns about GHG emissions from the continued use of conventional fossil fuels as the primary energy source for seawater desalination plants.

During desalination with RO membranes, brackish water or seawater is pressurized against a semi-permeable RO membrane that allows water to pass through while rejecting salt. In order to produce desalinated water, the osmotic pressure of the feed water needs to be exceeded. The feed water to the RO is pressurized using a high pressure feed

pump to supply the necessary pressure to force water through the membrane to exceed the osmotic pressure and overcome differential pressure losses through the system (Stover, 2007). In seawater desalination applications, an energy recovery device (ERD) in combination with a booster pump is used to recover the pressure from the concentrate and reduce the required size of the high pressure pump (Stover, 2007). In brackish water applications, ERDs are seldom utilized due to the low total dissolved solids (TDS) levels, while certain full-scale plants have installed turbochargers or isobaric devices to act as interstage booster pumps (Drak and Adato, 2014).

A theoretical minimum energy exists that is required to exceed the osmotic pressure and produce desalinated water. As the salinity of the feed water or as feed water recovery increases, the minimum energy required for desalination also increases. For example, the theoretical minimum energy for seawater desalination with 35,000 mg/L of salt and a feed water recovery of 50% is 1.06 kWh/m<sup>3</sup> (Elimelech and Phillip, 2011). However, the actual energy consumption is larger for full-scale plants. The energy required for desalination using RO membranes is a function of the feed water recovery, intrinsic membrane resistance (permeability), operational flux, feed water salinity and temperature fluctuations, product water quality requirements, and system configuration (Subramani et al., 2011). The lowest energy consumption reported for an RO system is 1.58 kWh/m<sup>3</sup> at a feed water recovery of 42.5% and a flux of 10.2 L m<sup>-2</sup> h<sup>-1</sup> (Seacord et al., 2006). In addition, pre- and post-treatment contributes to additional energy requirements (Wilf and Bartels, 2005). Typically, the total energy requirement for seawater desalination using RO (including pre- and post-treatment) is on the order of 3–6 kWh/m<sup>3</sup> (Semiat, 2008; Subramani et al., 2014a,b).

Established techniques for minimizing energy usage for RO are classified according to enhanced system design, high efficiency pumping and energy recovery (Subramani et al., 2011). Desalination energy minimization techniques have also focused on feedback controls linked to the feed water salinity to optimize energy consumption in RO applications (Bartman et al., 2010; Gao et al., 2014). Control schemes utilized real-time updates on RO membrane permeability to adjust feed pressure requirements to maintain operational flux and lowest specific energy consumption (Gao et al., 2014). In recent years, significant improvements in the salt rejection capacity and permeability of membranes for treating high salinity feed waters have been achieved. Today, the average energy consumption for seawater desalination using RO is still higher than the theoretical minimum energy required and improvements in desalination membranes show promise for lowering energy consumption. New desalination technologies offer reduced feed pressure requirements while maintaining salt rejection (Subramani et al., 2011; Pendergast and Hoek, 2011). In an analysis of the impact of RO permeability and energy minimization, Zhu et al. (2009) found that when the cost of energy and membrane is considered, the benefit of developing membranes with higher permeability is less likely to be a significant driver for lower seawater desalination costs. Thus, other factors such as process improvements, development of fouling resistant membranes, lesser pretreatment and effective brine management need to be considered to lower overall desalination costs (Zhu et al., 2009, 2010).

Three major reviews on emerging desalination technologies and methods to reduce energy consumption have been recently published (Subramani et al., 2011; Peñata and García-Rodríguez, 2012; Elimelech and Phillip, 2011). Subramani et al. (2011) performed a detailed review of energy optimization techniques available for seawater desalination along with a review of renewable energy resource utilization. Peñata and García-Rodríguez (2012) reviewed the current trends and future prospects for seawater desalination to improve process performance and obtain high productivity but their review considered only RO technology and limited information was provided on innovative technologies. Elimelech and Phillip (2011) reviewed strategies to reduce energy consumption for seawater desalination and concluded that optimization of pretreatment and post treatment is the best method for energy reduction. However, pretreatment and post treatment processes contribute less than 10% of the overall energy consumption during seawater desalination (Wilf and Bartels, 2005). In the above reviews, only certain innovative technologies, such as nanocomposite reverse osmosis, carbon nanotubes and forward osmosis membranes, were included. Numerous emerging technologies have been developed recently with more performance data published in the literature specific to desalination. Thus, in our review a comprehensive description of emerging desalination technologies is provided to complement those previously published.

Specifically, the objective of this review is to critically compare emerging desalination technologies that show promise for energy minimization and improved performance; it is divided according to the principle of operation

(membrane-based and thermal-based) while discussing alternative technologies as well. The first category consists of new desalination technologies that utilize membranes for separation and the second on those that utilize a temperature gradient for separation to occur. Finally, alternative technologies are reviewed and consist of those that utilize mechanisms different from membranes or thermal technologies. Application potential of these three technology categories in municipal and industrial water sectors are discussed along with their implementation challenges.

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## 2. Membrane-based technologies

In this section, emerging desalination technologies based on membrane processes is discussed. This section is divided into two sub-sections: the first sub-section deals with development and application of new generation membrane material for desalination and the second sub-section provides a review of emerging technologies based on membranes for desalination. Certain membrane-based technologies are close to commercialization whereas others are still under developmental stages. A comparison of membrane-based technologies is provided in Table 1.

### 2.1. Novel membranes

#### 2.1.1. Nanocomposite membranes

A thin film nanotechnology (TFN) membrane incorporates Linde type A zeolite nanoparticles into the thin film layer of the membrane to enhance permeability of water while maintaining salt rejection (Jeong et al., 2007). Linde type A is an aluminosilicate zeolite that exhibits a three dimensional pore structure with the pores perpendicular to each other in the x, y and z planes. The utilization of these nanoparticles increases the flux through the membrane, and thus provides an opportunity to reduce energy consumption through a lowered feed pressure while maintaining the same water production levels. TFN technology utilizes an interfacial polymerization process with benign nanoparticles dispersed in one or more of the monomer solutions in order to create the nanocomposite membranes (Kurth et al., 2014). These membranes have a measurably smoother, more hydrophilic, and more negatively charged surface in comparison with a typically pure polyamide thin film composite (TFC) membrane due to the presence of the nanoparticle pores (Jeong et al., 2007). These surface properties improve the permeability of the membranes, essentially creating molecular, hydrophilic tunnels across the membrane matrix which water preferentially passes through, while the greater negative charge on the nanoparticle pore walls enhance ion exclusion, and thus maintain salt rejection (Pendergast et al., 2013). The hydrophilic nanoparticles make the membrane as a whole – which is typically hydrophobic in its pure polyamide composition – more hydrophilic, leading to less susceptibility to membrane fouling. In an early study on TFN technology, at the highest levels of nanoparticle loading, permeability was reported to be almost twice that of a pure polyamide thin film composite formed by the same polymerization process while the salt rejection was maintained for the TFN membrane (Jeong et al.,

**Table 1 – Comparison of membrane-based technologies.**

Technology	Advantages	Drawbacks	Recovery range	Feed water quality	Treated water quality	Energy consumption	Cost impacts
Nanocomposite Membranes	<ul style="list-style-type: none"> <li>- Increased permeability while maintaining salt rejection.</li> <li>- Reduced feed pressure requirement.</li> <li>- Reduced footprint at high flux operation.</li> </ul>	<ul style="list-style-type: none"> <li>- More expensive membrane elements.</li> <li>- Retrofitting of existing plants may require a variable speed drive (VFD) on pumps.</li> </ul>	Variable, 40–50%.	32,000–34,000 mg/L (TDS). Brackish water membranes are under development.	Similar to TFC RO membranes.	1.73 kWh/m <sup>3</sup> –2.49 kWh/m <sup>3</sup> for seawater desalination with TDS of 32,000 mg/L (Subramani et al., 2014a).	<ul style="list-style-type: none"> <li>- Potential to reduce costs through: decreased energy with same water production, increased flux with same feed pressure, decreased footprint with same water production.</li> <li>- Currently applicable only for seawater desalination.</li> </ul>
Aquaporin membranes	<ul style="list-style-type: none"> <li>- High permeability (an order of magnitude higher than commercial RO membranes).</li> <li>- 100% rejection of solute molecules.</li> <li>- Osmotically-driven process without the need for applied pressure.</li> </ul>	<ul style="list-style-type: none"> <li>- Synthetic approach to producing and purifying aquaporin in large quantities is essential.</li> <li>- Limited experimental data with real feed water sources.</li> <li>- Chemical resistance of aquaporin is unknown. Structural strength of membranes is unknown.</li> </ul>	Not known.	No limitation on feed water TDS.	100% rejection of TDS.	Not known. Expected to be low due to absence of feed pressure requirement.	Not known. Technology still at bench-scale level. Costs will depend on the production of aquaporins on a large scale to synthesize membranes.
Nanotube membranes	<ul style="list-style-type: none"> <li>- High permeability (10 times higher than commercial RO membranes);</li> <li>- High rejection of salt.</li> </ul>	<ul style="list-style-type: none"> <li>- Packing density of nanotubes on substrate not known for practical applications.</li> <li>- Limited experimental data with real feed water sources.</li> <li>- Rejection of specific contaminants is not known and functionalization of nanotubes is not known.</li> <li>- Stability of nanomaterial within support/substrate layer is not known.</li> <li>- Associated health risks with release of nanomaterial into treated water stream is not known.</li> </ul>	Not known.	Not known.	More than 95% rejection of salt.	Not known. Expected to be similar to RO membranes. Desalination applications limited by thermodynamic restriction.	Not known. Technology still at bench-scale level. Costs will depend on packing density of nanotubes.
Graphene-based membranes	<ul style="list-style-type: none"> <li>- Good mechanical properties.</li> <li>- Fast water transport and high rejection capability.</li> </ul>	<ul style="list-style-type: none"> <li>- Requires applied pressure.</li> <li>- Only bench-scale and modeling studies have been performed.</li> </ul>	Not known.	Not known. Up to seawater salinity must be possible.	Not known.	Not known. Expected to be similar to RO membranes. Desalination	Not known. Technology still at bench-scale level. Costs will depend on the ability to synthesize large quantities

(continued on next page)

Table 1 – (continued)

Technology	Advantages	Drawbacks	Recovery range	Feed water quality	Treated water quality	Energy consumption	Cost impacts
	<ul style="list-style-type: none"> <li>- Membranes can be tuned to be ion selective.</li> </ul>					<p>applications of graphene material to limited by thermodynamic restriction.</p> <p>of form membranes.</p>	
Semi-batch RO	<ul style="list-style-type: none"> <li>- Reduced energy consumption.</li> <li>- Energy recovery devices are not required.</li> <li>- Higher feed water recovery for brackish and wastewater applications (&gt;90%).</li> <li>- Higher operational flux (&gt;30%) with fewer membrane elements.</li> <li>- Reduced plant footprint.</li> <li>- Less susceptibility to fouling due to high cross-flow velocity. Potential for lesser pretreatment.</li> </ul>	<ul style="list-style-type: none"> <li>- Only pilot and demonstration scale testing data is available.</li> <li>- Effect of high cross flow and brine circulation on membrane life is unknown.</li> </ul>	<ul style="list-style-type: none"> <li>- Up to 55% for seawater desalination.</li> <li>- Up to 95% for brackish water and wastewater desalination.</li> </ul>	Up to 45,000 mg/L (TDS).	Similar to conventional RO.	<p>2.74 kWh/m<sup>3</sup> for seawater desalination with TDS of 37,000 mg/L (Subramani et al., 2014b).</p>	<ul style="list-style-type: none"> <li>- The utilization of fewer membranes and no requirement for ERDs reduces capital expenditures substantially for seawater desalination.</li> <li>- Lower fouling potential could reduce operating costs with respect to frequency of chemical cleanings.</li> </ul>
Forward osmosis	<ul style="list-style-type: none"> <li>- Osmotically-driven process without the need for applied pressure.</li> <li>- Multiple applications.</li> <li>- Applicable for high salinity desalination.</li> <li>- Potential savings in energy consumption when combined with RO.</li> <li>- Can utilize waste heat source for regeneration of draw solution.</li> <li>- High feed water recovery.</li> <li>- Lower fouling potential due to lack of applied pressure. Potential for lesser pretreatment.</li> </ul>	<ul style="list-style-type: none"> <li>- Limited full-scale installations.</li> <li>- Difficult to choose optimal osmotic agent (draw solution).</li> <li>- Lower flux rates than RO leading to higher membrane area requirement.</li> <li>- Requires membranes specific for FO applications.</li> </ul>	<ul style="list-style-type: none"> <li>- 91.9% at leachate treatment plant.</li> <li>- 35% at full-scale seawater facility.</li> <li>- 96% in FO/RO hybrid systems for wastewater.</li> </ul>	500 to 175,000 mg/L (TDS).	Similar to TFC RO membranes.	Similar to RO for seawater desalination.	<ul style="list-style-type: none"> <li>- The costs depend on the application of the technology. In strictly FO applications with gaseous mixtures as draw solution, the primary cost will be thermal energy required for recovery/re-concentration of the draw solution.</li> <li>- In FO/RO hybrid systems using reuse water as feed to FO and RO for seawater desalination, the cost of desalinating water will be lower as less electrical energy will be required in the RO stage due to the dilution of feed seawater.</li> </ul>

2007). The highest TFN element permeate flow rate reported was 52 m<sup>3</sup>/d and a minimum NaCl rejection of 99.7% (NanoH<sub>2</sub>O, Inc., 2011).

At bench scale, Pendergast et al. (2013) evaluated two different types of TFN membranes, which were developed to improve water permeability and salt rejection along with improved resistance to physical compaction. When zeolite nanoparticles were embedded within the polyamide active layer, compaction of the membrane was suppressed. Incorporation of the nanoparticles in the polysulfone support layer also resulted in a smaller water contact angle and higher ultimate tensile strength when compared to an unmodified polysulfone support layer. Although water permeability was enhanced with the incorporation of zeolite nanoparticles in the polyamide matrix while maintaining the salt rejection, comparisons were made with hand cast TFC membranes. It is important to note that results based on these bench-scale studies may not be directly comparable to TFC membranes obtained from commercial manufacturers. Thus, other studies have compared TFN membranes with commercially available TFC membranes.

Hofs et al. (2013) compared TFN and TFC membrane elements at pilot scale and reported that TFN elements exhibited 1.4 times higher permeability when compared to TFC membrane elements. In this study, a TFN membrane element SW365ES was compared with a TFC membrane element SW30XHR-440i from DowFilmtec. Although the TFN membrane exhibited higher water permeability while maintaining similar salt rejection, boron rejection and low molecular weight nitrosamines rejection was lower when compared to the TFC membrane. New generation TFN membranes with improved boron rejection have been recently introduced in the market but the water permeability of these new generation TFN membranes are similar to TFC membranes. It is also unclear if the concentration of nanoparticles (<6 wt%) in the TFN membrane's active layer results in the increased permeability.

In a recent study, Subramani et al. (2014a) compared NanoH<sub>2</sub>O's TFN membranes Qfx400R and Qfx400ES with DowFilmtec's TFC membranes SW30XLE and SW30ULE for desalination of Pacific Ocean seawater with a TDS of 34,000 mg/L. The specific energy consumption for the TFN membranes was 2.24–2.55 kWh/m<sup>3</sup> for fluxes of 11.9–15.3 L m<sup>-2</sup> h<sup>-1</sup> and a system recovery of 40–55%. The specific energy consumption for the TFC membranes was 2.28–2.61 kWh/m<sup>3</sup> for the same flux and recovery conditions. Thus, the savings in energy consumption was less than 6% using TFN membranes. The use of TFN membranes also resulted in lower boron rejection when compared to TFC membranes. However, in seawater desalination a second pass RO system with brackish water membranes operated at a pH of approximately 10.3 is utilized to achieve very low levels (<0.5 mg/L) of boron in the treated water stream. Selection of TFN RO membranes over TFC RO membranes also requires a careful consideration of life cycle costs. When the TFN RO membrane element cost is higher, capital costs will be higher. However, life cycle costs of the plant could potentially be lower due to savings in energy costs over the plant operational life.

### 2.1.2. Aquaporin membranes

Aquaporins are the protein channels that control water flux across biological membranes. They are found widely in human tissues with the purpose of rapid, passive transport of water molecules across cell membranes (Pendergast and Hoek, 2011). Water movement in an aquaporin is mediated by selective, rapid diffusion and caused by osmotic gradients (Agre, 2003). Aquaporin-1 (AQP1), with selective extracellular and intracellular vestibules at each end, allows water molecules to pass rapidly in a single-file line, while excluding proteins and ions by an electrostatic tuning mechanism (Agre, 2003; Sui et al., 2001). The result leads to only water molecules being transported through the aquaporin channels and charged ions being rejected (Sui et al., 2001; Bowen, 2006).

Aquaporin membranes are considered to be 100 times more permeable than commercial RO membranes (Kaufman et al., 2010). Highly permeable and selective membranes based on the incorporation of the functional water channel protein Aquaporin Z into a novel triblock copolymer have been shown to have significantly higher water transport than existing RO membranes (Kumar et al., 2007). Kumar et al. (2007) utilized Aquaporin-Z from *Escherichia coli* bacterial cells in a polymeric membrane. The aquaporin was selected based on the ability for high water permeation and selectivity. A symmetric triblock copolymer with a high hydrophobic to hydrophilic block ratio was selected to mimic a lipid-bilayer membrane. The resulting protein-polymer membrane demonstrated over an order of magnitude increase in water permeability over a purely polymeric membrane. The aquaporin membrane also rejected glucose, glycerol, salt and urea to detection limits. In another study, Zhu et al. (2004) simulated the permeation of water molecules through AQP1 (Zhu et al., 2004). Two factors were proposed for the transport of water molecules: molecular and diffusion permeability. The former was a result of concentration differences leading to mass transfer while the latter was due to random movement of molecules with no net transfer (Zhu et al., 2004). Wang et al. (2012) constructed an aquaporin membrane on a porous support by a combination of pressure assisted vesicle adsorption and covalent-conjugation-driven vesicle fusion. The water flux through the membrane ranged between 34.1 and 73.8 L m<sup>-2</sup> h<sup>-1</sup>. The experimental obtained water flux was <10% of the theoretical water flux obtained using computer modeling.

Studies have also been performed where aquaporins were deposited onto commercially available membranes. Kaufman et al. (2010) deposited an aquaporin onto commercially NF270 and NTR7450 membranes via vesicle fusion at a pH of 2.0. The investigators demonstrated supported lipid bilayers formed atop dense water permeable nanofiltration (NF) membranes that can be operated under a mechanical driving force as with RO membranes. NF membranes were chosen as the support due to their high permeability and low surface roughness that allowed for minimal distortion of the lipid bilayer.

Membranes based on aquaporins show promise for desalination where the driving mechanism is an osmotic pressure gradient (salt concentration), rather than a mechanically applied pressure gradient as in RO (Pendergast and Hoek, 2011). With 75% coverage of aquaporins on a membrane, an

order of magnitude increase in hydraulic permeability has been predicted (Kaufman et al., 2010). Due to the absence of applied pressure, energy consumption is expected to be substantially lower as compared to RO membranes. Due to the difficulty of attaining large quantities of proteins and producing large areas of membrane material, aquaporin-based membranes are not widely available for commercialization (Pendergast and Hoek, 2011).

### 2.1.3. Nanotube membranes

Carbon nanotubes have been evaluated for desalination due to their rapid water transport properties, large surface area and ease of functionalization (Majumder et al., 2005; Hummer et al., 2001; Humplik et al., 2011; Hinds et al., 2004; Corry, 2008). Desalination energy consumption using carbon nanotubes can be significantly lower when compared to RO due to the nanotubes' water mass transport being 2 to 5 times higher than theoretical predictions by the Hagen–Poiseuille equation (Holt et al., 2006; Ahadian and Kawazoe, 2009). Water and ions are transported through membranes formed from carbon nanotubes that range in diameter from 6 to 11 Å. The high flow rate has been attributed to the atomic smoothness and molecular ordering of the nanotubes through which water molecules are passed on a one dimensional single-file procession (Hummer et al., 2001; Kalra et al., 2003). The challenge with the use of carbon nanotubes for desalination has been due to the complexities involved in the fabrication of sub-nanometer tubes.

Carbon nanotubes have been incorporated onto several types of substrates using catalytic chemical vapor deposition (CVD) (Holt et al., 2006; Kim et al., 2007; Yoshikawa et al., 2008). Results for desalination applications showed that narrow carbon nanotubes could completely reject ions due to the large energy barrier at the nanotube openings created by stable hydrogen bond formation (Corry, 2008). On the contrary, water does not form stable hydrogen bonds with the nanotubes and permeates rapidly. Membranes incorporating carbon nanotubes have been found to be promising candidates for water desalination, as the size and uniformity of the tubes can achieve the desired salt rejection (Corry, 2008). A 10-fold permeability increase is expected using a carbon nanotube RO membrane (Corry, 2008; Holt et al., 2006; Sholl and Johnson, 2006).

Ion rejection by carbon nanotube membranes is governed by the steric effects between nanopores and the hydrated diameter of ions along with the Donnan equilibrium of the membrane surface (Ahn et al., 2012). Corry (2008) found that the rejection of ions by carbon nanotubes was dependent on the pore size of the nanotube (Corry, 2008). As the inner diameter of the nanotubes increased from 0.32 nm to 0.75 nm, salt rejection efficiencies of the membrane declined from 100% to 58%. However, these results were based on molecular dynamics simulation and not based on actual experimental results. Ahn et al. (2012) found that the rejection efficiency of a carbon nanotube membrane improved when the surface charge of the membrane was elevated to increase electrostatic interactions. Thus, modifying the surface properties of the carbon nanotube could result in higher desalination efficiency. Compared to conventional membranes, another advantage is the longer lifetimes due to excellent mechanical

properties (Salvetat et al., 1999a,b). Hilder et al. (2009) showed that boron nitride nanotubes had superior water flow properties when compared to carbon nanotubes while also achieving 100% salt rejection (Hilder et al., 2009). The use of a nanotube radius of 4.14 Å can functionalize the membrane to become cation-selective. When a nanotube radius of 5.52 Å was used, the membrane was functionalized to become anion-selective (Hilder et al., 2009).

Carbon nanotubes have also been evaluated for their salt adsorption capacity. Yang et al. (2013) showed that plasma treatment of carbon nanotubes resulted in ultrahigh salt adsorption capacity exceeding 400% by weight. Modified carbon nanotubes were fabricated with the deposition of a thin layer of nanotubes onto a mixed cellulose ester porous support (Yang et al., 2013). The adsorption capacity of these modified nanotubes was two orders of magnitude higher than activated carbon material. The salt adsorption capacity was recovered completely by a tap water rinse. The increase in salt adsorption capacity of the modified nanotubes was attributed to the defective sites created on the surface due to the plasma treatment. In addition to the high surface area, the modified surface enhanced surface hydrophilicity and ion binding properties due to the functionalization of carboxylic and hydroxyl groups (Yang et al., 2013). Since the salt is adsorbed rather than rejected, there is no requirement for applied pressure. Hence, the energy consumption can be reduced substantially.

Significant advantages of aligned nanotube membranes over conventional membranes through reduced hydraulic driving pressure, and lower energy costs have been reported, but the productivity is limited by osmotic pressure via thermodynamic restriction (Song et al., 2003). It is also uncertain if the nanotubes can be aligned with a high packing density to obtain the projected permeability. Carbon nanotubes are a material that is producible in large quantities; however, fabrication of large surface areas after incorporation of nanotubes will be a key step to enabling their commercialization (Pendergast and Hoek, 2011).

### 2.1.4. Graphene-based membranes

Graphene-based membranes are being developed for desalination due to their fast water transport properties and good mechanical properties (Nair et al., 2012; Xue et al., 2013; Choi et al., 2013; Mi, 2014). Similar to the water permeation mechanism in carbon nanotubes, two-dimensional graphene nanocapillaries allow a low-friction flow of monolayer water with size exclusion as the dominant sieving mechanism (Nair et al., 2012). Nair et al. (2012) prepared graphene oxide (GO) sheets by dispersing graphene through sonication and formation of laminates by spray-coating or spin-coating (Nair et al., 2012). Although graphene is impermeable to water molecules, transport occurs through capillaries and can be as fast as water molecule transport through an open aperture. The capillaries formed within graphene laminates are attributed to the functional groups, such as hydroxyl and epoxy, which are responsible for the creation of nanocapillaries (Nair et al., 2012). Such groups create a cluster and leave large, percolating regions of graphene sheets not oxidized. These GO laminates have spaces formed between non-oxidized regions of graphene sheets. Joshi et al. (2014) found that GO sheets are

vacuum-tight in the dry state but swell and act as molecular sieves when immersed in water and reject all solutes with a hydrated radii larger than 4.5 Å. Nanocapillaries are opened up in the hydrated state and result in a low frictional flow of water (Joshi et al., 2014).

Xue et al. (2013) studied graphyne, a one atom thick carbon allotrope of graphene. Graphyne was formed by replacing certain carbon–carbon bonds in graphene with acetylenic linkages to form  $\alpha$ -graphyne,  $\beta$ -graphyne,  $\gamma$ -graphyne and its analogs. Results proved that 100% rejection of common ions present in seawater were rejected by the graphyne monolayers with a water permeability that was two orders of magnitude higher than commercially available RO membranes (Xue et al., 2013). Molecular dynamics and computer simulations have been used for studying the transport of water molecules through GO layers and its application in desalination. Nicolai et al. (2014) utilized molecular dynamics and computer simulations to study the transport of water molecules through GO layers. They showed that water permeability through GO framework membranes increases by two orders of magnitude when the capillary pore size increases with 100% salt rejection capability.

O'Hern et al. (2014) showed that the selectivity of GO membranes can be tuned through the generation of sub-nanometer pores. Oxidative etching resulted in pores with diameters of  $0.40 \pm 0.24$  nm and densities exceeding  $10^{12}$  cm<sup>-2</sup>. At short oxidation times, the pores were cation selective with electrostatic repulsion due to the negatively charged functional groups in the pore edges. At longer oxidation times, the pores prevented the transport of larger organic molecules but allowed the transport of salt, indicating steric size exclusion (O'Hern et al., 2014). In an effort to fabricate GO membranes for desalination applications, Choi et al. (2013) created an assembly of GO nanosheets on polyamide (PA) thin film composite (TFC) RO membranes. The GO material was coated onto the PA-TFC membrane surface via layer-by-layer deposition of oppositely charged nanosheets which resulted in increased hydrophilicity and reduced surface roughness of the RO membrane (Choi et al., 2013). The altered properties of the RO membrane due to the GO nanosheets resulted in enhanced resistance to protein fouling and increased chlorine resistance (Choi et al., 2013; Kim et al., 2013a,b,c).

Graphene can be mass produced and it is possible to make laminates with high mechanical strength and flexibility (Nair et al., 2012). Functionalized graphene has also been utilized as forward osmosis membranes to decrease internal concentration polarization (ICP) and increase water flux (Gai and Gong, 2014; Gai et al., 2014). However, water productivity, similar to carbon nanotubes, will be limited by osmotic pressure via thermodynamic restriction. Commercialization of graphene-based membranes for desalination applications will depend on the ability to synthesize large quantities of graphene material and the mechanical strength of the nanolayers when an applied hydrostatic pressure is present.

## 2.2. Membrane-based processes

### 2.2.1. Semi-batch RO

The semi-batch RO process combines raw feed water with circulating concentrate at defined ratios (Song et al., 2012).

The process utilizes a combination of variable operating pressure with internal concentrate recirculation and a membrane configuration consisting of only three or four elements per pressure vessel to reduce energy consumption (Efraty et al., 2011). This process lowers the feed pressure required for desalination, and hence, reduces energy consumption. The process starts with a low initial feed pressure that is gradually increased, while equal pressurized feed and permeate flow rates are maintained. In a typical 6.5 min cycle, the operating pressure can vary between 40 and 70 bar (Stover and Efraty, 2011). The recirculation of concentrate allows a feed water recovery of 50% or more for seawater desalination and more than 90% for brackish water desalination. The feed water recovery depends on the time of concentrate recirculation. Next to the re-circulation loop is an isobaric chamber filled with feed water. At the end of a cycle, valves open and the membranes are flushed with the pressurized water from the isobaric chamber without stopping the pumps or permeate flow. The side chamber is then closed off, depressurized by letting out a few drops of concentrate, recharged with feed water, and re-pressurized with water from the desalination loop. No pressurized concentrate stream is released from the process. Thus, the pressure available in the concentrate is (almost completely) utilized before discharge and energy recovery devices (ERDs) are not required (Stover and Efraty, 2011). As the system is operated at high cross-flow velocities, fouling of the membranes is potentially reduced.

The semi-batch RO process has been utilized for both brackish and seawater desalination. Song et al. (2012) demonstrated that the semi-batch RO process consumed similar energy when compared to full-scale brackish water desalination plants. For brackish water desalination, a SEC of 1.0 kWh/m<sup>3</sup> was reported using the semi-batch RO system at a flux of 26.1 L m<sup>-2</sup> h<sup>-1</sup>. However, at a flux of 43.7 L m<sup>-2</sup> h<sup>-1</sup>, the SEC of semi-batch RO system was 150% of a full-scale RO system operated with a conventional configuration (Song et al., 2012). Stover (2013) utilized semi-batch RO for brackish water desalination and achieved a SEC of 0.64–0.76 kWh/m<sup>3</sup>. For the semi-batch RO system, only four elements were utilized per pressure vessel when compared to seven elements per pressure vessel for the conventional RO configuration. The semi-batch RO process was operated an average flux of 20.1–28.4 L m<sup>-2</sup> h<sup>-1</sup> and a final feed water recovery of 94% (Stover, 2013).

The semi-batch RO process has been commercialized as closed-circuit desalination (CCD) by Desalitech, LLC and reported to reduce desalination energy consumption up to 20% (). Subramani et al. (2014b) evaluated the semi-batch RO process for seawater desalination and compared its specific energy consumption with a conventional RO system for the same operating conditions using TFN RO elements. The semi-batch RO process with new TFN RO membranes exhibited 12–16% savings in SEC when compared to a conventional RO process for seawater desalination. For an operational flux of 12.7 L m<sup>-2</sup> h<sup>-1</sup> and a feed water recovery of 44% and 53%, the SEC for the semi-batch system was 2.16 kWh/m<sup>3</sup> and 2.24 kWh/m<sup>3</sup>, respectively at a feed water temperature between 16 and 18 °C. For the same operational flux and feed water recovery of 44% and 53%, the theoretical SEC for a



conventional RO system (based on modeling) was 2.46 kWh/m<sup>3</sup> and 2.67 kWh/m<sup>3</sup>, respectively (Subramani et al., 2014b).

The permeate water quality of the semi-batch RO system was also similar to a conventional RO system. Another consideration during the selection of a semi-batch RO is the equipment requirement (Subramani et al., 2014b). The semi-batch RO system requires additional pressure vessels that are used as side conduits to replace the system with fresh feed water and reject brine to enable the desalination cycle to be continuous. Although an ERD is not required for the semi-batch RO system, additional equipment in the form of automated pneumatic valves are required to continuously operate the system. The cost of these additional valves must be considered during evaluation of the capital cost. All the pumps utilized in the conventional RO system are also required for the semi-batch RO system with the addition of a side conduit pump.

### 2.2.2. Forward osmosis

Forward osmosis (FO), a process that has been recognized as a practical commercial process since the 1930's (Semiat, 2008) and has been investigated for a wide range of applications to desalinate water. In the FO process, instead of using hydraulic pressure, as in conventional RO desalination processes, a concentrated draw solution is used to generate high osmotic pressure, which pulls the water across a semipermeable membrane from the feed solution (McCutcheon et al., 2005). The draw solutes are then separated from the diluted draw solution to recycle the solutes and to produce a final product water. A mixture of ammonia and carbon dioxide gas has been used as the predominant draw solution (McCutcheon et al., 2006). When ammonia and carbon dioxide are mixed in the right proportion, a solution with a high osmotic pressure can be formed. This solution has been used for drawing water saline feeds. The advantage of using such a mixture is that it has been shown to have the ability to be regenerated when heated, and reused for the FO process. Thus, the FO can be considered as a combination of membrane and thermal processes.

While a variety of osmotic agents can be utilized, it is imperative that draw solutions are non-toxic, stable, near neutral pH, highly soluble to avoid precipitation, and can be removed from water at a low cost using existing technology (Cath et al., 2006; Liu et al., 2010; Achilli et al., 2010; Yen et al., 2010; Klaysom et al., 2013). Volatile solutes such as KNO<sub>3</sub>, SO<sub>2</sub>, or NH<sub>3</sub>/CO<sub>2</sub> mixtures are viable osmotic agents as their temperature dependent solubility allows for their thermal separation from the draw solution and subsequent reuse. Magnetoferritin is also a viable osmotic agent for reuse as this material can easily be separated from draw solutions with the application of a magnetic field (Liu et al., 2010). However, while reusing these osmotic agents minimizes waste, the separation of these agents from draw solutions remains the primary consumer of energy in the FO process (Zhao et al., 2012).

To further decrease FO energy requirements, draw solutions that do not require separation treatment have been developed. When fertilizers (i.e. KCl, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, etc.) are employed as the osmotic agent, the product of FO desalination is a diluted draw solution that can be applied to crops via

fertigation. As chemical fertilizers continue to be widely used, this method serves as an effective and cost-efficient way to supply water and nutrients to crops (Phuntsho et al., 2011). In a similar FO application, sugars (glucose, fructose, sucrose) and partially dehydrated food have been used as osmotic agents in portable applications where the draw water does not require treatment and becomes a nutrient solution for end use (Liu et al., 2010). In another approach, switchable polarity solvents that can be mechanically separated have been evaluated. Stone et al. (2013) utilized a mixture of CO<sub>2</sub>, water and tertiary amines as draw solutes in forward osmosis. The primary advantage with this method lies in the utilization of waste CO<sub>2</sub> at atmospheric pressure to alter the properties of switchable polarity solvents (Jessop et al., 2005, 2012). Once the draw solution is diluted, the switchable polarity solvent is mechanically separated using simple low-pressure filtration techniques. In this approach, 1 atm of CO<sub>2</sub> along with mild heating results in the conversion of the switchable polarity solvents from polar to nonpolar phase, which is then followed by mechanical separation. The energy consumption with switchable polarity solvents has been reported to be 35–48% lower than using NH<sub>3</sub>/CO<sub>2</sub> for the draw solution (Wilson et al., 2013). When membranes with cellulose triacetate (CTA) were used, the draw solution containing switchable polarity solvents degraded the membrane. However, polyamide membranes were stable and did not degrade (Stone et al., 2013). Thus, membrane material compatibility needs to be further studied before this process is applied at larger scales.

In certain FO applications, saline water is used as the draw solution rather than the feed solution. The most simple of these applications is FO for RO pretreatment. In this case, seawater serves as the draw solution and freshwater (or a solution with lower osmotic pressure) serves as a feed solution which will pressurize and dilute seawater for more favorable RO conditions (Cath et al., 2009). This pretreatment process greatly reduces the energy required to desalinate water. In a similar process, pretreatment of RO water can be carried out using impaired water (i.e. wastewater, leachate, etc.) as the feed solution (Cath et al., 2009). The benefit of using this type of water is that in addition to diluting RO feed water to more favorable operating conditions, impaired water is concentrated for more effective handling. In a similar manner, a novel process that uses ocean water to dewater an algae/nutrient solution for the generation of algal biofuels has been under investigation (Hoover et al., 2011).

In addition to choosing the optimal osmotic agent, there are a variety of membrane types and configurations that will affect FO performance. As internal and external concentration polarization (ICP/EXP) can significantly affect performance, ideal FO membranes should be designed with a high density active layer that will achieve an elevated solute rejection, a thin support layer with minimal porosity that will limit ICP, and hydrophilic properties to maximize flux and minimize fouling (Coday et al., 2013). Examples of membranes used for FO include cellulose triacetate (CTA) with embedded polyester mesh, aromatic polyamide polymer RO membranes, and proprietary membranes developed to minimize EXP/ICP/fouling and maximize flux and solute rejection (Cath et al., 2006; Miller and Evans, 2006). In order to improve performance of the FO process, membranes have also been

fabricated in hollow fiber and flat sheet configurations. Fang et al. (2012) fabricated hollow fiber FO membranes with poly (amide-imide) material and created a double-skinned fiber with an inner skin and outer skin similar to an RO and NF membrane, respectively. A 2.0 M NaCl solution was used as the draw solution. The hollow fiber membrane exhibited a flux of  $41.3 \text{ L m}^{-2} \text{ h}^{-1}$  by minimizing internal concentration polarization (Fang et al., 2012). Qui et al. (2012) fabricated flat sheet FO membranes with polyamide-imide via phase inversion followed by polyelectrolyte polyethyleneimine post-treatment to form nanofiltration-like rejection layer with a positive charge. These flat sheet membranes achieved a water flux of  $29.7 \text{ L m}^{-2} \text{ h}^{-1}$ . When the rejection layer was oriented towards the draw solution, a water flux of  $54 \text{ L m}^{-2} \text{ h}^{-1}$  has been reported (Wei et al., 2011). The hollow fiber and flat sheet FO membranes not only achieved high water fluxes but also superior rejection properties.

The overall energy utilized by the FO process has been reported to be approximately 25–45% of the thermal energy needed for multieffect distillation (Cath et al., 2009). FO has the added capability for using heat at a much lower or higher temperature than multieffect distillation processes. The FO process can use heat as low as  $40^\circ\text{C}$  and as high as  $200\text{--}250^\circ\text{C}$ . A specific energy consumption of less than  $0.25 \text{ kWh/m}^3$  for the membrane portion of FO was reported by Cath et al. (2009). However, after consideration of the energy consumption associated with draw solution recovery, the specific energy consumption was similar to an RO process ( $\sim 3.5 \text{ kWh/m}^3$ ).

In an innovative approach to reducing energy consumption, Cath et al. (2009) used FO in combination with RO to form a hybrid process (Cath et al., 2009). In this novel approach, recycled water (tertiary treated effluent) was passed through an FO system, with seawater used as the draw solution. The seawater was diluted by the recycled water within the FO process. The diluted seawater was then passed through a RO system where the feed pressure requirement was lowered by dilution of the seawater; hence, lower energy consumption was obtained for the seawater desalination process. The concentrate (brine) from the RO process was further treated through a second stage FO process and the final seawater brine was discharged to the ocean. By using a combination of FO and RO, seawater desalination was performed with a lower energy consumption and the recycled water was simultaneously treated through two physical barriers (FO and RO) (Cath et al., 2009). Using the same approach, Yangali-Quintanilla et al. (2011) desalinated Red Sea water using FO and RO. Secondary wastewater effluent was used as the feed water and Red Sea water was used as the draw solution. The system was reported to consume only 50% of the energy ( $\sim 1.5 \text{ kWh/m}^3$ ) when compared to a high pressure seawater RO system desalinating the same seawater. Although the FO/RO process had lower energy consumption, a cost analysis suggested that a minimum average flux of  $10.5 \text{ L m}^{-2} \text{ h}^{-1}$  was necessary to compete with a conventional RO process (Yangali-Quintanilla et al., 2011).

In another study, Shaffer et al. (2012) reported a specific energy consumption of  $2.93 \text{ kWh/m}^3$  at 50% recovery for an integrated FO/RO process for producing water that can be employed for agricultural purposes requiring low boron levels. For the same conditions, a two-pass RO system will require

$3.79 \text{ kWh/m}^3$  of energy (Shaffer et al., 2012). However, the combination of FO and RO will result in a substantially higher membrane area requirement due to the operational flux for the FO membrane being low. For example, Shaffer et al. (2012) reported a total membrane area of  $972,000 \text{ m}^2$  for the FO/RO process at 50% total system recovery when compared to only  $74,000 \text{ m}^2$  for a two-pass RO process. Recently, Kim et al. (2013a,b,c) utilized crystallization and RO for draw solution recovery. The first step involved the FO process with the diluted draw solution cooled in a crystallization unit. Due to the crystallization step, the feed salinity to the RO recovery system was reduced and a total energy consumption of  $2.15 \text{ kWh/m}^3$  for seawater desalination was obtained. The total energy consumption was reported as the sum of cooling energy in the crystallization process and pumping energy for the RO process.

In a recent analysis, McGovern and Lienhard (2014) compared the specific energy consumption of a two-pass RO system for seawater desalination with forward osmosis. For desalination of seawater with  $35,000 \text{ mg/L}$  of TDS at 50% recovery, the two-pass RO energy consumption was  $3.0 \text{ kWh/m}^3$  including ultrafiltration (pretreatment), 1st and the 2nd pass RO. For the same conditions, the energy consumption for the FO process was calculated to be  $3.58 \text{ kWh/m}^3$  with the draw solution dilution and regeneration process consuming  $0.10$  and  $3.48 \text{ kWh/m}^3$ , respectively (McGovern and Lienhard, 2014). Thus, for FO to be competitive with RO in terms of energy consumption, the regeneration process must be significantly more efficient than RO. However, the FO process has the advantage of lesser fouling propensity when compared to RO due to the absence of a hydraulic driving pressure. The FO process is also suitable for niche applications where the salinity levels of the water that needs to be treated is higher than the salinity that can be handled with the RO process.

### 3. Thermal-based technologies

The principle of thermal-based desalination processes depends on phase transition by energy addition or removal to separate fresh water from saline water. The most important thermal distillation processes are multistage flash (MSF), multieffect distillation (MED) and vapor compression (VC) (Al-Sahali and Ettouney, 2007). In recent years, modifications to thermal-based desalination technologies have resulted in increased process efficiency. Development has focused on technologies that combine a thermal phase change with a membrane. These technologies include membrane distillation and pervaporation. In order to reduce the energy consumption of purely thermal processes, technologies such as humidification-dehumidification and adsorption desalination have been developed. These emerging technologies along with their application in desalination is presented in this section. A comparison of these thermal-based technologies is provided in Table 2.

#### 3.1. Membrane distillation

Membrane distillation (MD) is a thermally driven, membrane-based process (El-Bourawi et al., 2006; Alkhudhiri et al., 2012;

**Table 2 – Comparison of thermal-based technologies.**

Technology	Advantages	Drawbacks	Recovery range	Feed water quality	Treated water quality	Energy consumption	Cost impacts
Membrane distillation	<ul style="list-style-type: none"> <li>- Absence of applied pressure.</li> <li>- High rejection capacity with the removal of non-volatiles.</li> <li>- Lower operating temperatures when used in vacuum.</li> <li>- Possibility of utilizing plastic material to avoid corrosion.</li> <li>- Minimal effect of performance due to feed salt concentrations.</li> <li>- Possibility of utilizing different energy sources, such as waste heat, solar energy and geothermal.</li> </ul>	<ul style="list-style-type: none"> <li>- Only bench-scale or pilot-scale studies have been performed.</li> <li>- Lack of membranes and modules designed specifically for MD.</li> <li>- Fouling of hydrophobic membranes is an issue when the membrane is wetted. Requires pretreatment of feed water source.</li> </ul>	Up to 80%.	No limitation on feed water TDS. Up to 300,000 mg/L TDS can be treated.	Up to 100% rejection.	43 kWh/m <sup>3</sup> without waste heat (Walton et al., 2004). 10.3 kWh/m <sup>3</sup> with waste heat.	Not known. Technology still at bench or demonstration scale. Costs depend on the availability of a waste heat source to heat feed water stream.
Humidification–dehumidification	<ul style="list-style-type: none"> <li>- Simple operation and maintenance.</li> <li>- Can utilize solar energy or waste heat source.</li> <li>- High rejection capacity.</li> <li>- Lower operating temperatures when compared to conventional thermal desalination.</li> <li>- Ideal for small-scale remote applications when combined with solar energy.</li> </ul>	<ul style="list-style-type: none"> <li>- Requires waste heat or renewable energy source for cost-effective desalination.</li> <li>- High thermal energy consumption (300–550 kWh/m<sup>3</sup>).</li> <li>- Large footprint requirement due to humidifier and dehumidifier chambers.</li> <li>- Optimization of carrier gas flow rate and feed water type is essential.</li> </ul>	More than 97.5%.	Up to seawater salinities have been evaluated.	Up to 100% rejection.	45.3 kWh/m <sup>3</sup> (Mahmoud, 2011).	Less than \$5/m <sup>3</sup> for the treatment of oil and gas frac flowback water. Costs for other applications are not known.
Adsorption desalination	<ul style="list-style-type: none"> <li>- Low energy consumption.</li> <li>- Utilization of low temperature heat source or solar heat.</li> <li>- Stationary operation without any moving parts.</li> <li>- Production of two effects, distillation and cooling.</li> </ul>	<ul style="list-style-type: none"> <li>- Requires waste heat or renewable energy source for cost-effective desalination.</li> <li>- Robustness of silica gel adsorber beds is not known.</li> <li>- Data available only for pilot or</li> </ul>	Up to 65% for seawater desalination.	No limitation on feed water TDS.	Up to 100% rejection.	1.38 kWh/m <sup>3</sup> for seawater desalination (Ng et al., 2013).	Not known. Technology still at demonstration scale.

Pervaporation	<ul style="list-style-type: none"> <li>- Absence of applied pressure.</li> <li>- High rejection capacity.</li> <li>- Lower operating temperatures.</li> </ul>	<ul style="list-style-type: none"> <li>- Low flux.</li> <li>- Performance depends on selection of membrane material.</li> <li>- Lack of pilot-scale or demonstration scale data.</li> </ul>	No limitation on feed water TDS.	Up to 100%.	Up to 100% rejection.	Not known.	Not known. Technology still at bench or demonstration scale.
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Adham et al., 2013) that combines membrane technology and evaporation processing in one unit. It involves the transport of water vapor through the pores of hydrophobic membranes via the temperature difference across the membrane. This difference results in a vapor pressure differential, leading to the transfer of the produced vapor through the hydrophobic membrane to the condensation surface. In MD, performance is not affected by the salinity of the feed water (Wang and Chung, 2015). However, the permeate flux is strongly affected by the feed temperature (Pangarkar et al., 2014).

Membrane materials that have been considered for the MD process include polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, and polypropylene (Alkudhri et al., 2012). Typical values for the porosity are 0.06–0.85; for the pore size, 0.2–1.0  $\mu\text{m}$ ; and for the thickness, 0.06–0.25 mm. For almost three decades, MD has been considered an alternative to conventional desalination technologies such as MSF and RO. These two techniques involve high energy and high operating pressure, respectively, which result in excessive operating costs. MD offers the attraction of operation at atmospheric pressure and low temperatures (30–90 °C), with the theoretical ability to achieve 100% salt rejection.

Typical configurations utilized for MD are direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) and sweeping gas membrane distillation (SGMD) (Evans and Miller, 2002). Different configurations of the MD process are utilized to improve efficiency during desalination. In DCMD, the membrane is in direct contact with the liquid phase. It is the simplest configuration in MD and is considered to produce the highest flux among the various configurations (Cath et al., 2004). In AGMD, an air gap is present between the membrane and condensate side. This configuration is considered to exhibit the highest energy efficiency and is best suited for applications with low energy availability (Meindersman et al., 2006). In VMD, a vacuum pressure is maintained in the permeate side and is best suited when volatiles need to be removed in the feed water (Bandini et al., 1992). In the SGMD configuration, a sweeping/stripping gas is introduced in the permeate side of the membrane (Basini et al., 1987). A review of recent advances in membrane distillation with various configurations and applications in brackish water desalination, seawater desalination, removal of small contaminant molecules and recovery of valuable products has been provided in detail by Wang and Chung (2015). In this review, different MD configurations along with hybrid configurations have been discussed. Membranes based on polytetrafluoroethylene (PTFE) dominate in MD modules due to its high hydrophobicity and resistance to harsh chemical conditions. However, the cost of these membrane materials is prohibitive for their large-scale implementation and difficulties associated with module design, specifically module sealing (Wang and Chung, 2015). Thus, improvements in membrane material are warranted for MD processes.

The selection of membrane material is critical for MD processes. The selected membrane should be porous, must be hydrophobic (should not be wetted by liquids) and must not have capillary condensation inside the pores. Only vapor should be transported through the pores and the membrane must not alter vapor equilibrium of the process liquids

(Tomaszewska, 2000). One of the major drawbacks of the technology is the low flux obtained (less than  $8.5 \text{ L m}^{-2} \text{ h}^{-1}$ ). In an experimental study conducted for flux enhancement, Cath et al. (2004) evaluated three hydrophobic membranes under DCMD mode with a turbulent flow regime and a feed water temperature of  $40 \text{ }^\circ\text{C}$ . In this process, the feed water at elevated temperature is in contact with one side of the membrane and colder water is in direct contact with the opposite side. The temperature difference and the solute concentration induces the vapor pressure gradient for mass transfer occurring in three steps: (1) diffusive transport from the feed stream to the membrane interface, (2) combined diffusive and convective transport for the vapors through the membrane pores, and (3) condensation of the vapors on the membrane interface on the product side of the membrane (Cath et al., 2004). Using this configuration with synthetic seawater resulted in a 99.9% salt rejection and a doubling of the flux (up to  $34 \text{ L m}^{-2} \text{ h}^{-1}$ ) when compared to conventional DCMD processes. Due to the temperature gradient occurring across the membrane, heat transfer across the boundary layer often limits the rate of flux transfer in MD systems. In order to improve mass transfer, Teoh et al. (2014) modified module design using spacers and baffles for turbulence promotion. Turbulence promoters aid in the increase of heat and mass transfer coefficients resulting in increased flux transfer. Use of baffles, external helix, inner helix and sieve designs have shown a 11–49% increase in the flux at  $75 \text{ }^\circ\text{C}$  when compared to an unaltered module design (Teoh et al., 2014).

In an effort to enhance the overall feed water recovery of RO processes, Qu et al. (2009) integrated DCMD with accelerated precipitation softening to treat RO. The RO concentrate was pH adjusted with sodium hydroxide along with calcite seeding, followed by microfiltration to avoid crystal seeds clogging the DCMD module. The overall feed water recovery of the desalination process was enhanced to 98.8% and the DCMD flux declined only by 20% after 300 h of operation. In a similar configuration, Mariah et al. (2006) integrated MD and crystallization (MDC) to treat RO brine from seawater desalination. In this approach, pure crystalline products were obtained from RO concentrate as the vapor pressure driving force during the process allowed a solution to be concentrated up to saturation.

With SGMD, Evans and Miller (2002) evaluated Celgard Liqui-Cel<sup>®</sup> Extra-Flow 2.5X8 membrane contactors with X-30 and X-40 hydrophobic hollow fiber membranes. Results showed that the system was capable of producing low TDS water, typically  $10 \text{ mg/L}$  or less, from seawater using low grade heat. However, large air flows were required to achieve significant water yields, and the costs associated with transporting this air were prohibitive. To overcome this barrier, new and different contactor geometries are necessary to achieve efficient contact with an extremely low pressure drop. Second, the temperature limits of the membranes must be increased. In the absence of these improvements, SGMD will not be economically competitive.

Kim et al. (2013a,b,c) coupled MD with solar energy, geothermal energy, or waste heat to reduce energy consumption and cost. Even with the availability of a waste heat source that can be utilized for the MD process, there are limited studies on the MD process and a direct cost

comparison with conventional technologies (such as RO) is not available. Moreover, the industry has not fully embraced MD for several reasons: low water flux (i.e., productivity), energy efficiency and a shortage of long-term performance data due to the wetting of the hydrophobic microporous membrane (Mathioulakis et al., 2007). Wetting of the membrane surface leads to accelerated deposition of organics on the membrane surface resulting in robust pretreatment requirements. Eventually, the pretreatment requirements increase the cost of treatment. Innovative materials that offer microporous membranes with desired porosity, hydrophobicity, low thermal conductivity, and low fouling are essential to bring MD closer to commercialization. Opportunities, therefore, beckon membrane researchers to improve the flux in the process and increase its durability by fabricating highly permeable superhydrophobic membranes and/or modifying the MD module configurations.

There are several pilot and demonstration scale studies being proposed to evaluate MD for brackish water treatment and wastewater from oil and gas fields. In a study conducted by through the National Center for Excellence in Desalination (Australia), a MD system was employed for treatment of brackish groundwater at Tjuntjunjarra, a remote corner state of Western Australia where the primary contaminant is nitrate. At the Singapore Membrane Technology Center, MD is being evaluated for treatment of water contaminated with oil from petroleum refineries consisting of a waste heat source. In both these studies, a vacuum gap multi-effect membrane distillation (V-MEMD) is being utilized. In the Australian study, a  $1 \text{ m}^3/\text{d}$  pilot system was utilized which can be operated with a solar thermal or a waste heat source. Pretreatment consisted of filtration depending on the water quality. With a feed water conductivity of  $28,000 \text{ } \mu\text{S/cm}$ , a distillation quality of  $1.8 \text{ } \mu\text{S/cm}$  was produced (Pryor, 2012). In MEMD, warm water passes through a series of MD effects working at progressively lower pressures ( $\Delta$ ). This increases the gain output ratio (GOR) to the level that it could deliver large units with a GOR of 10, comparable to commercially available multi-effect distillation systems. Due to the vacuum, water boils at a much lower temperature ( $50\text{--}80 \text{ }^\circ\text{C}$ ). The specific energy consumption for MD systems has been reported to be about  $43 \text{ kWh/m}^3$  of water produced (Walton et al., 2004). However, this energy consumption will be substantially lower when waste heat is available to heat the source water that requires treatment.

Research in MD needs to be focused on preparation of membrane material with more structured morphology to facilitate mass transfer and enhance flux. In this effort, Gethard et al. (2011) studied desalination using carbon nanotube enhanced MD. In this study, carbon nanotubes were immobilized in the pores of a hydrophobic membrane which favorably altered the water–membrane interactions to promote vapor permeability while preventing liquid penetration into the membrane pores. With the incorporation of carbon nanotubes, the flux and salt rejection was enhanced by 1.85 and 15 times, respectively with seawater (Gethard et al., 2011).

### 3.2. Humidification–dehumidification

Humidification–dehumidification (HDH) is a distillation process and is based on the increased ability of air to carry water

vapor at higher temperatures (Kabeel et al., 2013). A heated air flow (carrier gas) is brought in contact with the feed water that needs to be treated. The air extracts a certain quantity of vapor in the humidification zone. Distilled water is recovered at the dehumidification zone by maintaining contact of humid air with a cooling surface causing the condensation of a part of the vapor mixed with the air (Kabeel et al., 2013). The system consists of a humidifier, a dehumidifier and a heater to heat either the carrier gas or the feed water stream (Narayan et al., 2009). Due to the high energy consumption associated with this type of desalination technology, various modifications and improvements have been evaluated. These innovations have included the use of multi stage air heated cycle, mechanical compression driven systems, thermodynamic balancing, systems with a common heat transfer wall and hybrid systems with RO (Narayan et al., 2011).

Chafik (2003) used a solar collector to heat the air and saturate it before further heating and humidification. This cycle was repeated in four or five stages to increase the exit humidity from 4.5% to 9.3% for a four stage system. However, the gain out ratio (GOR) increased only by 9% (Narayan et al., 2010). Narayan et al. (2011) utilized a variable pressure HDH system to increase the humidity ratio in the humidifier alone without changing the pressure in the dehumidifier. This configuration leads to an increased vapor content of the moist air at sub-atmospheric pressures, leading to higher efficiency. Holst (2007) balanced the temperature difference in HDH system by circulating air by natural convection. This configuration resulted in lower thermal energy consumption (120 kWh/m<sup>3</sup>) for the HDH system. HDH with a common heat transfer wall enhances heat recovery between the humidifier and dehumidifier with an increased GOR and operation at atmospheric pressure. This method of operation is known as dewvaporation (Hamieh and Beckman, 2006; Beckman, 2008). Although high energy recovery is possible with dewvaporation, a large surface area is required for condensation to occur. This will result in higher footprint requirement for dewvaporation systems.

Further developments have included the use of reverse osmosis systems to desalinate the brine from the humidifier (Narayan et al., 2009). In this configuration, the HDH system is operated using a thermal vapor compression system. The carrier gas from the humidifier is compressed in a thermal vapor compression system using a steam supply and then sent to a dehumidifier. The dehumidified carrier gas is expanded to recovery energy in the form of work which is then utilized to operate a reverse osmosis system. This configuration showed lower thermal energy consumption. However, the availability of medium pressure steam is essential.

### 3.3. Adsorption desalination

Adsorption desalination is a thermal-based technology which employs low temperature waste heat sources or solar heat to power the sorption cycle using a highly porous silica gel (Ng et al., 2013). In this method, water vaporization occurs in an evaporator followed by vapor adsorption/desorption onto silica gel and condensation at the condenser (Ghaffour et al., 2014). The adsorption desalination cycles are operated in

batches in one or more pairs of reactors. In one reactor (one half-cycle), the silica gel adsorbent is used to adsorb the vapor generated in the evaporator. The saturated silica gel in another bed (next half-cycle) is regenerated by low temperature heat source (typically 50–85 °C) or solar heat. The desorbed vapor is then condensed on tube surfaces of a condenser. The major components involved are the evaporator, the adsorber beds with silica gel and the condenser. This emerging desalination method produces high quality potable water and cooling power with only one heat input source.

The silica gel adsorbent has a high affinity towards water vapor due to the double bond surface forces that exist between the meso-porous silica gel and the water vapor. This results in a high uptake of water vapor and regeneration by a low temperature waste heat source which would otherwise be purged into the atmosphere without utilization (Ng et al., 2013). A solar powered system has been installed at the demonstration-scale in Saudi Arabia and Singapore (Ng, 2014). Another prototype has been installed in Singapore that utilizes a waste heat source. Three large-scale systems are also being planned for implementation in the Saudi Arabia (Amy et al., 2013). Specific energy consumption <1.5 kWh/m<sup>3</sup> has been reported for seawater desalination using this technology, which is substantially lower (with the presence of a waste heat source) than seawater desalination using conventional thermal-based and membrane-based technologies (Ng et al., 2013).

### 3.4. Pervaporation

Pervaporation processes separate mixtures in contact with a membrane via preferential removal of one component from the mixture due to its higher affinity with, and/or faster diffusion through the membrane. In desalination applications, pervaporation has the advantage to achieve near 100% salt rejection with potential low energy consumption. It is a combination of membrane permeation and evaporation. Pervaporation of an aqueous salt solution can be regarded as a separation of pseudo-liquid mixture containing free water molecules and bulkier hydrated ions formed in solution upon dissociation of the salt in water (Kuznetsov et al., 2007).

Several membrane materials have been evaluated for the process. Polyvinyl alcohol (PVA) membranes have been studied extensively as pervaporation material in various applications due to its excellent film-forming and highly hydrophilic properties and high degrees of swelling due to the presence of hydroxyl groups (Kittur et al., 2003). In other studies, hybrid organic-inorganic membranes based on PVA, maleic acid and silica have been utilized. Hybrid membranes showed higher water flux and up to 99.9% salt rejection (Xie et al., 2010). The introduction of silica nanoparticles in the polymer matrix enhanced both the water flux and salt rejection due to increased diffusion coefficients of water through the membrane.

Polyetheramide-based polymer film of 40 μm thickness has also been evaluated for pervaporation (Zwijenberg et al., 2005). The membrane in tubular configuration was used in a direct solar membrane pervaporation process with seawater as the feed. The retention of ions (sodium, chloride, calcium, arsenic, boron and fluoride) was higher than RO (Zwijenberg

et al., 2005). Results indicated that the measured fluxes were independent of fouling and concentration up to 100 g/L of solids. In another study, grafted poly (ethylene terephthalate) films with styrene exhibited better selectivity to toluene when compared to ungrafted membranes for pervaporation (Khayet et al., 2006). The process has also been evaluated using PEBA membranes with 100  $\mu\text{m}$  thickness with an operating temperature of 50 °C that allowed a water flux of 26.4 L m<sup>-2</sup> h<sup>-1</sup> (Hamouda et al., 2011). Pervaporation has also been implemented for irrigation where a network of subsurface pipes is filled with water that needs to be desalinated. The pipes are lined with a unique DuPont material that allows water vapor to diffuse through the pipe walls, while the contaminants are retained within the pipes (DTI-r, 2012).

The main disadvantage of the process is the low water flux achieved. Xie et al. (2010) showed that at low temperatures, the salt concentration in the feed solution showed negligible effects on water flux and diffusion coefficients. At high feed temperatures (50–60 °C), flux and diffusivity of water decreased with increasing salt concentration due to the decreased water vapor pressure and water concentration at the membrane surface. The feed water temperature is a crucial parameter due to the increase in diffusivity and reduction in viscosity that occurs on heating. In addition, presence of vacuum and membrane thickness and inherent permeability of the membrane polymer are important parameters determining the performance of the process.

#### 4. Alternative technologies

Technologies discussed in this section include those that operate using a mechanism different from the membrane or thermal based technologies discussed in the previous sections. These alternative technologies are in the initial stages of development and only a few pilot- or demonstration-scale evaluations have been conducted. A comparison of these desalination technologies is provided in Table 3.

##### 4.1. Microbial desalination cell

Microbial desalination cells (MDCs) are based on the transfer of ionic species from water in proportion to the current generated by bacteria (Cao et al., 2009; He, 2012; Luo et al., 2012). The two primary purposes of the MDCs are to generate electricity and remove contaminants. MDCs consist of three chambers, with an anion exchange membrane (AEM) next to the anode, a cation exchange membrane (CEM) adjacent to the cathode, and a middle chamber between the membranes filled with the water to be desalinated. When current is generated by the bacteria growing on the anode, positively charged ionic species are prevented from leaving the anode by the AEM. Simultaneously, negatively charged ionic species (such as Cl<sup>-</sup>) move from the middle chamber to the anode. Simultaneously, as the cathode chamber protons are consumed, positively charged species ionic species (such as sodium ion) migrate from the middle chamber to the cathode chamber (Cao et al., 2009). Thus, the loss of ionic species from the middle chamber results in the desalination of the water without any feed pressure or draw solution and

electricity requirements. Instead, electricity is generated while the water is desalinated, a process similar to electrolysis without the use of an external energy source (Cao et al., 2009). The sludge generated during the process can be dewatered and used as a substrate for the anode to enhance the stability of desalination and electricity generation (Meng et al., 2014).

Initial proof-of-concept studies involved different initial salt concentrations (5, 20 and 35 g/L) with acetate used as the substrate for the bacteria (Cao et al., 2009). The MDC produced a maximum of 31 W/m<sup>3</sup>, while at the same time removing approximately 90% of the salt in a single desalination cycle. In another study, Jacobson et al. (2011) desalinated artificial seawater using a MDC; an increased removal of TDS (about 70%) was observed with an increase in hydraulic retention time. It was determined that electricity generation was a predominant factor in the removal of TDS and that other factors such as water osmosis contributed to desalination. Zhang et al. (2011) integrated MDC with forward osmosis for wastewater treatment. In this approach, an osmotic microbial fuel cell (OsMFC) was developed by using a FO membrane as a separator (absence of the middle chamber in a conventional MDC). A NaCl solution or artificial seawater was used as the draw solution and it was found that the OsMFC produced more electricity than a conventional MDC in both batch and continuous operation. Higher efficiency was attributed to better proton transport with water flux through the FO membrane. The OsMFC has applications in water reuse with re-concentration of draw solutions using RO concentrate or in seawater desalination using a MDC for further wastewater treatment and desalination (Zhang et al., 2011).

Efforts to improve the efficiency of MDCs have resulted in increased performance. In order to scale up MDCs, more compact reactor designs are necessary (Yang et al., 2012). Spacers can be used to minimize the reactor size without adversely affecting performance. A single 1.5 mm expanded plastic spacer produced a maximum power density (approximately 973 mW/m<sup>2</sup>) and was found to be similar to that of a MDC with the cathode exposed to air without a spacer (Yang et al., 2012). Use of a thinner spacer (1.3 mm) resulted in reduced power by 33%. In order to recirculate the solutions between the anode and cathode, a recirculation MDC (rMDC) was designed and evaluated (Qu et al., 2012). This adaptation avoided pH imbalances that could inhibit bacterial metabolism. A salt solution (20 g/L NaCl) was reduced in salinity by 37% with the rMDC when compared to a standard MDC with 25% reduction in salinity (Qu et al., 2012). Stacked MDCs resulted in efficient desalination of seawater when compared to single chamber MDCs (Kim and Logan, 2011). When 4 stacked MDCs were used in series, the salinity of seawater was reduced by 44%. The use of two additional stages resulted in an increase in salt removal capacity by 98% (Kim and Logan, 2011). In another interesting application, a three chamber MDC was used as a pretreatment to RO to reduce the salinity of the feed water (Mehanna et al., 2010). A single cycle of operation resulted in a 43% reduction in salinity and production of 480 mW/m<sup>2</sup>. Thus, the use of MDC before RO results in a reduction of salt concentration in the feed water with reduced energy demand for the downstream RO process; at the same time electrical power is produced (Mehanna et al., 2010). Although MDCs show promise for desalination, the

**Table 3 – Comparison of alternative technologies.**

Technology	Advantages	Drawbacks	Recovery range	Feed water quality	Treated water quality	Energy consumption	Cost impacts
Microbial desalination cell	<ul style="list-style-type: none"> <li>- Absence of applied pressure.</li> <li>- Absence of external electricity source.</li> </ul>	<ul style="list-style-type: none"> <li>- Low efficiency.</li> <li>- Requires a carbon source.</li> <li>- Only bench-scale studies have been performed.</li> </ul>	Recovery depends on the hydraulic retention time.	Up to seawater salinity.	Up to 98% removal of salinity with multi-staged systems.	No energy consumption. However, electricity production efficiency is dependent on several factors.	Not known. Technology still at bench-scale level. Costs will depend on scalability and performance of technology with real feed water sources.
Capacitive deionization technologies	<ul style="list-style-type: none"> <li>- Absence of applied pressure.</li> <li>- High rejection of salt.</li> <li>- More efficient for low salinity feed water sources (TDS &lt; 15,000 mg/L).</li> <li>- Polarity reversal results in self-cleaning of electrodes.</li> </ul>	<ul style="list-style-type: none"> <li>- Efficiency of electrodes for salt separation requires optimization.</li> <li>- Limited data available for seawater desalination.</li> </ul>	Up to 90%.	TDS <15,000 mg/L.	Up to 99% removal of salt.	1.8 kWh/m <sup>3</sup> for seawater desalination using a combination of electro dialysis and continuous electrodeionization (Siemens, 2014).	Not known. Costs will depend on the feed water TDS and associated energy consumption.
Ion concentration polarization	<ul style="list-style-type: none"> <li>- Absence of applied pressure.</li> <li>- Absence of membranes and fouling.</li> <li>- High rejection of salt and microorganisms.</li> <li>- Efficient for small-scale desalination modules.</li> <li>- Can be operated using battery power in remote locations.</li> </ul>	<ul style="list-style-type: none"> <li>- Limited data available.</li> <li>- Applicable only for small-scale systems.</li> <li>- Scaling of microchannels due to hardness ions could be an issue.</li> </ul>	Up to 50% for seawater desalination.	TDS <40,000 mg/L.	More than 99% removal of salt.	3.5 kWh/m <sup>3</sup> for seawater desalination (Kim et al., 2010).	Not known. Technology still at bench-scale level.
Clathrate hydrates	<ul style="list-style-type: none"> <li>- Low pressure requirements.</li> <li>- High rejection of salt.</li> </ul>	<ul style="list-style-type: none"> <li>- Process has not been evaluated on a continuous basis.</li> <li>- Separation of hydrates from brine requires optimization.</li> <li>- Elimination of salt molecules from hydrate cages.</li> </ul>	Up to 100%.	Up to seawater salinity has been evaluated.	Up to 100% removal of salt.	Not known. Estimated to be significantly lower than RO process due to absence of feed pressure requirement.	\$0.46–\$0.52/m <sup>3</sup> for seawater desalination.



process is still under development and only bench-scale studies have been performed to date. Further pilot-scale systems need to be setup with a continuous mode of operation with actual seawater or wastewater in order to prove the efficacy of this technology.

#### 4.2. Capacitive deionization technologies

Although capacitive deionization (CDI) technology is not a recent concept, several challenges exist for the identification of an optimum material for electrode manufacture (Farrar et al., 1997). CDI technology was developed as a nonpolluting, energy-efficient, and cost-effective alternative to desalination technologies such as reverse osmosis and electrodialysis (Welgemoed, 2005). In this technology, a saline solution flows through an unrestricted capacitor-type module consisting of numerous pairs of high-surface-area electrodes. The electrode material, typically a carbon aerogel, has a high specific surface area (400–1100 m<sup>2</sup>/g) and a very low electrical resistivity (less than 40 mΩ cm). Anions and cations in solution are electrosorbed by the electric field upon polarization of each electrode pair by a DC power source. After the adsorption of ions, the saturated electrode undergoes regeneration by desorption of the adsorbed ions under zero electrical potential or reverse electric field (Seo et al., 2010). Thus, the adsorption ability of the electrode is the key parameter for the performance of CDI technology.

##### 4.2.1. Membrane-based systems

When a potential is applied to CDI electrodes, counter-ions are attracted onto the electrode surface; simultaneously co-ions are expelled from the counter electrode (Kim and Choi, 2010). This leads to higher energy consumption and a lower operation efficiency because of the mobility of unwanted ions. Recently, a modification of capacitive deionization has resulted in higher recovery and efficiency in a membrane-CDI (MCDI) technology (Kim and Choi, 2010; Biesheuvel and van der Wal, 2010) where ion-exchange membranes are used for selective transport of ions to the electrodes. This advance has resulted in higher efficiency and lower energy consumption.

##### 4.2.2. Flow through systems

In another method, called flow-through electrode CD system, the feed water flows through the electrodes, instead of flowing between them (RWL, 2012). This method is four to ten times faster than conventional CDI, is more energy efficient, and requires no membrane components. The system also uses a new electrode material called hierarchical carbon aerogel monoliths in lieu of carbon aerogels. The porous carbon material eliminates the limitations typically associated with conventional capacitive deionization. It also has less separation between electrodes to further increase the system's performance. The entire process can be executed in only the time needed to charge the electrodes (RWL, 2012).

##### 4.2.3. Hybrid systems

Energy consumption as low as 0.1 kWh/m<sup>3</sup> has been reported in using CDI for brackish water treatment (Welgemoed, 2005). For seawater desalination, an energy consumption of 1.8 kWh/m<sup>3</sup> using a combination of ED and continuous

electrodeionization (CEDI) was recently reported (Siemens, 2014). In the hybrid approach, an electric field is used to draw sodium and chloride ions across ion-exchange membranes. As the water itself does not pass through the membranes, the process can be operated at lower pressure and lower energy consumption. Seawater is pretreated with a self-cleaning disk filter, followed by UF modules. The ED–CEDI system consists of ED units arranged in series to remove high concentrations of salt, followed by CEDI units arranged in parallel to remove smaller amounts of salt. Besides energy savings, other claimed advantages of the ED–CEDI technology include lower vibration and noise levels, improved safety, and minimal pre- and post-treatment (Siemens, 2014).

In another application, the Voltea process, the technology combines ED and CDI (Voltea, 2012). A three-step process is utilized, with the water flowing in a cell containing positively and negatively charged electrodes. The electrode surfaces are covered with ion-selective membranes, so ions in the feed water are attracted to the oppositely charged electrodes, pass through the membrane, and finally accumulate within the porous electrode structure. Up to 99% salt rejection has been reported using the process. When the electrodes become saturated, their polarity is reversed. The process is estimated to use less than 1.0 kWh/m<sup>3</sup> when removing 3000 mg/L of salt from water. The system can operate at 90% recovery and can be equipped with an energy recovery system to reuse the energy stored in ions on the electrodes.

##### 4.2.4. Entropy battery systems

Similar to the CDI technique, a desalination battery has been evaluated (Pasta et al., 2012). The system was previously reported as a “mixing entropy battery” (La Mantia et al., 2011; Lee et al., 2014). Instead of storing charge in the electrical double layer at the surface of the electrode, it is held in the chemical bonds, which is the bulk of the electrode. Battery electrodes offer higher specific capacity and lower self-discharge than capacitive electrodes (Pasta et al., 2012). The desalination battery operates by performing cycles in reverse when compared to the mixing entropy battery. Rather than generating electricity from salinity differences, as in the mixing entropy battery, the desalination battery uses an electrical energy input to extract sodium and chloride ions from seawater to generate fresh water. The system consists of a cationic sodium insertion electrode and a chloride capturing anionic electrode. It utilizes a Na<sub>2–x</sub>Mn<sub>5</sub>O<sub>10</sub> nanorod positive electrode with Ag/AgCl negative electrode (Pasta et al., 2012). A four step charge/discharge process allows these electrodes to separate seawater into fresh water and brine streams. In the first step, the fully charged electrodes are immersed in seawater. A constant current is then applied in order to remove the ions from the solution. In the second step, the fresh water solution in the cell is extracted and then replaced with additional seawater. The electrodes are then recharged in this solution, releasing ions and creating the brine in the third step. In the fourth step, the brine solution is replaced with fresh seawater and the cycles are repeated (La Mantia et al., 2011). Steps 1–2 results in the production of fresh water while steps 3–4 in brine production. *Wire-based systems* Recently, desalination with capacitive wire-based technology with anode/cathode wire pairs was constructed from coating a thin porous carbon electrode layer on

top of electrically conducting wires (Porada et al., 2012). Using this novel approach, feed water with a salinity of 20 mM was reduced by a factor of 3–4. By alternately dipping an array of electrode pairs in freshwater with and in brine without an applied cell voltage, an ion adsorption/desorption cycle is created. The wires used are rigid graphite rods having a length of about 40 times their thickness, chosen specifically for their property of being inert, cheap and highly conductive. When a voltage difference is applied between the wires, the cathode adsorbs cations and the anode adsorbs anions. During the process, ions are temporarily stored in the electrical double layers (EDLs) formed within the micropores inside the carbon particles that constitute the electrode. The voltage required can be produced by solar panels and recoveries up to 50% can be achieved by the process. The process also has the advantage of producing fresh water continuously as opposed to being produced intermittently by CDI, thus avoiding mixing of freshwater and untreated feed water. The wires can be placed close to each other without requiring a spacer layer in between, thus reducing pressure drops and fouling (Porada et al., 2012).

#### 4.3. Ion concentration polarization

Ion concentration polarization has been utilized to desalinate seawater using an energy-efficient process (Kim et al., 2010). In this process, micro- and nanofluidics in combination with ion concentration polarization are used to desalinate seawater. Ion concentration polarization is a fundamental transport mechanism that occurs when an ionic current is passed through an ion-selective membrane. But, in the newly developed process, no membranes are utilized. Polydimethylsiloxane (PDMS) microfluidic chips with permselective nanojunctions are used for desalination (Kim et al., 2010). An electrical potential is used to create a repulsion zone that acts as a membrane separating charged ions, bacteria, viruses, and microbes from seawater flowing through a  $500 \times 100 \mu\text{m}$  microchannel. Water flows through the microchannel tangential to a nanochannel where the voltage is applied. The resulting force creates a repulsion zone and the stream splits into two smaller channels at the nanojunction. The two streams created are the treated water and concentrate. More than 99% salt rejection and 50% recovery have been reported using this process (Kim et al., 2010). When seawater was used for the experiments, a depletion zone was created within 1 s to divert charged ions into the brine stream. The ICP layer acted as a virtual barrier for any charged particles, both positive and negative, including biomolecules due to their non-zero zeta potential (Kim et al., 2010). Thus, the process removes both small salt ions and large microorganisms simultaneously. The process worked efficiently for 1 h without any clogging of the microchannels. The ion concentration polarization process has been reported to consume approximately  $3.5\text{--}3.75 \text{ kWh/m}^3$  of energy (Kim et al., 2010). The process will ultimately be most appropriate for small-scale systems, with the possibility of battery-powered operation.

#### 4.4. Clathrate hydrates

Clathrate hydrates are crystalline inclusion compounds of water (majority species-water molecules) and a guest

molecule (minority species-gas molecules) that form spontaneously at conditions of temperature and pressure particular to each guest molecule (Bradshaw et al., 2008; Park et al., 2011). Typically, the temperatures at which clathrate hydrates are stable are slightly above the freezing point of water, although certain guest molecules stabilize hydrates at nearly ambient temperature (Bradshaw et al., 2008). Three types of crystalline structures that clathrate hydrates possess are structure I, structure II and structure H. Each of the structures contains cage-like sub structures that are formed by water molecules and enclathrate the guest molecule (Bradshaw et al., 2008). Hydrogen bonding is the primary mechanism of interaction between the water–water molecules while van der Waals forces are responsible for the stabilization of the guest molecules. After occupation of a sufficient number of cages, a thermodynamically stable crystalline unit cell structure is formed. These are referred to as gas hydrates and often contain guest molecules that exist in the gas phase at standard temperature and pressure. Common types of naturally occurring gas hydrates are methane, carbon dioxide, hydrogen sulfide, ethane, ethylene and propane (Bradshaw et al., 2008).

The use of clathrate hydrates to facilitate freeze desalination of saline water has been investigated since the 1960's. Processes based on propane and a variety of hydrates were investigated for kinetics and separations in continuous flow systems (Knox et al., 1961; Barduhn et al., 1962). In the 1990's, the Bureau of Reclamation commissioned work from Thermal Energy Systems, Inc., to explore the feasibility of this technology and construct of pilot plant facilities in Hawaii and San Diego (McCormack and Niblock, 2000, 1998; McCormack and Andersen, 1995). In the Thermal Energy Systems study, the hydrochlorofluorocarbon (HCFC) refrigerant, R141b, was pressurized in a tank of seawater at hydrate forming conditions (100 psig and  $5^\circ\text{C}$ ). A complex slurry of hydrates and brine was formed. In order to obtain potable water, the hydrates need to be separated from the brine. The hydrates formed were small in size and dendritic in nature with a high amount of salt entrapped in the interstitial spaces. In order to remove the salt, filtration was utilized to remove the smallest hydrates and a wash column to remove excess salt. The wash step results in the production of potable water quality and an estimated cost of  $\$0.46\text{--}\$0.52/\text{m}^3$  was reported (McCormack and Niblock, 2000).

In another study (Bradshaw et al., 2008), the problem of interstitial salt formation and the necessity of using wash columns was eliminated. Novel hydrate formers, utilizing R141b and HFC-32, resulted in hydrate formation significantly above the freezing point of water. Additives were utilized to inhibit dendritic hydrate growth and thus minimize interstitial salt entrapment. The rate of R141b hydrate formation in the presence of a heat exchange fluid depended on the degree of supercooling and the use of perfluorocarbon heat exchange fluid assisted separation of R141b hydrates from the brine. The use of clathrate hydrates shows promise for desalination with a production cost similar to commercially available desalination technologies but the process is yet to be operated on a completely functional level and there are no continuously operating facilities, even at a pilot scale. Drawbacks related to the control of hydrate nucleation, hydrate size and

morphology, agglomeration, amount of entrapped salt, and the efficient recovery of hydrates from the brine is necessary for process optimization.

## 5. Application potential of emerging technologies in the treatment of challenging wastewater sources

A combination of two technologies (hybrid) has shown to be more efficient than the utilization of a single technology by its own. Several hybrid configurations are currently being evaluated for treatment of challenging wastewater sources. These feed water sources include: flowback and produced water from the upstream oil and gas industry; cooling tower blow down water or refinery wastewater from the downstream oil and gas industry and power industry; leachate and acid mine drainage water treatment from the mining industry; high organics laden wastewater during the production of syngas and biofuels; and metals laden wastewater in the metals manufacturing industry. All of these industrial sectors require potable water for various processes and applications. An integration of emerging desalination technologies will not only provide a means to treat these challenging wastewater sources, but also potentially treat wastewater at higher feed water recoveries with low operational and maintenance costs associated with electricity consumption and cleaning chemicals usage.

A few hybrid configurations that can be utilized for the treatment of various industrial wastewater sources are shown in Fig. 1. In configuration (A), a forward osmosis system is combined with a reverse osmosis system for treatment of high fouling wastewaters (Holloway et al., 2007; Hickenbottom et al., 2013). Since applied pressure is absent in forward

osmosis, deposition of foulants on the membrane is lower leading to the elimination of pretreatment. Due to lack of applied pressure, osmotic cleaning using a low salinity stream in the draw solution side will result in transport of water from the draw solution side to the feed solution side (Chung et al., 2012). This will dislodge loosely held foulant deposits on the membrane surface leading to more efficient cleaning. Concentration of the draw solution is accomplished using a conventional reverse osmosis system. Due to the maximum feed pressure limit associated with the reverse osmosis, the hybrid configuration of FO and RO can only be utilized for treatment of low salinity feed water streams. For feed water streams with a TDS >40,000 mg/L, draw solution recovery using a gaseous mixture of  $\text{NH}_3/\text{CO}_2$  could be utilized. In this case, additional energy requirements for the recovery of the draw solution using heat or other thermal means must be considered. This configuration will be especially applicable for the treatment of flowback water in oil and gas industries if beneficial reuse is desired. The treated water can be reused for beneficial reuse purposes, such as feed water for boilers or irrigation.

In configuration (B), a forward osmosis system is combined with a membrane distillation system. The membrane distillation system is used for concentration of the draw solution (Wang et al., 2011; Xie et al., 2013). Based on the salinity of the feed water stream, various draw solutions can be used. Since the membrane distillation system performance is not restricted by salinity, this configuration can be used for treatment of high salinity wastewater streams. A typical application would include treatment of flowback or produced water in oil and gas industry (USDOE, 2014). This hybrid configuration promises minimal energy requirements when a waste heat source is available to heat the draw solution and re-concentrate using membrane distillation.

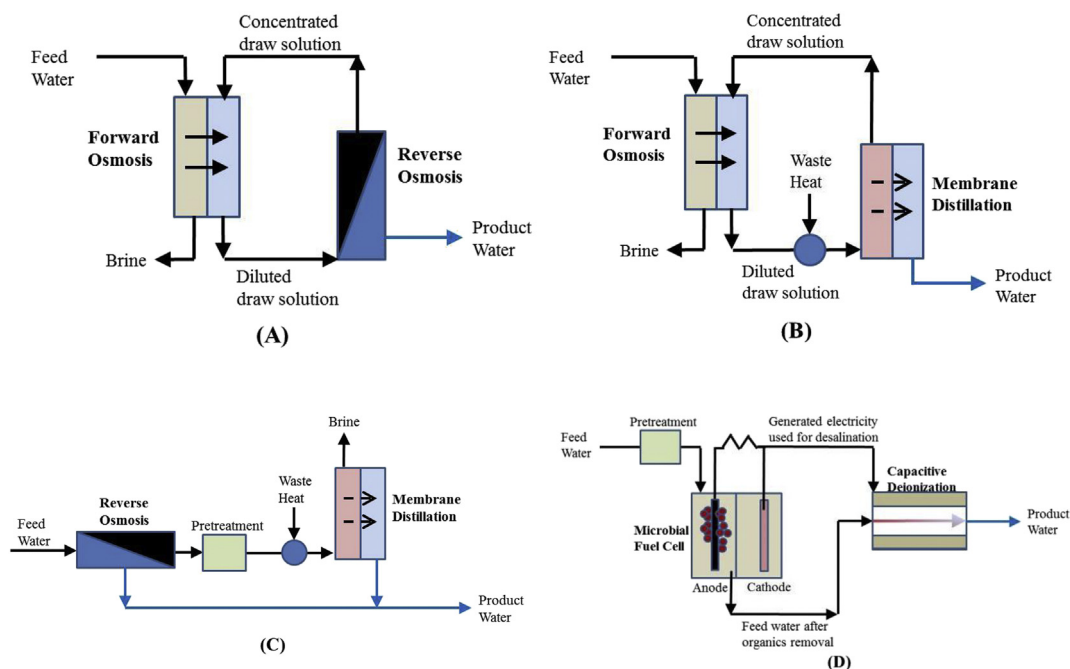


Fig. 1 – Application of hybrid technologies for treatment of challenging wastewater sources.

In configuration (C), membrane distillation is used for treatment of concentrate of RO systems (Camacho et al., 2013; Dow et al., 2008). In this configuration, the RO concentrate may require pretreatment to remove organics and scale forming ions present to reduce fouling and scaling of the membrane in the membrane distillation system. Further treatment of the RO concentrate using a membrane distillation system can reduce the brine volume generated and increase the overall feed water recovery of the desalination process. When zero liquid discharge is desired, the final brine from the membrane distillation system can be sent to a brine crystallizer. Utilization of a membrane distillation system prior to the crystallizer can reduce costs substantially due to lower brine volume treatment requirement in the crystallizer. Several oil and gas facilities currently operate reverse osmosis system and the feed water recovery is restricted due to the salinity of the feed water stream (Adham, 2013). Using a combination of RO and MD can potentially result in high feed water recoveries while reducing energy costs required for concentrate treatment.

In configuration (D), flowback water from the oil and gas industry is pretreated and fed to a microbial fuel cell system (Barole and Tsouris, 2013; Barole, 2014). In this system, electricity is generated which is then utilized for desalination in a capacitive deionization system. The microbial fuel cell is also utilized for removal of biodegradable organics in the feed water and the second step utilizes a desalination step to remove dissolved solids. This hybrid configuration is energy self-sufficient by generating electricity on-site. The microorganisms present in the fuel cell anode chamber degrade the organics present in the feed water and hence this step acts as a pretreatment to the capacitive deionization system. The advantage of using this hybrid configuration is the absence of an external electricity source since the electricity required by the capacitive deionization system is provided by the microbial fuel cell. Additional energy generated through the microbial fuel cell can be utilized for other applications on-site. The primary drawback with this configuration is the TDS limit of the feed water. Capacitive deionization systems are efficient only for low TDS (<15,000 mg/L). Also, the scalability of this hybrid configuration is not known and only bench-scale experimental data are currently available.

## 6. Conclusions

Several new technologies have been developed for desalination in recent years. Certain emerging membrane-based technologies, such as nanocomposite membranes and closed circuit desalination, show substantial promise for energy reduction and have been recently commercialized. Although technologies based on aquaporins and nanotubes show promise for high permeability and minimum energy consumption, these technologies are not developed to the point of commercialization and further studies are required at a larger scale to determine their sustainable operation. In addition, technologies based on nanotubes will still be restricted due to the thermodynamic and osmotic pressure restrictions and it is not clear if significant energy reduction is possible beyond the minimum theoretical energy

consumption. Membrane-based technologies, such as forward osmosis, can achieve lower energy consumption only if a waste heat source is available for regeneration of the draw solution. Other process configurations with FO and RO for simultaneously treating wastewater and seawater shows promise, but water quality parameters related to mixing of emerging contaminants with the treated seawater must be considered. Technologies related to microbial cells do not require an external energy source but the efficiency of these technologies for full-scale desalination applications is questionable. Among the thermal-based technologies, membrane distillation is innovative and shows the most commercial opportunity if the operational flux can be improved. Among alternative technologies evaluated in this review, capacitive deionization based technologies can potentially provide lower energy consumption as well as superior performance when compared to other desalination technologies, but require operation in combination with other technologies for sustainable performance.

## Acknowledgments

The authors would like to thank the WaterReuse Research Foundation for project funding (Project # WaterReuse-11-04), the Foundation's project advisory committee and its project officer, Kristan Cwalina.

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