Sustainability in Water Desalination

Manish Kumar, Tyler Culp and Yuexiao Shen

Penn State University

Abstract

Desalination is commonly defined as the removal of salt and contaminants from water. It includes a broad range of technologies that can enable access to marginal sources of water such as seawater, brackish groundwater and surface water, and wastewater. Given the reduction in access to freshwater in recent decades and the uncertainty in availability imposed by climate change, desalination is critical for ensuring the future of humanity.

This paper presents an overview of the advances that have made desalination more sustainable in recent decades, and summarizes the exciting directions that could make this technology more accessible, energy-efficient, and versatile. It will describe the emergence of membrane technology as the preferred technology for desalination and the current challenges facing the sustainable implementation of membrane desalination. It will end with a discussion of the novel directions that membrane technology researchers and practitioners are exploring and their potential impact on the future of this important technology.

Introduction

Desalination represents a promise of near unlimited water supply and is an attractive potential solution to the age-old conundrum of visual seawater abundance and practical inaccessibility for potable use in coastal areas. In recent years, desalination has come to include both the removal of salts from water (such as from seawater) as well as the removal of dissolved contaminants from any aqueous streams. It thus encompasses seawater, brackish surface and groundwater, industrial and municipal wastewaters. The primary descriptor of importance for desalination processes is the amount of dissolved solids (primarily inorganic salts) represented by the total dissolved solids (TDS) content. TDS is simply the solids left over after water is evaporated from particle free water. **Table 1** lists the typical range of TDS levels in waters subjected to desalination-based water treatment processes.[1] In addition to being a measure of usability (such as for consumption), TDS as a descriptor is important as it set the bounds for the minimum energy that is needed to remove these solutes from water (or water away from these solutes). Just as energy is released when a solute is dissolved in a compatible solvent, energy has to be provided to separate the same solute from the solvent and is dependent on the concentration of the solute. It is clear from **Table 1** that higher salinity water (such as seawater) fundamentally requires larger amounts of energy input for desalination while water obtained from low salinity streams such as those used in wastewater reuse could be much lower.

Table 1:Typical water sources for desalination and their TDS ranges as well as the calculated minimum energy for separation per unit volume (Specific energy consumption).

Water Source*	Total Dissolved Solids (mg/L)	Minimum energy for separation (kwh/m^3)**
Seawater	15,000 - 50,000	0.67
Brackish water	1,500 -15,000	0.17
River Water	500 - 3,000	0.04
Pure Water	< 500	< 0.01
Wastewater (untreated domestic)	250 - 1000	0.01
Wastewater (treated domestic)	500 - 700	0.01

** From reference 1, ** calculated based on average TDS of the range

The growing pressure on freshwater sources has focused the world's attention on seawater and in recovering water from marginal water sources such as brackish groundwater and surface water. It has also raised awareness and catalyzed the implementation of wastewater reuse where wastewater is treated to a high quality and in some cases used for direct or indirect potable reuse. Thus, desalination is a critical technology for humanity to allow for sustainable development.

Background and History

Desalination has had a long history in both mythology and practice. An early and illustrative reference is in the Bible and is widely considered to be an example indicating desalination.

"*…When they came to Marah, they could not drink the water of Marah because it was bitter; therefore it was named Marah. And the people grumbled against Moses, saying, "What shall we drink?" And he cried to the LORD, and the LORD showed him a log, and he threw it into the water, and the water became sweet.*" - Exodus, 15:22-26

The early scientific descriptions of desalination centered around the application of distillation. In his Meteorologica, Aristotle wrote that "Salt water when it turns into vapour becomes sweet and the vapour does not form salt water again when it condenses".[2] This is the definition of distillation, which was used historically for creating freshwater from seawater at larger scales starting in the 1930s.[3] Distillation-based technologies continued to be a major technology for water desalination till the advent of membranes. A brief overview of these technologies is provided in the next section.

Historic importance of distillation-based technologies

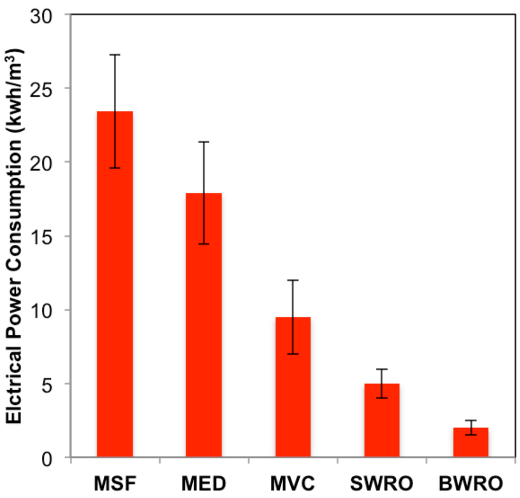


Figure 1:Typical equivalent (specific) electrical power consumption for thermal and membrane distillation strategies (from Ref 4). MSF: Multistage flash distillation, MED: Multiple-effect distillation, MVC: Mechanical vapor compression, SWRO: Seawater reverse osmosis, BWRO: Brackish water reverse osmosis

In terms of technologies used for desalination, historically the most common technologies were thermally driven technologies based on distillation. These technologies include Multi-stage Flash (MSF) Distillation, Multiple-effect Distillation (MED) and Mechanical Vapor Compression (MVC) processes. Several large plants, primarily in the Middle East have historically utilized the distillation beginning in the 1930s.[3] In these processes water is evaporated by addition of heat and in many cases is assisted by the use of vacuum. The evaporated water is then condensed to recover desalinated.

However thermal desalination has very high-energy consumption and is increasingly being replaced by the use of membranes, specifically reverse osmosis (RO) membranes. **Figure 1** shows the energy consumption per unit volume of water for several commonly used water desalination techniques.[4] As is evident from this figure, RO has emerged as a substantially more energy-efficient technology for water desalination.

Emergence of Membrane technology. Membrane technologies arose as a result of a breakthrough in the use of polymer films for

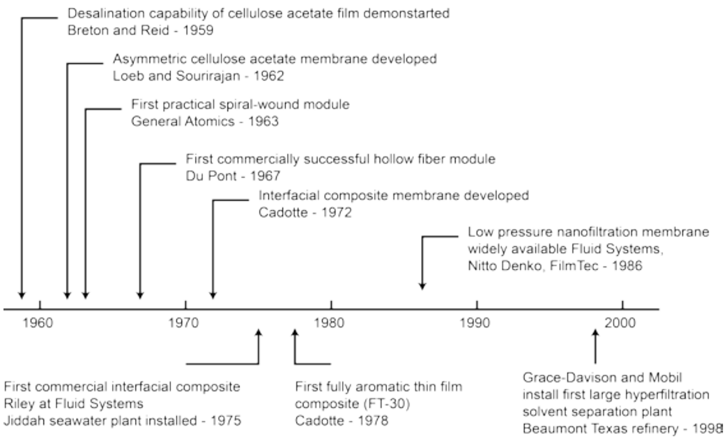


Figure 2: A brief timeline of the development of RO membranes. MSF: Multistage flash distillation, MED: Multiple-effect distillation, MVC: Mechanical vapor compression, SWRO: Seawater reverse osmosis, BWRO: Brackish water reverse osmosis. Reproduced with permission from Ref. 5. Copyright 2004

separating salt from water in the late 1950s/early 1960s. A brief history of the development of reverse osmosis membranes is shown in **Figure 2**[5] and the following discussion closely follows a description by Baker.[5] Reid and Breton first demonstrated the possibility of desalination using polymeric cellulose films[6] and thus the first polymeric reverse osmosis (RO) membranes were created.

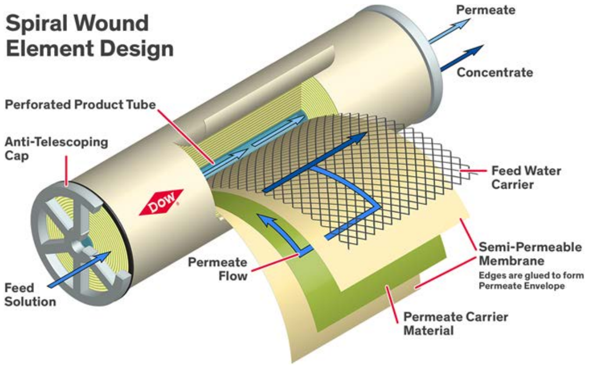


Figure 3: A typical spiral wound module design (used with permission from Dow Chemical)

Loeb and Sourirajan then showed that an asymmetric cellulose acetate membrane can be used for desalination.[7] During these early attempts the permeabilities of these membranes were low and RO membranes were considered a novelty separation technique rather than a solution to desalination. An innovation in the packaging of large membrane areas in a small volume was the development of the spiral wound module that is now common in RO applications in 1963 by General Atomics.[8,9] In this module, “leaves” of membranes along with feed and permeate spacers are connected to a perforate permeate tube and rolled up in a “jelly roll” configuration (**Figure 3**). Hollow-fiber modules containing thin fibers were developed a few years later by DuPont, but this configuration is less commonly used for RO.

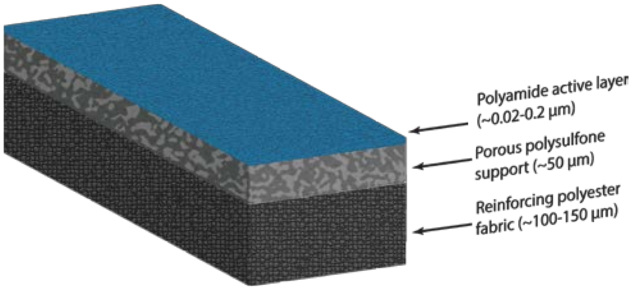
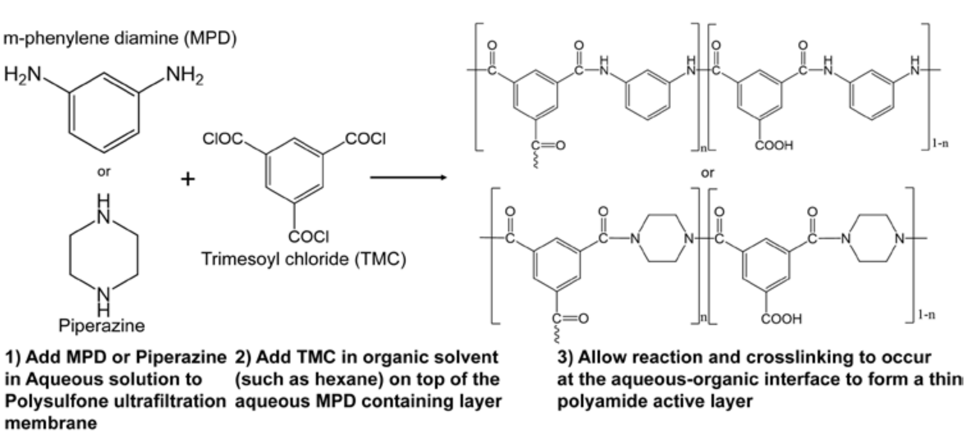


Figure 5: The overall architecture a thin film composite (TFC) RO membrane. A crosslinked polyamide nonporous active layer is supported on a microporous polysulfone membrane which is cast on a polyester fabric

A major advance in membrane chemistry that has made the current state of application of RO membrane possible is the development of the thin film composite (TFC) architecture. Previously, membranes were either several-micron-thick polymer layers with a uniform architecture or similar size polymer layers with an "asymmetric" structure with a non-porous salt-rejecting top surface opening up to a more porous support. In a design first patented by Cadotte[9] a three-layer thin film composite membrane was proposed and has since become the industry standard. This membrane provides a high permeability while maintaining selectivity for water (vs. salt or other solutes). The major innovation was to make the crosslinked "active layer" of the membrane of nanoscale thickness and support it on a microporous membrane. A schematic of this membrane is shown in **Figure 5**. A 20 -200 nm thin crosslinked polyamide layer is supported on (or indeed grown from) a microporous polysulfone layer which is in turn supported on a polyester fabric.



1) Add MPD or Piperazine in Aqueous solution to Polysulfone ultrafiltration membrane

2) Add TMC in organic solvent (such as hexane) on top of the aqueous MPD containing layer

3) Allow reaction and crosslinking to occur at the aqueous-organic interface to form a thin polyamide active layer

Figure 6: The reaction scheme and procedure most commonly used for synthesizing thin film composite (TFC) reverse osmosis (RO) and nanofiltration membranes (NF). RO membranes are typically synthesized using the MPD aqueous monomer while NF membranes are more commonly synthesized using the piperazine monomer. TMC is used for both types of membranes.

The most common chemistry for modern RO membranes is interfacial polymerization, another major advance in RO membrane manufacturing. The procedure is described in **Figure 6** and has been the standard procedure for making RO membranes for a few decades.

The energy consumption of RO technology has been dramatically decreased in the last few decades (**Figure 7**, data from Gude[32] as well as Elimelech and Phillip[10])This has been made possible through various improvements in formulation and tweaks in manufacturing procedures and process improvements such as energy recovery from the pressurized brine. This has led to rapid improvement in the sustainability and has resulted in exponential increase in the implementation of these membranes for seawater and brackish water desalination as well as wastewater reuse in the last three decades.

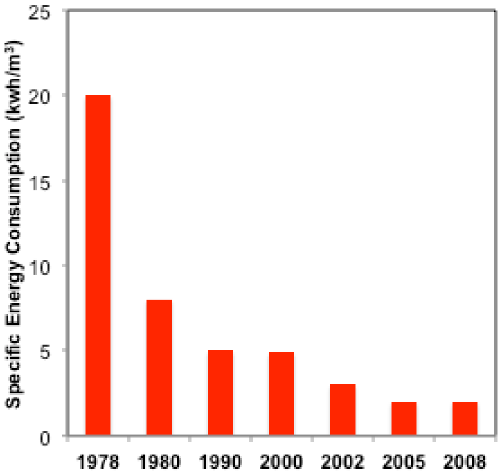


Figure 7: A rapid reduction in the specific energy consumption of RO membranes has taken place in the last three decades.

For some cases such as in seawater reverse osmosis, it is argued that current membranes have reached very close to the thermodynamic limit of ~ 1 kwh/m^3 and that further improvement in materials might not lead to additional energy sustainability.[10] On the other hand, improvements in permeability and selectivity can still lead to major gains in brackish water treatment and wastewater reuse. Ultra-permeable membranes with very high salt rejection appropriate for reverse osmosis (RO) have the potential to substantially reduce the energy (~45 %) or plant infrastructure (pressure vessels, up to 65%) in low salinity streams[12] such as brackish water desalination and water reuse. The energy advantage is significantly lower for high salinity seawater applications (15% less energy) but the plant size can be reduced by 44%.[12] A focus on increasing selectivity rather than simple increasing permeability of membranes has been proposed in recent work as a sustainable approach to improving membrane materials.[13]

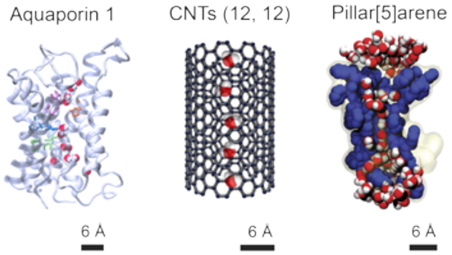
Recent advances in RO desalination

Several recent advances have been made in the area of desalination membranes in recent years that promise a path to higher sustainability, a few of which are summarized below

Channel based membranes as an alternative to current solution-diffusion RO membranes. RO membranes rely on the solution-diffusion mechanism to separate solutes from water. Solution-diffusion refers to transport where components of the solution first dissolve into the membrane matrix and then diffuse across the membrane by “jumping” between transiently connected pores. In contrast to this strategy, biological membranes conduct efficient and selective channel-based transport where water or selected solutes are transported through “straight through” protein channels (membrane proteins, MPs). Membrane protein channels are approximately 4 nm in length in comparison to the tortuous un-connected pores in the 20-200 nm thick RO membrane active layers.

Relevant to desalination, special attention has been recently focused on the water channel proteins, Aquaporins (AQPs), and their current synthetic analogs Carbon nanotubes (CNTs). AQPs are proteins that selectively transport water across cell membranes in many forms of life (including in humans).[14] Both AQPs and CNTs efficiently transport water at the rate of several billions of molecules per second. Both these types of channels consist of narrow pores that are lined with hydrophobic surfaces, which result in single-file water transport.[15,16] While carbon nanotubes cannot be made at dimensions that are substantially less than 10 Å in diameter and thus cannot reject salt (hydrated sodium and chloride ions are ~ 7.2 and 6.6 Å[17] in diameter respectively), AQPs are highly water selective due to their small pore size (~3 Å) and the presence of amino-acid residues that reject charged ions.[18] The exceptional permeability and selectivity of AQPs has led to research on their incorporation into water purification membranes over the last decade.[19] These membranes, termed AQP-based biomimetic membranes, were proposed in the mid to late 2000s in several patents. There have been many advances in this area since, including methods to incorporate AQPs in stable lipids and lipid-like block copolymers (BCPs), their packing at high density into membranes, the integration of such layers into various membrane architectures and finally the development of a scalable membrane where AQPs are inserted into the active layer of RO membranes.[20] The final strategy has resulted in commercially available membranes at small scale, however they face significant challenges to scale-up due to the concerns about stability and cost.

Another area inspired by biological channels and arguably more scalable is the development of artificial water channels and recent proposals to develop membranes around them.[21] Bioinspired artificial water channels are a new class of channels that are made synthetically using organic synthesis and have till recently been a less studied area of research with only a few architectures reported.[19] We recently demonstrated, for the first time that artificial water channels can approach the permeabilities of AQPs and CNTs while providing several advantages



	Aquaporin 1	CNTs (12, 12)	Pillar[5]arene
Scale bar	6 Å	6 Å	6 Å
Permeability (# H_2O/channel/s)	4.0 billion	0.9 billion	0.4 billion
Scale-up considerations			
Stability	Low	High	High
Alignability	High	Low	High
Synthesis	Challenging	Challenging	Simple
Sovlent compatibility	Low	High	High
Effective crosssectional area	Low	High	High

Figure 8. Biological water channels, Aquaporins (AQPs), and their current synthetic analogs, Carbon nanotubes (CNTs) have high water permeabilities of ~ billion water molecules per second. They have been integrated into membranes but these membranes face scale-up challenges. We have recently shown that specific artificial water channels, peptide appended pillar[5]arenes (PAPs), have transport rates similar to those of AQPs and CNTs. PAPs also have several advantages for scale-up including high usable cross section, simple synthesis, organic solvent compatibility and stability (both chemical and biological).

(Figure 8).[22,23] The channels tested were peptide–appended pillar[5]arene channels (PAPs) and Imidazole-quartet artificial proton channels. Artificial channels provide distinct advantages for scale-up when compared to CNTs and AQPs due to their compatibility with organic solvents and chemical and biological stability and are proposed for incorporation into selective high permeability membranes.

Graphene -based membranes can also be considered as channel based membranes and have also been proposed as next generation RO membranes.[24,25,26] Graphene is a single thin layer of sp2 hybridized carbon that has unusual mechanical, thermal and electrical properties and is being proposed for a variety of applications in various fields. Pores drilled into graphene have been proposed as filtration membranes but currently the pores cannot be made small enough to reject salt.[27] A more practical use of graphene for desalination is the use of oxidized graphene or graphene oxide (GO) sheets stacked together so that the distance between the layers can be small enough to reject solutes.[26] This work is rapidly progressing and could be a potentially new material for sustainable desalination.

Fouling Resistant Membranes. A major challenge during operation of RO membranes is the deposition of colloidal materials and organic macromolecules on the membrane surface and the growth of microbes. This deposition leads to cake formation, irreversible adsorption and growth of persistent biofilms, collectively referred to as fouling. Fouling can cause substantial increase in power consumption due to the additional resistance to flow provided by the fouling layers. Salt also accumulates in fouling cake layers and the effective osmotic pressure to be overcome increases thus decreasing the driving force for membrane filtration. This also leads to an increase in power consumption and is known as cake enhanced concentration polarization and for biofilms biofilm enhanced osmotic pressure.[28,29] Several membrane modification strategies have been proposed to reduce membrane fouling in RO systems including the grafting of superhydrophilic or amphiplilic molecules that can prevent adsorption of macromolecules and biological cells, use of nanoparticles and carbon based materials such a CNTs and graphene oxide flakes to impact biocidal properties to the RO membrane surface, and use of electroactive or magnetically actuated surfaces to prevent deposition or cause cell death. In addition methods that interrupt or manipulate cell-to-cell communication have been proposed for biofouling control.

Desalination powered by renewable energy. Desalination has always been considered incompatible with renewable energy infrastructure because of the need for high energy density to drive energy intensive desalination processes.[30] However, with the rapid improvement in RO membranes and systems, and concomitant decrease in energy use for desalination, more attention is being paid to the coupling of desalination units to solar (using photovoltaics) or wind energy sources. The applications are so far limited to small plants and proposed for “off-the-grid” applications.

Critical Challenges in Desalination

While there has been rapid progress in development and deployment of membrane desalination in recent year, there are still persistent fundamental and practical challenges to the sustainable implementation of desalinations. Some of these challenges are briefly summarized below

The inscrutability of desalination membranes. While crosslinked TFC RO membranes have been used for a few decades now, the microstructural details of these membranes remain unknown. This prevents a direct link between modifications in chemistry to the resulting microstructure which drives transport properties. Efforts are ongoing to develop tools to gain an understanding of RO membrane structure.

Concentration Polarization. Whenever salt is rejected from the surface of RO membranes it forms a concentrated layer adjacent to the membrane immediately reducing the driving force for transport across the membrane. The thickness of this concentration polarization layer can be reduced by enhancing the back transport of solutes. Several ideas have been proposed but their implementation in a sustainable manner has been challenging.

Seawater Intakes and Discharges. A particular challenge to development of seawater desalination plants (including RO plants) is the impingement and entrainment of marine microorganisms during intake to the plant. Impingement is the collision and trapping of marine organisms that are larger than intake screens while entrainment is the passage of small organisms through these screens and subsequent destruction. Also, when dense brine is discharged back to the ocean, it can have detrimental effects on the marine environment if proper mixing does not occur. Efforts need to be made to understand these challenges in more depth and understand the effect of intake designs and discharge diffusers on the marine environment.[31]

Inland desalination Brine disposal. While coastal plants can discharge concentrated brine to the ocean, inland RO plants need to be able to find a sustainable avenue to manage their brine which could be as high as 20% of the feed flow. Brine minimization and beneficial reuse of brine components as sustainable alternatives to deep well disposal, disposal to municipal sewers, and use of evaporation ponds need to be evaluated carefully.

Lack of chlorine resistance in polyamide membranes. Sodium hypochlorite (in simple terms bleach) is ubiquitous in water treatment plants for preventing growth of biofilms on surfaces in contact with water including for several types of water treatment membranes. However this is not an option for commonly used polyamide membranes used for desalination due to their high susceptibility to damage from chlorine. Development of chlorine-resistant membranes is an important practical need.

Translation of new materials. While a host of new materials have been developed for RO desalination, their translation in to products and use at larger scales is limited. Efforts should be made to translate innovations in materials and process design to actual products and plants.

High salinity streams. There are a variety of high salinity streams that are emerging from energy operations such as from fracking operations, proposed underground CO_2 storage, unconventional oil development and from flue gas desulfurization applications that frequently have TDS values in excess of 100,000 ppm. These pose unique challenges to RO materials, RO process components and operating strategies.

Outlook

Membrane desalination as a technology is growing rapidly and is becoming a critical technology to ensure long-term water sustainability around the world. There is intense scientific interest in improving the sustainability of this technology and several current innovations are looking to further drive down the power consumption and the barriers to acceptability of this technique. The future of this technology is bright and it is expected to play a major role in the resource-limited future facing the world in the near future.

REFERENCES

(1) Emerging Trends in Desalination: A Review. November 2008. Waterlines Report Series No 9, October 2008. UNESCO Centre for Membrane Science and Technology. University of New South Wales, 2008.

(2) Forbes, R.: Short History of the Art of Distillation fromthe beginnings to the Death of Cellier Blumenthal. Leiden: EJ Brill, 1948.

(3) Zander, A.; Elimelech, M.; Furukawa, D.; Gleick, P.; Herd, K.; Jones, K. L.; Rolchigo, P.; Sethi, S.; Tonner, J.; Vaux, H. J. Desalination: A national perspective. *National Research Council, The National Academies* **2008**.

(4) Al-Karaghouli, A.; Kazmerski, L. L. Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes. *Renew Sust Energ Rev* **2013**, *24*, 343-356.

(5) Baker, R. W. Reverse osmosis. *Membrane Technology and Applications, Second Edition* **2004**, 191-235.

(6) Reid, C.; Breton, E. Water and ion flow across cellulosic membranes. *Journal of Applied Polymer Science* **1959**, *1*, 133-143.

(7) Loeb, S.; Sourirajan, S.: *Sea water demineralization by means of a semipermeable membrane*; University of California, Department of Engineering, 1963.

(8) Westmoreland, J. C.:Spirally wrapped reverse osmosis membrane cell. US Patent number US3367504 A, 1968.

(9) Cadotte, J. E.: Interfacially synthesized reverse osmosis membrane. US Patent number US4277344 A, 1981.

(10) Gude, V. G. Energy consumption and recovery in reverse osmosis. *Desalination and water treatment* **2011**, *36*, 239-260.

(11) Elimelech, M.; Phillip, W. A. The future of seawater desalination: energy, technology, and the environment. *Science* **2011**, *333*, 712-717.

(12) Cohen-Tanugi, D.; McGovern, R. K.; Dave, S. H.; Lienhard, J. H.; Grossman, J. C. Quantifying the potential of ultra-permeable membranes for water desalination. *Energy & Environmental Science* **2014**, *7*, 1134-1141.

(13) Werber, J. R.; Deshmukh, A.; Elimelech, M. The critical need for increased selectivity, not increased water permeability, for desalination membranes. *Environmental Science & Technology Letters* **2016**, *3*, 112-120.

(14) Agre, P. Aquaporin water channels (Nobel Lecture). *Angewandte Chemie* **2004**, *43*, 4278-4290.

(15) de Groot, B. L.; Grubmuller, H. Water permeation across biological membranes: mechanism and dynamics of aquaporin-1 and GlpF. *Science* **2001**, *294*, 2353-2357.

(16) Hinds, B. Molecular dynamics: a blueprint for a nanoscale pump. *Nature nanotechnology* **2007**, *2*, 673-674.

(17) Israelachvili, J. N.: *Intermolecular and surface forces: revised third edition*; Academic press, 2011.

(18) Agre, P.; King, L. S.; Yasui, M.; Guggino, W. B.; Ottersen, O. P.; Fujiyoshi, Y.; Engel, A.; Nielsen, S. Aquaporin water channels--from atomic structure to clinical medicine. *The Journal of physiology* **2002**, *542*, 3-16.

(19) Shen, Y.-x.; Saboe, P. O.; Sines, I. T.; Erbakan, M.; Kumar, M. Biomimetic membranes: A review. *Journal of Membrane Science* **2014**, *454*, 359-381.

(20) Zhao, Y.; Qiu, C.; Li, X.; Vararattanavech, A.; Shen, W.; Torres, J.; Helix-Nielsen, C.; Wang, R.; Hu, X.; Fane, A. G. Synthesis of robust and high-performance aquaporin-based biomimetic membranes by interfacial polymerization-membrane preparation and RO performance characterization. *Journal of membrane science* **2012**, *423*, 422-428.

(21) Barboiu, M. Artificial water channels. *Angewandte Chemie International Edition* **2012**, *51*, 11674-11676.

(22) Shen, Y.-x.; Si, W.; Erbakan, M.; Decker, K.; De Zorzi, R.; Saboe, P. O.; Kang, Y. J.; Majd, S.; Butler, P. J.; Walz, T.; Kumar, M. Highly permeable artificial water channels that can self-assemble into two-dimensional arrays. *Proceedings of the National Academy of Sciences* **2015**, *112*, 9810-9815.

(23) Licsandru, E.; Kocsis, I.; Shen, Y.-x.; Murail, S.; Legrand, Y.-M.; van der Lee, A.; Tsai, D.; Baaden, M.; Kumar, M.; Barboiu, M. Salt-excluding artificial water channels exhibiting enhanced dipolar water and proton translocation. *Journal of the American Chemical Society* **2016**, *138*, 5403-5409.

(24) Werber, J. R.; Osuji, C. O.; Elimelech, M. Materials for next-generation desalination and water purification membranes. *Nature Reviews Materials* **2016**, *1*, 16018.

(25) Cohen-Tanugi, D.; Grossman, J. C. Water desalination across nanoporous graphene. *Nano letters* **2012**, *12*, 3602-3608.

(26) Mi, B. Graphene oxide membranes for ionic and molecular sieving. *Science* **2014**, *343*, 740-742.

(27) Wang, E. N.; Karnik, R. Water desalination: Graphene cleans up water. *Nature nanotechnology* **2012**, *7*, 552-554.

(28) Herzberg, M.; Elimelech, M. Biofouling of reverse osmosis membranes: role of biofilm-enhanced osmotic pressure. *Journal of Membrane Science* **2007**, *295*, 11-20.

(29) Hoek, E. M.; Elimelech, M. Cake-enhanced concentration polarization: a new fouling mechanism for salt-rejecting membranes. *Environmental science & technology* **2003**, *37*, 5581-5588.

(30) Charcosset, C. A review of membrane processes and renewable energies for desalination. *Desalination* **2009**, *245*, 214-231.

(31) Szeptycki, L.; Hartge, E.; Ajami, N.; Erickson, A.; Heady, W. N.; LaFeir, L.; Meister, B.; Verdone, L.; Koseff, J. R. *Marine and Coastal Impacts of Ocean Desalination in California*2016.