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Synthetic Membranes for Water Purification: Status and Future

Anthony G. Fane, Rong Wang, and Matthew X. Hu*

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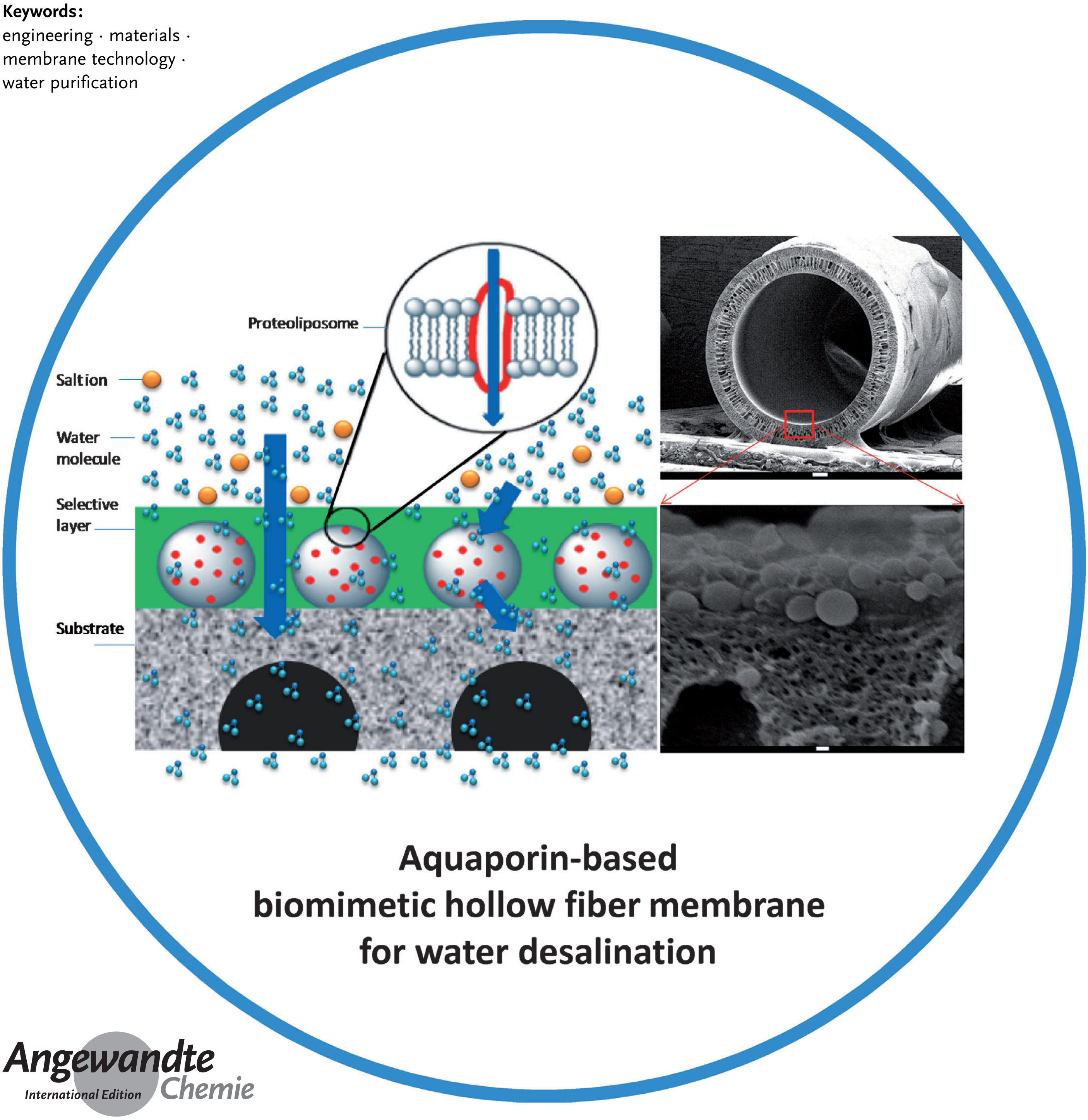

Aquaporin-based biomimetic hollow fiber membrane for water desalination

Membrane technology offers the best options to "drought proof" mankind on an increasingly thirsty planet by purifying seawater or used (waste) water. Although desalination by reverse osmosis (RO) and wastewater treatment by membrane bioreactors are well established the various membrane technologies still need to be significantly improved in terms of separation properties, energy demand and costs. We can now define the ideal characteristics of membranes and advances in material science and novel chemistries are leading to increasingly effective membranes. However developments in membranes must be matched by improved device design and membrane engineering. It is likely that limitations in fluid mechanics and mass transfer will define the upper bounds of membrane performance. Nevertheless major advances and growth over the next 20 years can be anticipated with RO remaining as the key to desalination and reclamation, with other membrane processes growing in support and in niche areas.

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1. Introduction

1.1. Historical Perspective

Thanks to polymer chemistry and advanced engineering, synthetic membranes have significantly improved our quality of life.[1] Since its invention 50 years ago reverse osmosis (RO) has become the dominant method for desalination, fulfilling the hope of President J. F. Kennedy who said, in 1962, "*If we could ever competitively, at a cheap rate, get fresh water from salt water, this would be in the long-range interests of humanity (and) really dwarf any other scientific accomplishments*". RO desalination now produces fresh water from seawater at less than US $ 1.00 per cubic meter (1000 liters), using a fraction of the energy required in the 1960s.[2] Additionally, other membrane processes, microfiltration (MF) and ultrafiltration (UF), have become major technologies for water treatment from non-saline sources, pretreatment for RO processes and in wastewater treatment in membrane bioreactors. Membranes are now mainstream separation processes in industry, including chemicals, minerals, food, biotechnology, and pharmaceuticals. Biomedical separations, such as hemodialysis, are based on membranes[3] and gas separation is another major application of membranes.[4] This Review focuses on synthetic membranes applied to water purification, the largest application of membranes and a $ 6 billion business growing at 10 to 15 % per year.[5] We give a brief review of the drivers for development, describe the characteristics of membranes for water and identify features that could be improved. We consider the status and developments in material science and membrane engineering and how improvements can be achieved. From these perspectives we discuss future prospects of synthetic membranes in the water industry.

1.2. Drivers for the Future

The development of membranes will be driven by several factors (Table 1). Water purification by membranes is likely to continue with growing water scarcity, but is challenged by the need to reduce energy usage. Membrane processes involve vast amounts of controlled nanostructures and this provides exciting opportunities for novel materials and novel membrane engineering.

1.3. Membranes and Their Characteristics

A definition of a membrane is a "thin barrier or film that exhibits permselectivity" when subject to a driving force.[6] Membranes can be natural or synthetic and either dense (effectively nonporous) or porous. Figure 1 illustrates common forms of membranes and shows asymmetric or composite membranes comprising a "skin-like" separation layer on a porous substrate layer; the composite membrane

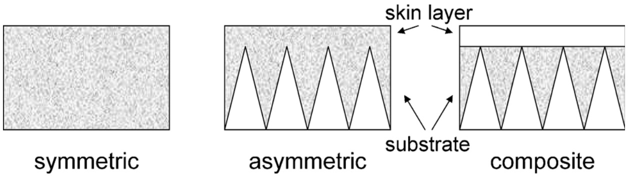

Figure 1. Common forms (cross-sections) of synthetic membranes.

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[*] Prof. A. G. Fane, Prof. R. Wang, Prof. M. X. Hu
Singapore Membrane Technology Centre, Nanyang Environment & Water Research Institute, Nanyang Technological University
Singapore 639798 (Singapore)
E-mail: agfane@ntu.edu.sg

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Table 1: Drivers for membrane development in the water domain.

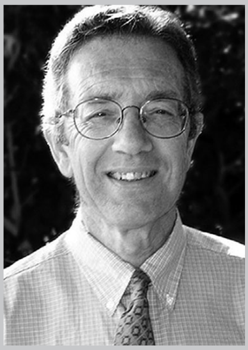
Drivers	Comments
Water scarcity	● 50% of global population facing water scarcity by 2030. ● Depleting groundwater and climate change reducing available fresh water. ● $>40\%$ of population live within 100 km of the ocean.
Energy demand, sustainability	● Low carbon future requires processes to reduce or produce energy. ● Desalination energy has thermodynamically defined minimum. ● Wastewater has lower energy demand for purification.
Novel materials and manufacturing	● Material science developing novel materials and ways to form controlled nanostructures. ● Additive manufacturing provides novel fabrication options.

has layers of different materials allowing separate optimization of the layers. While the skin layer directly effects separation the substrate may be more than a support and also influence performance. Membrane technology is based on a range of synthetic membranes with various functions made from polymers or inorganic materials or mixtures thereof (mixed matrix membranes). There are a few examples of mixed matrix membranes incorporating biomaterials. Currently polymeric membranes dominate membrane technology applications. Tables S1 and S2 in the Supporting Information provide summaries of materials used to make membranes.

The range of membrane processes relevant to water purification is summarized in Table 2 which lists essential properties for each membrane and process and additional "desired" properties, which are goals for future membranes, as explained below. The pressure-driven processes (MF, UF, NF, and RO) have decreasing pore sizes so that MF can remove particulates, bacteria and turbidity, UF can remove macrosolutes, fine colloids and virus, and NF and RO can remove ionic species and low molecular weight organics. NF retains large hydrated ions, typically multivalent, and RO retains most monovalent ions including Na^+ and Cl^-. MF, UF, and NF have pores identifiable by electronmicroscopy, and RO is effectively nonporous but with free volume, identified by positron annihilation lifetime spectroscopy (PALS).[7]

Current MF/UF membranes, typically produced by polymer phase inversion, have a relatively wide pore size distribution (PSD). A wide PSD has significant disadvantages, including greater sensitivity to fouling because the largest pores initially take a disproportionate flux (flow $\propto d_{\mathrm{pore}}^{4}$) making them susceptible to blocking.[8] Large pores also allow transmission of species that should be retained. Isoporosity of MF/UF membranes is therefore a main target of membrane technology. A high pore density (pores/area) is also required to achieve high water permeability. It is important to note that high water permeability does not necessarily mean high flux, but rather operation at conventional fluxes with lower net pressures. This is because flux-driven fouling can negate the benefit of high flux. Table 2 notes that MF and UF membranes should be robust over a wide range of pH and be insensitive to oxidizing agents (cleaning agents including acids, alkalis, and hypochlorite are used). Mechanical strength is desirable, particularly for hollow fibers subject to backwash and induced movement (by bubbling, vibrations etc.). Hydrophilicity usually renders membranes less prone to fouling and more easily cleaned. While some current MF/UF membranes are relatively hydrophilic, several have contact angles of 60 to 80° where $<30°$ is more desirable. Fouling is the bane of membrane processes and another important goal is the "anti-fouling" membrane. Experience suggests that this may be "mission impossible" but we may be able to learn from low-fouling surfaces in nature. Related to this are membranes with tunable or responsive properties such as surface charge, pore size, and morphology. Finally, the next generation MF/UF membranes should be low cost if they are to provide water for the growing global population.

The bulk of NF and RO membranes are thin-film composites of an interfacially produced polyamide layer on a UF-like support layer.[2,9] These are produced in continuous flat sheets and then incorporated into spiral wound modules (SWMs) that fit into cylindrical pressure vessels. In terms of properties for NF it would be desirable to improve the



Tony Fane has worked on membranes since 1973. He is former Director UNESCO Centre for Membrane Science and Technology at University of New South Wales and former Head of Chemical Engineering. Since 2002 he has directed membrane research at NTU, Singapore, as Temasek Professor (2002–2006), then Founding Director (2008–2012), now Director-Mentor (2013–), of the Singapore Membrane Technology Centre (SMTC). He is on the Advisory Board of J. Memb. Sci. (a former editor) and Editorial Board of Desalination. He received the IWA Membrane Technology Award in 2013.

Rong Wang graduated from Zhejiang University, China, and the Chinese Academy of Sciences. She is Full Professor and Chair in the School of Civil and Environmental Engineering (CEE), Nanyang Technological University (NTU), Singapore. She is also Director, Singapore Membrane Technology Centre (SMTC). She has over 25 years of experience in chemical and environmental engineering as well as water and energy-related research and innovation. She specializes in novel membrane development and hybrid membrane systems and process simulation. She was a co-recipient of the Minister for National Development R&D Award (Merit) 2013 in Singapore.

separation between mono- and divalent ions and to have a sharper molecular weight cut-off for organic species. However it is known that organic selectivity can relate to solute–membrane partitioning[9] and improved control of these interactions is desirable. For RO there is an unfulfilled goal for commercial ultrapermeable membranes (UPMs) that have water permeabilities significantly higher than conventional membranes, without sacrificing salt retention. However there are practical limits to use of UPMs such that significant advances in membranes may require significant advances in module design and operation. The option to produce UPMs in hollow fiber format, as well as flat sheets (for SWMs) could become desirable (see Section 3). Our RO wish list includes controlling biofouling, either by developing "anti-fouling" membranes or chlorine-resistant RO membranes for biofilm control. A chlorine tolerant hollow fiber RO membrane exists, based on cellulose triacetate,[10] but its permeability is far from desired UPM properties.

In forward osmosis (FO) water transfers across a membrane driven by an osmotic pressure difference. Interest in FO has blossomed in the past decade[11] due to potential for low energy separations or the use of low grade heat; typical FO schematics and flowsheets can be found.[11] FO membranes are similar to RO membranes; the main difference is in the support layer. In FO, both sides of the membrane are susceptible to concentration polarization (CP), including internal concentration polarization (ICP) within the support layer that reduces the effective osmotic pressure difference across the "skin layer". Minimal ICP needs a thin and highly porous support, characterized by its structural parameter, S, (see footnote [e], Table 2).[12] Next-generation FO should have smaller S values, without compromising mechanical strength. Pressure retarded osmosis (PRO) is a form of FO that can generate power from osmotic gradients.[13] The higher osmotic pressure (draw) solution is pressurized to (optimally) half the osmotic pressure difference (i.e. ca. 12 bar for a seawater/fresh water mix, ca. 24 bar for SWRO brine/wastewater brine). Water transfers into the pressurized draw and this additional high-pressure water is used to drive a turbine. PRO membranes require greater strength to withstand 15 to 25 bar. A power density of $\geq 5\,\mathrm{W\,m^{-2}}$ has been suggested,[13b] but a value $\geq 20\,\mathrm{W\,m^{-2}}$ would allow for module losses.

Membrane distillation (MD) is a temperature-driven membrane process, suitable for solar or waste heat[14] (this reference provides typical schematics and flowsheets). A vapour pressure difference, between heated feed and cool permeate, drives water vapor through the membrane pores. To avoid pore wetting the membrane needs hydrophobic properties (contact angle $>90°$); enhanced performance could come from superhydrophobicity. Effective membrane transport coefficients require relatively porous and thin membranes. Fabricating an anti-fouling MD membrane is challenging, given the need for bulk hydrophobicity.

Electrodialysis (ED) differs from all the other processes discussed because the solutes (ionic species) transfer across the membrane and the water does not. Process heuristics suggests that removal of the minor species has an intrinsic attraction, but ED has been disadvantaged by relatively costly flat sheet ion exchange membranes, typically housed in stacks and geometric constraints imposed by the electrodes providing the voltage gradient. Nevertheless ED has the attraction of "tunable" salt removal and potentially better fouling tolerance due to electrodialysis reversal (EDR), with intermittent switching of polarity to remove incipient scale.[15] Interestingly, ED predates RO by >10 years as a membrane desalination process. The advent of TFC-RO membranes (mid 1970s) gave RO a commercial advantage so that ED/EDR now has more niche applications. This could change due to improvements in membrane costs, electrical resistance, and chemical stability (see Section 4.6).

In the above discussions and Table 2 we have identified essential and desired characteristics of various membranes used in water purification. Section 2 describes developments in novel materials and membranes that could lead to some of the desired properties. Section 3 considers engineering challenges to be tackled to exploit next-generation membranes, and in Section 4 we look into the crystal ball and discuss the future prospects of membranes in water purification.

2. Materials and Membranes

2.1. Generic Issues

Developments in membranes have always been prompted by the availability of new materials, particularly new polymers, new synthetic routes for inorganic materials, and more recently the promise of nanotechnology. For example, the development of block copolymer self-assembly provides a new concept for preparing isoporous membranes. New low-temperature synthesis of inorganic materials allows growth of inorganic or ceramic layers directly onto porous polymer substrates without need for high-temperature sintering. The integration of smart and responsive polymers into or onto membranes leads to added functionalities. Developments in polymer nanocomposites has led to new mixed matrix membranes with better performance and should enable the development of membranes with enhanced strength and robustness. In terms of modeling, molecular dynamic simulation (MDS) is providing valuable insights and guidance in the design of membranes.[16] Finally, additive

Xiao Hu (Matthew) is Professor at the School of Materials Science and Engineering, Nanyang Technological University (NTU) in Singapore. He received his Ph.D. from the University of Manchester in the UK, and joined NTU in 1992 as one of the founding members of its Materials programme. His group studies the underlying principles for design, synthesis and processing of functional materials for targeted end uses. He has been a member of the Singapore Membrane Technology Centre since 2009. One of his efforts is using materials science approach to tackle challenges in desalination and water purification processes.

Table 2: Membrane types and processes, essential and additional desired properties.

Membrane process	Essential properties (State-of-the-art)	Additional desired properties
Microfiltration (MF)	● Mean pore sizes: 50–1000 nm ● Water permeability[a] $> 10^3$ ● Robust (good pH range, oxidants) ● Good mechanical strength ● Not hydrophobic ● Readily fabricated (FS and/or HF)[b] ● Modest cost	● Isoporous (very narrow distribution) ● Water permeability $> 2\times10^3$ ● Suit wide pH and strong oxidants ● Mechanically very strong & durable ● Very hydrophilic ● Easily fabricated (FS and HF) ● Low cost ● Intrinsically anti-fouling ● Tunable (surface charge, pore size) ● Self healing (integrity)
Ultrafiltration (UF)	● Mean pore sizes: 20–50 nm ● Water permeability[a] > 500 ● As for MF	● – ● Water permeability $> 10^3$ ● As for MF
Nanofiltration (NF)	● Mean pore size: ≤ 2 nm ● Water permeability[a] ≤ 10 ● Retention: M^+(partial), M^{++}(good) ● Partial fractionation of organics ● Relatively robust (good pH range) ● Good mechanical strength ● Not hydrophobic ● Readily fabricated (FS)[c,d] ● Modest cost	● – ● Water permeability > 15 ● Retention: M^+(zero), M^{++}(complete) ● Fractionation of organics ● Suit wide pH and strong oxidants ● Mechanically very strong & durable ● Very hydrophilic ● Easily fabricated (FS and HF) ● Low cost ● Intrinsically anti-fouling ● Tunable (surface charge)
Reverse osmosis (RO)	● Mean pore size: ≤ 1 nm ● Water permeability[a] ≤ 5 ● Retention: NaCl ($>99\%$) ● Retention: boron ($>90\%$) ● Relatively robust (good pH range) ● Good mechanical strength ● Not hydrophobic ● Readily fabricated (FS)[c,d] ● Modest cost	● – ● Water permeability > 5 ● Retention-NaCl ($>99.9\%$) ● Retention-Boron ($>95\%$) ● Suit wide pH and strong oxidants ● Mechanically very strong & durable ● Very hydrophilic ● Easily fabricated (FS and HF) ● Low cost ● Intrinsically anti-fouling ● Tunable (surface charge)
Forward osmosis (FO)	● As above, and with support layer S factor[e] < 500 μm	● As above, and with S factor < 200 μm
Pressure retarded osmosis (PRO)	● As above, and with power density, PD ≥ 5 W m^{-2}[f] ● Able to withstand pressure differential of > 15 bar	● As above, and with PD ≥ 20 W m^{-2} ● Able to withstand pressure differential of > 25 bar[g]
Membrane distillation (MD)	● Maximum pore size < 500 nm ● Porosity $> 50\%$ ● Hydrophobic ● Readily fabricated (FS)[c] ● Modest cost	● Isoporous ● Porosity $\geq 85\%$ ● Super hydrophobic pores ● Easily fabricated (FS and HF) ● Low cost ● Intrinsically anti-fouling
Electrodialysis (ED)	● Dense membranes with low water permeability ● Ion exchange character with both anionic and cationic properties ● Low electrical resistance ● Robust (mechanically and chemically)	● Improved permselectivity ● Lower electrical resistance ● Improved chemical stability ● Reduced cost

[a] Water permeability = liters m^{-2} h^{-1} bar^{-1} (LMH per bar). [b] FS = flat sheet (flexible), hollow fiber. [c] FS as in spiral wound modules (the predominant module concept). [d] HF is available, but not as thin film composite. [e] S = structural parameter of support = tortuosity × thickness/porosity (units μm). [f] PD of 5 W m^{-2} is a bench mark based on analysis by Statkraft.[13b] [g] Assumes osmotic pressure difference is 50 bar.

manufacture, also known as 3D printing, offers methods of rapid prototyping to develop new module designs[17] and optimize components such as flow channel spacers. 3D printing does not yet have the degree of fine resolution required to prepare membranes but that will likely evolve.

2.2. Thin-Film Composites and Nanocomposites

The concept of in-situ interfacial polymerization (IP), first introduced by Morgan in 1965,[18] is now the preferred technique for manufacturing commercial thin-film composite (TFC) RO and NF membranes. This technique is also used for novel FO and PRO membranes with a RO-like or NF-like selective layer.[12,19] The basic principle of IP involves polymerization or polycondensation reaction between two monomeric reactants, one dissolved in an aqueous phase and the other in an organic phase. The most common monomer pairs are polyfunctional amine and polyfunctional acyl chloride. When the two phases are brought into contact on the porous membrane substrate, amine (aqueous phase) penetrates into the organic phase near the interface and is acylated at both ends.[20] The reaction proceeds by an irreversible coupling of acid chloride-terminated oligomers by the amine. With increase in concentration and size of the oligomers, a polyamide network forms and precipitates on the surface of the support layer.[21] The growth of the cross-linked thin film inhibits further contact between the two reactants at a later stage, so IP is a self-limiting process, resulting in the formation of an ultra-thin polyamide layer.[20a]

Considerable work has been carried out on the IP technique during the last three decades, as detailed in previous reviews.[9,22] In particular, Petersen[23] provides a comprehensive review of most commercially available RO and NF membranes up to 1992. Studies have revealed how the performance of polyamide TFC membranes is affected significantly by the polymerization process. The factors involved include monomer type, concentration, the ratio of monomer concentrations (aqueous to organic phase), organic solvent type, reaction rate, reaction time, etc. For instance, high monomer concentrations, high reaction rates, and long reaction time usually lead to lower water permeability and higher solute rejections.[24] Also, aromatic amines normally produce better solute rejections but lower water fluxes than aliphatic amines.[25] Since the IP reaction occurs in the organic phase, different solvents or mixed solvents affect the diffusion rate of monomers in the organic phase, resulting in variations of membrane properties.[26] Table S.3 (Supporting Information) lists commonly used and newly developed monomers, and common organic solvents and additives used for the IP reaction.

Additives are used in the aqueous or organic phases, aiming to control the polymerization reaction, or change the hydrophobicity, roughness, density, charge, and anti-fouling properties of the resultant IP layer. The additives used include surfactants,[27] acid acceptors,[28] phase-transfer catalysts,[24b,29] and nanoparticles.[30] The first effort to incorporate nanoparticles into RO membranes was anti-fouling purposes in 2001,[30a] where TiO_2 nanoparticles were introduced by self-assembly after the IP reaction. TFCs incorporating nanoparticles in the IP layer were first demonstrated by formation of zeolite–polyamide nanocomposite thin films by interfacial polymerization,[30b] and this is now referred to as the thin film nanocomposite (TFN) membrane. In this approach, superhydrophilic zeolite nanoparticles were used to enhance water permeation while maintaining high salts rejection. Since the unique functionality of various nanoparticles can be imparted into the conventional polymeric membranes to tailor the membrane properties, the concept of forming TFNs can be considered as a breakthrough in preparation of RO/NF membranes. This is a type of “mixed-matrix” membrane (see Section 2.6).

Preparation of interfacially polymerized composite membranes for FO and PRO has been reported recently.[31] The first TFC hollow fiber membrane specifically designed for FO was reported in 2010.[19b] The IP method used is similar to that for RO membranes, but the structure of the porous substrate affects the FO or PRO membrane performance significantly due to internal concentration polarization.[32] The substrate structure has to be tailored by various approaches with different materials, which in turn, affects subsequent IP on the top of the substrate.[33] In addition to incorporating nanoparticles in the polyamide layer,[34] adding porous zeolite nanoparticles into the polysulfone substrate can significantly improve the structure parameter of the substrate, leading to enhanced performance.[34b]

2.3. Bioinspired Membranes

Typical synthetic membranes do not have well-controlled nanostructures or multi-functional properties, which leads to suboptimal separations, high energy needs, and productivity loss over time. In contrast, thanks to evolution, biological membranes can achieve highly efficient separations, and provide ideal models for synthetic membrane design. Biomimetics or biomimicry is the imitation of the models, systems and elements of nature to solve challenging human problems.[35] Biomimetic membranes, that either incorporate biological elements, or mimic biological structures or use fundamental concepts from biological systems, have attracted increasing attention in recent years.

There is a considerable literature on biomimetic or bioinspired membranes, including review articles focusing on block copolymer-based biomimetic membranes,[36,37] solid supported lipid biomimetic membranes,[38,39] and aquaporin-based biomimetic membranes for desalination.[40] A recent review covers biological concepts and theories relevant to membranes for separations, and introduces strategies for the design and synthesis of biomimetic membranes targeted for practical applications.[41]

Although there are many types of biomimetic/bioinspired membranes,[41] for the purpose of water purification the following two types are of most interest: 1) biomimetic membranes for filtration performance enhancement in terms of permeation and retention; 2) bioinspired membranes for membrane fouling/wetting mitigation. Figure 2 depicts these two types of membrane.

Inspired by nature, one approach is to incorporate biological channel proteins[42] or artificial channels or nanopores, which mimic the function of natural channel proteins,[43] into the synthetic membranes. The aquaporin-based biomimetic membrane is an example. Aquaporins are “water channel” proteins that form pores in the cell membranes and can transport as many as 3 billion water molecules per second

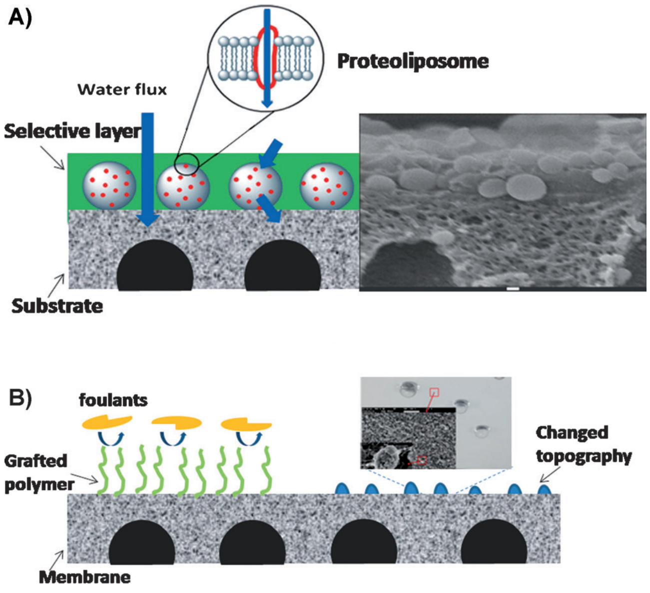


Figure 2. Schematic structures of biomimetic/bioinspired membranes. A) Incorporating channel proteins into synthetic membranes. B) Modifying the surface with bio-inspired molecules or altering the surface topography.

per molecule, while rejecting all other solutes.[44] If they can be successfully prepared, aquaporin-based biomimetic membranes are anticipated to have high water permeability and high solute retention,[42] an ideal combination for membranes for desalination or water reuse. These membranes should be much more efficient than conventional RO membranes. Ultrapermeable membranes (UPMs) would allow operation at "close to osmotic pressure", with significant energy savings for seawater desalination (see Section 3.4). This has motivated extensive effort worldwide in recent years.[45] The most promising protocol developed to date is to embed aquaporin-based proteoliposomes in a cross-linked polyamide matrix by means of IP;[46] permeability enhancements of 50 to 100% have been achieved.

Bioinspired anti-fouling and anti-wetting membranes promise to overcome the challenges of membrane fouling in water/liquid filtration and membrane wetting in membrane distillation applications, respectively. For example, surface modification with bio-inspired molecules such as phospholipid moieties[47] provides an energy barrier for foulant attachment to the membrane surface. Another way is to alter the surface topography to achieve super-superhydrophilic or hydrophobic membrane surfaces, that can meet specific requirements.[48]

2.4. Responsive Membranes

Responsive membranes belong to smart systems whose characteristics can be tuned and manipulated by external stimuli. The flux and solute selectivity become tunable via changes in conformation of polymer chains effected by stimuli such as pH, ionic strength and temperature. These responsive membranes utilize the conformational change of polymer chains between extended and contracted states under different pH,[49] ionic strength,[50] and temperature[51] to switch between "on" and "off" states. Another group of responsive separation membranes can be modulated by light. These membranes rely on *cis–trans* conformation changes or polarity changes of functional groups including azobenzene,[52] spiropyran,[53] diarylethene,[54] and viologen[55] using a photon stimulus to effect the reversible tuning of membranes. Other stimuli including biological molecules, electrical and magnetic fields[56] have been used in responsive membranes for molecules sensor, capture–release, and separation. It is envisaged that combining various stimuli-induced molecular level changes with the versatility of membrane design would unlock the potential of smart responsive membranes not only with better performance but also with unprecedented functionalities for a wider range of applications. For example, smart membranes with zwitterionic properties, responsive to ionic strength, were shown to have anti-fouling potential for proteins.[57] To date, porous responsive membranes are almost always fabricated by either grafting of responsive polymer chains on the external surface of the membrane or on the pore walls or by filling stimuli responsive materials into the pores. Non-porous responsive membranes are prepared by incorporating responsive functional groups onto the polymer chains during synthesis prior to membrane fabrication. No matter how the responsive membranes are prepared or the stimuli required for tuning properties, the common features lie in modulation of membrane resistance to convection or diffusion of solvent or solute by a stimuli that changes the polarity, porosity or free-volume in the membrane.

One of the challenges lies in how to achieve functionality while maintaining membrane stability and mechanical integrity. Using approaches of chemical modification and new membrane material design, other functionalities such as reactive, catalytically and enzymatically active membranes can be synthesized and fabricated which render multifunctionality to cater for specific applications. Responsive membranes which can respond in more complex and less defined situations and mimic the functionalities of living systems[58] is a research area that has not been fully explored. Utilizing the design principles, exemplified in Figure 3, suggests many possible routes to developing responsive membranes, whereby the "passage" and "rejection" can be effectively tuned in various ways. Another approach to responsive membranes is the development of piezoelectric membranes that vibrate under an AC field.[59] The out-of-plane surface vibration achieves increased flux and fouling control.

2.5. Isoporous Membranes

Isoporous membranes have uniformity in pore size and that is ideal for many applications including, but not limited to, molecular separation, drug delivery, pathogen detection, tissue engineering, and microfluidics.[60] The most obvious advantages of isoporous membranes over traditional membranes are that they have a sharp molecular weight cut-off for

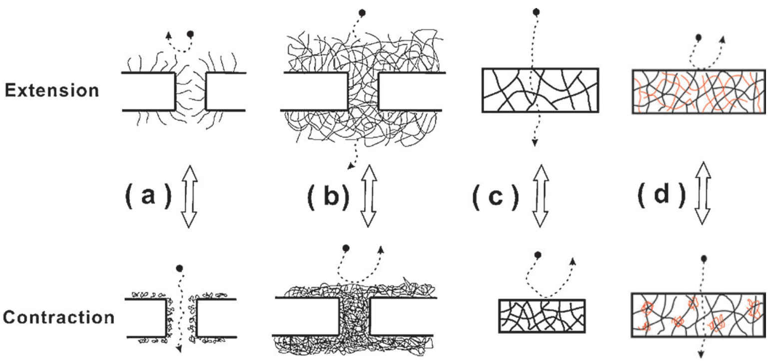


Figure 3. The effects of conformational change of polymer chains on the "on" and "off" switch of a) porous membrane with low grafting density on the pore surface; b) porous membrane with hydrogels filled in pores (or dense grafting density on pore wall) or casting on external surface; c) bulk nonporous responsive membrane; and d) nonporous IPN membrane with linear responsive polymers.

more precise separation and the isoporosity also decreases sensitivity to fouling. The traditional isoporous fabrication technique of track-etching is applied successfully to polymeric membranes, although the limited porosity can increase fouling issues; ideal membranes would be isoporous and highly porous. The techniques of microelectromechanical systems (MEMS) adapted from the semiconductor industry including electroplating[60] and lithography[61] are already mature enough to fabricate isoporous membranes using inorganic materials such as silicon, silicon oxide, and silicon nitride. The methods of embossing, micromolding, and nano-imprinting[62] have extended the possibility to organic and polymeric materials. Isoporous membranes made by MEMS are of high quality and can be scaled up albeit with high cost. The majority of MEMS-based membranes are relatively large pore size (MF range), although fine pores are possible.[60] Anodization is another isoporous membrane fabrication technology which exploits the growth of self-assembled porous oxide on metallic thin films (normally aluminum) by an appropriate voltage in an electrolyte solution. Apart from the limited choice of suitable metallic materials, producing large areas of defect-free isoporous membrane is still a challenge due to the fragility of metal oxides.

Organic isoporous membranes based on block copolymer self-assembly has promise. Smaller pore sizes are possible. Nano-scale domains with various morphologies such as sphere, lamellae and cylinders are tunable by volume fraction of each block in the polymer,[63] and various stimuli[64] can be applied to orient the nanostructure that is later dissolved in a specific solvent to form pores. Molecular self-assembly of copolymers is the only method that can effectively yield isoporous membranes with pore size smaller than 2 nm.[60] The formation of isoporous membranes from block copolymers is usually achieved semi-empirically depending on the molecular structures, solvent system and substrate chemistry used. Recent developments include tunable pore size, hollow fibers and robust UF membranes of improved permeability.[65] The future challenges of this promising method lie in the incorporation of such structures into robust systems that are compatible to roll-to-roll manufacturing and/or large-scale production without defects.

2.6. Mixed Matrix Membranes

Mixed matrix membranes combine organic and inorganic materials to take advantage of the distinct characteristics of both classes of materials. In summary, there are four types of mixed matrix membrane involving both organic or polymer materials and inorganic materials as illustrated in Figure 4.

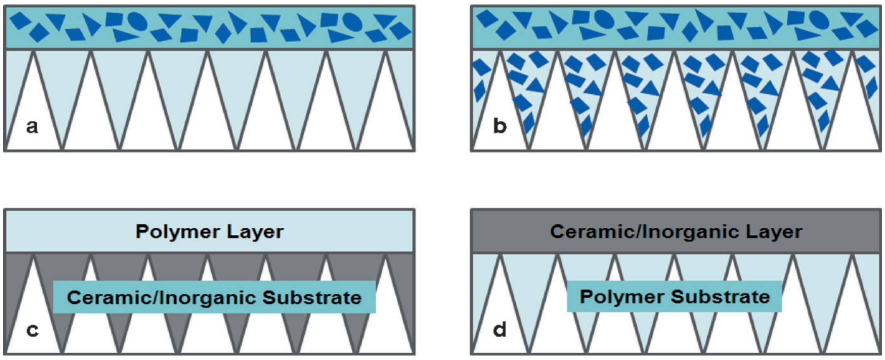


Figure 4. Several types of mixed-matrix membrane involving both organic or polymer materials and inorganic materials. a) Inorganic fillers including nanoscale fillers in the top rejection layer, b) fillers in both rejection layer and substrate, c) polymer layer on porous ceramic substrate, and d) low-temperature grown ceramic/inorganic layer on porous polymer substrate.

One approach involves encapsulating upright standing carbon nanotube (CNT) bundles into a polymeric matrix or growing a CNT forest on to a macroporous ceramic substrate.[66] Varying pore sizes from less than 1 nm to larger than 100 nm provide the possibilities for various applications including desalination and microfiltration. Mixed matrix membranes based on carbon materials such CNT and graphene are still in their infancy but are promising and there are several simulation studies supporting this notion.[67] Polymeric membranes have developed for decades but the formidable intrinsic compromise between selectivity and permeability[68] is still not yet resolved. Inorganic membranes have been hindered by the costs of producing large-scale defect-free membranes, even though inorganic nanoporous membranes have the potential to achieve high selectivity and permeability simultaneously. Therefore, mixed matrix membranes that incorporate nanoporous inorganic particles in a polymeric matrix are attractive and can combine the processibility of polymers with the superior selectivity and permeability of inorganic materials. Porous fillers of one dimension such as CNTs[67a,69] and inorganic nanotubes[70] have been incorporated into polymeric membranes for applications including desalination, gas separation, and pervaporation. Porous fillers of two dimensions, particularly zeolites, have been effectively incorporated into membranes for desalination[30] (see Section 2.2). The other important 2D filler is graphene, whose most potentially interesting application is desalination but not for gas separation because it is known to be air impermeable but water permeable.[71] Mixed matrix membranes containing nanoporous fillers have been shown to separate a broad range of molecules from protons to hydrocarbon with much higher permeability and selectivity than traditional membranes.[72] While the challenges and opportunities lie in the synthesis of novel mixed matrix membranes to cater for different needs, future success in this field also hinges on uniform dispersion and exfoliation of nano-scale particles into the membrane matrix and on better understanding of the mechanisms of selective permeation in the presence of nano-fillers.

2.7. Surface-Modified Membranes

The performance of a membrane depends not only on its surface pore structure but also its surface properties. For example, a common challenge for various membrane separations is fouling, which is associated with interaction of foulants in the feed with the membrane surface. Membrane surface modification is a simple and effective approach to realize the following: 1) to functionalize the membrane surface to either minimize undesired interactions such as adsorption or adhesion that cause membrane fouling in liquid filtration or membrane wetting in the MD process, or to introduce additional interactions such as affinity, responsiveness or catalytic properties for improving separation or creating a new separation function;[73] and 2) to adjust the surface pore characteristics (size and distribution) to allow the membrane to accommodate different separation requirements such as from ultrafiltration to nanofiltration.[74] Important modification methods comprise polymer grafting, classical chemical treatment, chemical cross-linking and surface coating, etc. Ulbricht provides a comprehensive overview of methods for surface functionalization of membranes.[73] Several other review articles on membrane surface modification are available.[75]

Polymer grafting is a process of covalent attachment of monomer or polymer onto the membrane surface. To initiate the process, the surface needs to be activated by chemical initiators or irritation with various energy sources such as ultra violet (UV),[76] plasma,[77] or ion-beam irradiation[78] to generate active sites on the backbone of the membrane surface. Next, the activated surface is exposed to selected monomers followed by polymerization. The surface characteristics of the resultant membrane are mainly determined by the grafted polymer layer. For instance, Akbari et al.[79] applied UV-photografting to modify polyethersulfone (PES) hollow fiber membranes using *p*-styrene sulfonate as a vinyl monomer. The resultant NF membrane possessed a negatively charged selective layer suitable for the treatment of anionic dye solutions.[79] Also, graft polymerization of methacrylic acid monomer increased the hydrophilicity and imparted negative charges on the membrane surface.[80] On the other hand, a cellulose acetate membrane was modified by irritation induced graft polymerization of styrene to turn its surface from hydrophilic to hydrophobic.[81] Yang et al. modified PVDF membranes by plasma treatment using the monomer 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate. The contact angle of the membrane increased from 88° to 105°, making it more suitable for MD applications.[82]

Classical chemical treatment, such as sulfonation, nitration, acid/base treatment, organic solvent treatment, etc. has been widely applied to UF and RO membranes to either tighten or open the surface pores, respectively. It has also been used to make the membrane surface chemically reactive for further treatment.[83] For instance, polysulfone UF flat-sheet membranes were transformed to NF membranes by nitration with NO and NO_2 followed by amination.[84] Polyamide (PA) composite RO membranes were modified using protic acids to hydrolyze the carbonyl groups and open the cross-linked structure, leading to more charges and increased water flux.[85] However, long-term stability of membranes made by this method should be examined, as the harsh treatment conditions may have damaged the membrane.

Chemical cross-linking is a popular treatment process applied on the membrane surface to interconnect the polymer chains to tighten the pore size and/or impart additional desired functional groups onto the membrane. Depending on the functionality of the membrane materials and choice of proper cross-linker, mild treatment conditions can be obtained. For example, poly(vinyl alcohol) (PVA) based composite NF membranes with enhanced chemical stability were obtained by cross-linking using glutaraldehyde.[86] In particular, polyimide or copolyimide based membrane surfaces can be cross-linked by diamine or polyamine cross-linkers to achieve NF-like selectivity. The mechanism for this reaction involves the opening of imide rings by the amine modifier. It was reported that the P84 polyimide flat sheet membrane was functionalized by the multiple amine groups of branched polyethyleneimine (PEI), forming a positively charged NF membrane.[87] Recently, Setiawan et al. reported the surface modification of FO poly(amide-imide) (PAI) hollow fiber membranes by amine-terminated polyelectrolyte post-treatment using poly(ethylene imine).[88] The treated membrane carried positive charges and showed both high rejection and water permeability. A similar method was also used to obtain hydrophobic MD membranes. An amine compound terminated with a long alkyl chain, for example, octadecylamine, was used as the modification reagent to generate long alkyl chains on the PAI membrane surface and throughout the cross section to enhance the membrane hydrophobicity.[89]

Surface coating is a simple physical method to coat a thin layer onto the membrane surface, aiming to increase/reduce the surface energy or to change the surface roughness. Gugliuzza et al. fabricated a superhydrophobic polyvinylidene fluoride (PVDF) membrane by surface coating a thin layer of tetra-fluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TIT) (Hyflon AD X60).[90] The resultant membrane presented strong hydrophobicity with a contact angle as high as 147°. Recently, Lv et al. fabricated a superhydrophobic PP membrane fiber by depositing a rough layer of dissolved granulated PP on the membrane surface.[91] However, the potential drawback of this technique is instability of the coating layer because of weak physical adsorption interaction of the coating layer.

A combination of methods is often utilized for membrane surface modification. A highly hydrophobic polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) membrane was obtained by modification with 10% sodium hydroxide (NaOH), followed by treatment with mixture solution of tetraethoxysilane (TEOS) and FS10, achieving an increase in contact angle of around 30°.[83] To make highly hydrophobic PAI hollow fiber membranes, an amine-functionalized silane coupling agent was used to impart the hydroxy groups on the PAI membrane surface by interaction of the imide group with the amine modifier, which further reacted with the silane perfluoro compound.[92] Plasma-induced grafting of polyethylene glycol followed by dip-coating into TiO_2 solution effectively reduced the hydrophobicity of a polyvinylidene fluoride (PVDF) membrane, thus enhancing the MD performance with oily feed.[93] Another example is direct incorporation of fluorinated silica ($fSiO_2$) on top of a PEI membrane surface by combination of chemical cross-linking and the sol–gel process to form inorganic–organic composite hollow fiber membranes for membrane contactor applications. The imide group in the PEI polymer chain reacts with amine-functionalized silane coupling agent and allows the silanol groups to attach on the membrane surface, making the treated membrane activated for the reaction with the $fSiO_2$ precursor solution.[94]

2.8. Inorganic Membranes

Inorganic MF and UF membranes were introduced to the water industry in the 1970s. The most common forms are ceramic monoliths (multibore) and flat sheets. Currently at least 15 companies globally produce commercial ceramic membranes.[95] Typically they have three layers, a macroporous support layer, an intermediate layer for a smoother interface, and a thin separation layer. They are produced by a multistep process involving extrusion or dip-coating and sol–gel processing including calcination and sintering.[96] Materials are usually oxides of Al, Ti, Zr or Si, or composites thereof. State-of-the-art ceramic membranes have some attractive properties. They usually have a very narrow pore size distribution, due to the closely sized precursors, allowing higher fluxes and are more mechanically, chemically, and thermally robust than polymer membranes. Their major perceived disadvantage is capital cost, but with their longer life times and potentially higher fluxes, their life-cycle costs are becoming attractive. Ceramic membranes are widely used for water treatment in Japan, and increasingly in Europe. High fluxes ($> 200\,L\,m^{-2}\,h^{-1}$) have been demonstrated,[97] particularly when associated with ozonation.[98] Ceramic NF membranes have also been developed[95,99] based on TiO_2 and SiO_2. Good retention of low molecular weight organics can be achieved but salt rejection decreases with increased salinity, presumably due to masked electrostatic interactions. Ceramic membranes have a developing role in surface water treatment and a wide range of industrial applications.[95] Emerging applications are for SWRO pretreatment and produced water treatment. Comprehensive reviews can be found elsewhere.[95,96]

Zeolites are aluminosilicate molecular sieves that have been evaluated for membrane separations.[100] Most attention has been on gas separations but zeolite-based desalination membranes are being developed.[101] To date reasonable retention of salts has been achieved (> 93% for NaCl), but water fluxes have been unattractive. A recent molecular dynamic simulation[102] suggests that much higher fluxes could be attained for an optimized zeolite thin film. However zeolite film membranes have struggled to achieve their potential and the most promising zeolite-enabled membranes are the “mixed-matrix” thin film nanocomposites (see Section 2.2).

3. Engineering Challenges

The future of membrane technology is not only dependent on developments in material science and membrane fabrication techniques. Successful exploitation of next-generation membranes requires advances in membrane engineering. In this section we take a brief look at some key issues.

3.1. Module Development

The module provides both a support for the membranes and fluid management for the input and output streams. The fluid management (more details in Section 3.2) has to deal with pressure drops and control of concentration polarization (CP) and fouling. Figure 5 illustrates the generic flow arrangements for membrane modules with cross flow (CF), dead-end (DE), counter-current (CC), and co-current (CoC).

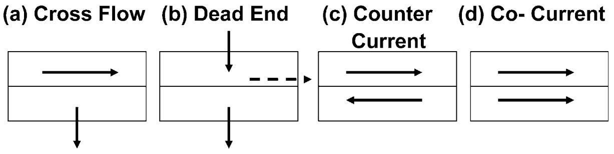


Figure 5. Generic flow arrangements for membrane modules.

The CF mode is common to all RO and NF applications and many MF and UF applications. The important role for CF is that it provides shear at the membrane surface that enhances back transport of retained solutes and reduces CP, where the CP modulus (M) can be expressed as the ratio of solute at the membrane surface to that in the bulk ($M = C_w/C_b$). In RO desalination, M is typically 1.1 to 1.2, which means that the osmotic pressure at the membrane surface, Π_w, is 10 to 20% higher than in the bulk fluid. The pressure to drive the RO process depends on Π_w so there is an incentive to minimize M. Herein lies the challenge for exploiting UPMs with the potential for fluxes 2-, 5-, or 10-fold higher than current membranes. The key parameter that defines M is the modified Peclet number[103] which is the ratio of flux (J) to boundary layer mass transfer coefficient (k), and the real challenge is to maintain constant (J/k) as higher fluxes are imposed. As explained in Section 3.2 it is not straightforward to increase k sufficiently to match J.

The dominant module design for RO (and NF) is the spiral wound module (SWM)[104] which uses flat-sheet membranes wrapped around a central permeate tube. Flow channel spacers positioned between membrane leaves define the height of the flow channels and generate eddies that enhance mass transfer, k. Increased crossflow velocity can increase k but it is currently impractical to increase by, say, 5-fold to match a 5-fold higher flux (see Section 3.2). RO modules are also produced in hollow fiber module (HFM) format, where a large number of fibers are potted in a "shell and tube" arrangement. The pressurized feed enters the shell and permeate passes out through the lumen. To withstand the high feed pressures of SWRO the fibers are small diameter (< 200 μm) with relatively thick walls. Fibers are wrapped to encourage good flow distribution.[10] In both SWM and HFM applications the permeate side geometry is important since it influences back pressures in the permeate side. The permeate side pressure reduces the driving force and in the SWM this can cause maldistribution of flux and localized fouling.[104] This would be exacerbated if UPMs are used at elevated fluxes, and some redesign of the SWM would be required. For the HFM to be operated at UPM fluxes would probably require shorter fibers, unless the lumen diameter could be increased, but that would then require much stronger membrane materials. However the HFM could be attractive for UPMs with enhanced fluid management (see Section 3.2). The above considerations also apply to NF. The "standard" RO module is 8 inch (200 mm) in diameter and 40 inch (ca. 1000 mm) long. Even larger, 16 inch, modules are commercially available and 24 inch modules are envisaged as SWRO plants get larger.[105] The claimed benefits of the larger modules are reduced capital costs. However as modules get larger the attention to flow distribution and pressure drops becomes more crucial. In principle even larger modules could be designed but the increased diameter of the pressure vessel becomes a constraint.

MF/UF membranes are most commonly used in HFMs, although some UF applications (dairy etc.) use SWMs. HFMs operate in both cross flow and dead end mode (Figure 5), the former typical of membrane bioreactors (bubble-induced CF) and the latter (DE) in water treatment or pretreatment where solids loads are low; regular backwash is used to remove deposited material. HFMs are either "contained", in a pressure vessel, with feed into the shell or lumen, or "submerged", with fibers immersed in a tank and permeate removed from the lumen under suction.[106] Current generation MF/UF have relatively high water permeabilities and could potentially be operated at higher fluxes if improved CP control was available (see Section 3.2). The other factor that could lead to better tolerance of higher fluxes would be the development of more isoporous membranes (see Sections 1.3 and 2.5). Indeed the reported high flux capability of inorganic MF/UF is partially explained by the narrower pore size distribution of inorganic membranes. Inorganic membranes can also be coupled with strong oxidants to control organic fouling.[107] Another reason maybe the sharper response to backwash events. Inorganic membranes are usually multibore monoliths and this approach has been adopted with some success for polymer membranes,[108] providing greater strength and integrity.

FO modules are challenging as the FO process requires crossflow on both sides of the membrane; counter current (CC, Figure 5c) is preferred. Flat-sheet FO membranes have been assembled into SWM formats with spacers/baffles on both feed and draw sides. However the SWM format may not be optimal as the lack of significant operating pressure would allow a flat geometry. There would be benefit in the HFM format and high performance hollow fiber FO membranes have been developed.[11] Fluid management on the shell-side needs to be very effective, and this could involve organized fiber packing, two-phase flow etc[109] (see also Section 3.2). PRO using modified FO membranes (see Section 1.3) brings an additional challenge with substantial pressure differences across the membrane. Membrane deformation can occur and this impairs performance.[110] If the SWM is used for PRO there needs to be a redesign of the channel spacers to provide added support, or the membrane itself needs to be strengthened without compromising performance. The HFM format would simplify mechanical design, but fibers would need to be strengthened to withstand 25 bar pressures.

The MD process can be operated in several modes,[14] direct contact (DCMD), vacuum MD, and air or sweep gas MD. In DCMD the membrane has liquid flow on both sides (Figure 5c), similar to FO, and this calls for special attention to shell-side fluid management.[109] Vacuum MD is currently commercialized in flat sheet format, but a HFM concept could be attractive.[111] To date the optimal strategy for commercial MD (DCMD vs VMD, flat sheet vs hollow fiber) has not been settled.

ED is based on flat-sheet geometry with flow on both sides of the membrane (diluate and concentrate) in a co-current mode (Figure 5d). The flow channels are narrow (0.5–2 mm) to minimize electrical resistance. Spacers, as used in the SWM for RO, are used to promote flow distribution and provide boundary layer mass transfer to control CP. The performance of ED can be compromised by the "limiting current density", $i_{\lim}$, which is the current beyond which CP causes problems such as water splitting, increased electrical resistance etc.[15] The value of $i_{\lim}$ is directly proportional to the mass transfer coefficient k, suggesting the need to develop more effective spacers or other mass transfer enhancing strategies (see Section 3.2).

3.2. Fluid Mechanics

Optimal use of a membrane needs the feed to be evenly distributed across the membrane surface, and for cross flow (Figure 5a), counter current (Figure 5c), and co-current flow

(Figure 5d) the flow-induced shear needs to limit the influence of concentration polarization (CP). For counter current flow, such as used for FO and DCMD, and co-current flow, used for ED, the downstream side requirements are similar to the feed side. The downstream side of the membrane for cross flow and dead end (Figure 5b) needs to be able to conduct permeate away without significant pressure drop, ΔP_{perm}. To illustrate the feed-side challenges of the future let us consider the spiral wound module (SWM) if novel UPMs with 2 to 5 times the flux potential are available. As noted in Section 3.1, the key parameter for controlling CP is the modified Peclet number (J/k). The boundary layer mass transfer coefficient can be increased by higher cross flow velocity (u_x), but this also increases the flow channel pressure drop, $\Delta P_{\text{channel}}$. Conventional spacers have the following properties:[104a]

$$k = f\,(\text{Re})^{0.5},\ \Delta P_{\text{channel}} = f\,(\text{Re})^{1.8},\ \text{where Re} = f\,(u_x)^{1.0} \qquad (1)$$

So to increase k two-fold requires a 4-fold increase in u_x, which would cause a 12-fold increase in $\Delta P_{\text{channel}}$. A 5-fold increase in k could lead to an impractical 300-fold increase in $\Delta P_{\text{channel}}$. Improved channel spacers are being developed with guidance from CFD simulations[112] but even a doubling of k without $\Delta P_{\text{channel}}$ penalty looks difficult. What other options are available to increase k? Unsteady-state shear may provide the answer with application of vibrations, two-phase flow or pulsations[109,113] which could potentially deliver 2-fold, or even 5-fold the mass transfer at modest energy penalty. However the enhancements may be difficult to achieve in the SWM and much more likely in HFM geometry.[113] The bottom line is that next-generation RO and NF using UPMs may require radically different module design to operate at enhanced flows.

For low pressure membrane processes (MF,UF) the unsteady-state shear stress techniques for fouling control are already well developed, in particular the benefit of bubbly flow. Even greater benefits are promised by vibratory operation of hollow fibers.[114] Future uses of these techniques are likely, including vibrations in anaerobic MBRs where bubbling is difficult. The down-stream side (Figure 5a,b) can also present constraints due to the pressure drop generated by ducting the permeate out of the module. For example, in a submerged MF/UF module with hollow fibers the permeate-side ΔP_{perm} can cause significant maldistribution of driving force and regions of high and low flux.[115] This is exacerbated by an elevated "average" flux and for long fibers of small diameter. Therefore module and fiber geometry need to be optimized. These considerations of flow distributions, polarization control and module pressure drops are common to all membrane processes for water purification and become more challenging at higher fluxes.

ED has similar mass transfer challenges to RO, except the flat-sheet geometry is the only option. To improve the mass transfer coefficient, k, would need better spacers and/or unsteady-state fluid flow. Indeed the use of bubbly flow, without a spacer, has been shown to give improved limiting current densities.[116]

3.3. Antifouling Strategies

Fouling is a serious inefficiency in membrane processing, and is unlikely to be eliminated. Antifouling membranes continue to be a goal (Table 2) and some advances have been made with development of smoother, more hydrophilic surfaces, or the use of polymer brushes.[117] One approach to control biofouling is to have antibacterial properties in membranes and/or spacers,[118] and another future strategy could be "biomimicry". Biofilms develop via quorum sensing and biofilm dispersal and involve chemical triggers; biomimicry control involves manipulating these triggers. For example, quorum quenching bacteria interfere with quorum sensing by producing enzymes that reduce biofouling in MBRs[119] and are being evaluated for RO. Nitric oxide is a dispersal trigger and shown to delay biofouling in RO.[120] Pretreatment in SWRO is an essential part of (bio)fouling control. In order to reduce the overall energy usage in SWRO plants there is incentive to minimize pretreatment energy (currently 10–15% of the overall energy). Beach wells deliver very good quality water at low energy, but may not be feasible geologically. Simple engineered systems combining biotreatment and gravity-driven membrane filtration could become low energy approaches.[121]

3.4. Systems and Processes

This section provides a brief discussion of "smart" systems, novel process engineering, and various enabling technologies that could impact future membrane applications.

The impact of fouling can be reduced by knowledge of the "fouling propensity of the feed" and/or the "state of the system". Online monitoring can provide this information and do this telemetrically allowing remote operation. For example, sensors mounted on a side-stream "canary cell" operating at the same conditions as the plant can provide preemptive fouling data; sensors include ultrasonic time domain reflectometry (UTDR),[122] electrical impedance spectrometery (EIS),[123] and optical detection of incipient scale.[124] It would also be feasible to embed sensors into a module to provide online data, and such a "smart module" (may be 1% of the modules in a large plant) could become a feature in the future. The development of telemetric sensors for membranes supports their use in decentralized treatment and water supply. Membrane technology is ideally suited to decentralized processing[125] and a growth in these applications is anticipated.

In SWRO and brackish RO the cascade designs are well established.[2b] However with the advent of UPMs there would be potential energy savings[126] of 20 to 30% by operating at "close to osmotic pressure", achieved by a multistage process where the pressure is stepped[2a] or by a batch process with steadily increasing pressure (closed-circuit desalination, CCD).[127] Another option being developed involves a combined reflux–recycle approach that manipulates osmotic pressure differences and can achieve extra product recovery without additional pressure.[128]

Renewable energy could have an important place in the future of membranes and water.[125b] For example, in Australia several large RO desalination plant are indirectly powered by wind power and a direct wave-powered RO demonstration plant is being evaluated.[129] Modest-sized RO plant can also be driven by photovoltaics where solar energy is abundant.[130] MD is a thermally driven process and can be run using waste heat or solar energy[131] with little electrical energy input. Similarly FO can desalinate or recover water from contaminated sources using thermal regeneration of the draw solute. The enabling technology includes use of thermolytic ammonium carbonate solution that can be regenerated by distillation;[132] this draw is in commercial use in the treatment of produced water. Thermally responsive polymers have also been developed that have good osmotic draw capability and can be regenerated by a temperature swing.[133]

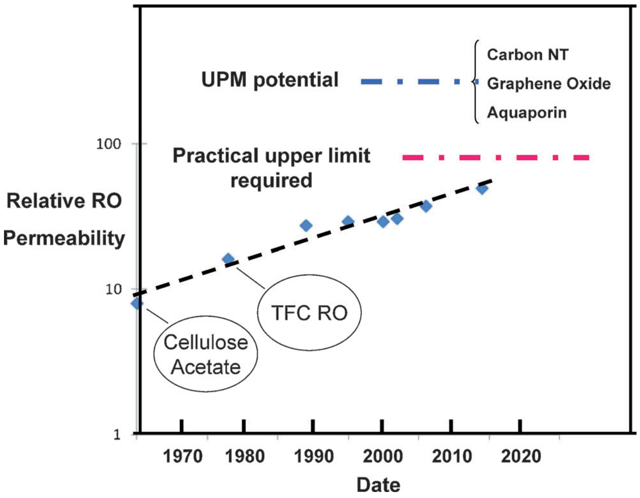


Figure 6. Evolution of relative RO permeability over time.

4. Prospects

The pressing need for increased supplies of potable and industrial water in the face of increasing water scarcity means greater reliance on water purification technologies. There are two inexhaustible sources of water, the sea and used (waste) water. Membranes offer the most feasible options for water purification from these sources, and this means that membrane-based water technology will be crucial for the global community in the future. This provides an incentive for improved membrane processes with lower costs and with energy minimization. In this section we "crystal ball" the various membrane processes relevant to the production of purified water. Table 3 summarizes possible futures over the short term (5 to 10 years) and longer term (10 to 20 years), highlighting technical advances and developing applications. A commercial perspective on market potential, applications, and recent patents is available.[5]

4.1. Reverse Osmosis and Nanofiltration

RO desalination has seen steady improvements over the past 50 years. A "figure of merit" (FoM), based on flux, salt passage, module cost and life time, was proposed by Birkett and Truby[134] who showed that from a baseline of 1 in 1978 the FoM had reached 480 by 2006, and the upward trend appeared to continue for cheaper and better modules. It is of interest to consider the membrane flux (permeability) trends. Figure 6 uses the normalized flux data from the FoM analysis, and includes estimates of earlier cellulose acetate data and recent improvements. The relative RO permeability has increased by an order of magnitude over about 50 years, and it is reasonable to assume this trend could continue. Novel chemistries and materials (CNTs, GO, aquaporins) promise to increase RO permeabilities over the short and longer term. However, Figure 6 also illustrates that the ultimate UPM potential of these novel materials may be well beyond the practical limit based on the constraints of fluid mechanics and membrane module engineering (see Sections 3.1 and 3.2). This means that efforts to develop defect-free sheets of aligned CNTs, aquaporins or graphene oxide, may not be required. A more likely scenario is that mixed-matrix membranes based on these novel materials as fillers in suitable polymer films will achieve the necessary performance. Within about 10 years RO permeabilities will probably be at the limit, even for novel hydrodynamics. In the longer term the potential of UPMs could cause a return to hollow fiber modules (HFMs) since this geometry is more favorable for novel hydrodynamics (vibrations etc).[113] There are two major challenges to a new generation of HFM RO; the first is the production of hollow fiber UPMs, presumably with externally skinned TFC structures, and the second is successfully developing the modules and modus operandi to achieve 2 to 5-fold increase in the boundary layer mass transfer coefficient, *k* (see Section 3.2). The HFM is a possible future, but the SWM will continue to evolve, particularly in terms of module size[105] and optimized spacer designs;[104b] taking *k* beyond 2-fold enhancement with novel spacers in the SWM seems to be unlikely.

The desire to reduce energy demand for SWRO will probably see some changes to system design with "close to osmotic pressure" operation offering energy savings; two approaches are the CCD concept[127] and multistaging.[2a] The use of reflux–recycle[128] could increase recovery without added energy input. Other strategies to reduce energy that are likely to be used include the FO/RO hybrid where seawater is diluted by used water pretreated by FO;[135] the final product includes a portion of reclaimed used water. This is likely to become more common as the idea of direct potable reuse (DPR) gains acceptance.[136] Indeed in terms of energy usage the used water reclamation process (conventional activated sludge + UF + RO + UV) uses only 50 % of that for SWRO. The strategy for the future should be SWRO followed by cycles of DPR.

The inefficiencies caused by biofouling are gradually being overcome, and it is a fair prediction that in the long term RO plant will operate with negligible biofouling. The control strategies emerging include coated membranes or spacers,[118] biomimicry,[119,120] nutrient limitation,[121] osmotic backwash,

Table 3: Possible futures for membrane processes in the water industry.

Process	Near term (5–10 years)	Longer term (10–20 years)
RO/NF	● Permeability rising incrementally (new chemistries, mixed matrix etc) ● Cost reduction ● More chemically robust membranes ● SWM development (spacers, size) ● Systems development (CCD, cascades) ● Improved biofouling strategies ● On-line fouling sensors introduced ● Direct potable reuse increases ● Hybrids NF/RO, FO/RO developing ● NF hollow fibers for water treatment	● Enhanced membranes (towards UPMs) ● (Possible) switch to HFMs with UPMs ● (Possible) use of vibrations (etc) with HFMs ● Chemically robust RO/NF ● Negligible biofouling possible ● Smart modules (inbuilt sensors) ● Direct potable accepted and common place ● Integrated SWRO and reclamation plant
UF/MF	● Membrane/module development ● Cost reduction ● Increased use of ceramic membranes ● Increased pretreatment for SWRO ● Vibratory systems in niche use ● Responsive membranes in niche use ● Low energy gravity-driven UF in niches (remote locations, developing countries) ● Increased decentralization (telemetrics)	● Isoporous membranes available ● Standardization of modules ● Ceramic membranes significant role ● UF/MF standard pretreatment for SWRO ● Application of vibratory systems common ● Wide use of responsive membranes
MBRs	● Commercial use of Anaerobic MBRs ● Improved nutrient (P) recovery ● Combined MBR + RO for reclamation ● Vibratory (etc) for fouling control ● Increased decentralization (telemetrics)	● Anaerobic MBRs common place ● AnMBR + RO (with P recovery) the preferred option for reclamation. ● High retention MBRs for reuse
MD	● Optimization of membranes and modules ● More use in niche areas (remote location, industrial reuse, renewable energy)	● Preferred membrane/module identified ● MD for zero liquid discharge common
FO/PRO	● Optimization of membranes and modules ● Practical draw solutes (DS) engineered ● Applications rationalized (FO/RO, waste, fertigation, renewable energy) ● PRO for osmotic power from SWRO/RO reclamation	● Preferred membrane/module identified ● Common place applications (available DS vs engineered DS) ● Component in FO/RO with seawater and used water inputs.
Membrane contactor	● Coupled with AnMBRs to recover and upgrade biogas	● Established role in niche
ED	● Optimization of membranes and modules ● Coupled with EDI for desalination ● Coupled with renewable energy for low carbon footprint	● Established role in niche

and air flush. (Cautionary note: an eminent biofilm expert[137] observed that "the bugs always win" when it comes to biofouling.) Fouling control and process optimization will be enhanced by use of on-line monitoring, and ultimately by "smart" modules with inbuilt sensors providing signals that preempt changes in pressures or flows.

Nanofiltration membranes are typically flat-sheet thin film composites in SWMs. Applications in water include natural organic removal and softening. They are also used as pretreatment for thermal desalination to remove scale formers, and NF could play a similar role prior for RO to increase recovery in SWRO. A potential application is in the proposed reflux-recycle process to improve recovery without added pressure.[128] Another anticipated development is the application of novel hollow fiber NF for water softening.[138]

4.2. Ultrafiltration and Microfiltration

UF/MF are well-established in the water industry. The choice between UF and MF is application dependent. There are also module options with pressurized (contained) membranes and submerged membranes. Both approaches are popular with a possible trend back to pressurized as this offers more range in driving force and a smaller footprint. Membranes continue to be improved and in some applications multibore hollow fibers have the advantage of strength. It is likely that in the longer term UF/MF membranes will become more isoporous (see Section 2.5), as this could reduce fouling tendency and allow for higher fluxes. The membranes may also be strengthened by mixed-matrix preparation. A current growing trend is application of ceramic UF/MF membranes in the water industry (potable water, pretreatment etc). The economics have shifted to make ceramic membranes more attractive on a lifecycle cost basis.

Vibratory membranes are involved in the VSEP process[139] which has a niche for difficult waste streams. However recent studies[114] (see Section 3.2) have shown the benefit of vibrations for submerged hollow fibers. This approach could become commercialized and eventually common in niche areas, as it can have energy benefits. The novel responsive membranes under development may have potential niche applications in future water processing.

An application of UF/MF that will develop is in pretreatment for the growing SWRO market; the advantages of membrane pretreatment have been analyzed.[140] Another application ready for growth is safe water production in developing countries, for example by gravity-driven UF[121c] which has very low energy demand and can avoid chemical usage. In the general context of water treatment the rapid urbanization globally provides an opportunity for decentralized processing, rather than extending centralized treatment plant. Telemetry is already established for remote monitoring of membrane plant.

4.3. Membrane Bioreactors

The aerobic MBR has developed rapidly since the early 1990s and shown advantages over the conventional activated sludge process (CASP) in terms of improved water quality and reduced foot print.[141] Energy demand is now only marginally greater than CASP. Growth in aerobic MBR plant can be anticipated. However the most likely major development for MBRs will be commercialization of anaerobic MBRs (AnMBRs) and their longer term establishment as the process of choice. The major attraction of the AnMBR is that it can be a net energy producer, even using municipal wastewater as feed.[142] The MBR permeate is better suited for RO reclamation than that from a CASP,[143] and this suggests that as new, "green field", reclamation plant are built they will combine MBR + RO. In the longer term this could be AnMBR + RO, along with recovery of nutrients, such as phosphorous compounds. Another type of MBR that has a potential future is the "high retention" MBR with a retentive membrane that delivers a high quality permeate, suitable for reuse. Examples are the FO MBR and MD MBR,[144] both of which could be driven by waste heat with lower carbon footprint than MBR + RO options.

4.4. Membrane Distillation

MD continues to attract interest as a potentially low-carbon process. However, it has achieved limited commercialization possibly because MD has several options, hollow fiber vs flat sheet, direct contact MD vs vacuum MD. It is likely that one of these combinations needs to dominate before commercial take off. MD will have niche applications, such as produced water, and could become common for zero liquid discharge through the MDC process[145]

4.5. Forward Osmosis/PRO

Forward osmosis has developed very rapidly over the past 10 years;[11] a major driver has been the potential for processing with a lower carbon footprint. Like MD the membranes are either flat sheet or hollow fiber, and for both types further development of the "best" module is required. For example, there is a need for optimal spacers for flat sheets and shell-side arrangement for hollow fibers. Several applications of FO can use available osmotic draws, but some applications need an efficient regenerable draw. Thermolytic ammonium carbonate is now used commercially, and other thermally regenerable draw agents are being developed.[133] Some of the future potential of FO hinges on the availability of better draw agents. Probable applications using available draws are FO pretreatment prior to RO (see Section 4.1) and FO fertigation where fertilizer solutions are the draw and water is obtained from brackish ground water.[146]

Pressure-retarded osmosis (PRO) is a special case using FO to extract power from an osmotic gradient.[13] Improved and strengthened FO-type membranes are needed for pressures up to 25 to 30 bar, and this may require a mixed-matrix approach (see Section 2.6). In addition, module development is required, with special feed spacers to avoid membrane deformation for SWM geometry. The HFM geometry could overcome this subject to availability of strengthened hollow fibers. However, it is likely that PRO will become an integral part of SWRO processing to extract the embedded energy in the seawater brine. Collocation with a wastewater reclamation plant would be required to provide a low salinity brine stream.[147]

4.6. Electrodialysis

ED has had a resurgence with a large plant (200 million liters per day) installed in Spain to produce drinking water from a saline river source.[148] In terms of seawater desalination ED has the potential for low energy processing, and this has been the subject of intensive R&D by Siemens Water Technology (now Evoqua Water Technologies) with support from the Singapore Environmental and Water Industry Programme Office.[149] It has been reported that improved membranes have been developed and that the module design has been optimized. Desalination energy demand (including pretreatment) of $1.65\ \mathrm{kWh\,m^{-3}}$ has been achieved, and this is marginally lower than the best reported for SWRO ($1.58\ \mathrm{kWh\,m^{-3}}$, without including energy for pretreatment).[2c] There are few published details of the process other than it combines the optimized ED with continuous deionization (CDI) to produce a water of acceptable salinity. It is likely that this will lead to commercialization in the short term[149] and could become an important application in the long term. Reverse electrodialysis (RED)[150] is another technology for extracting power from salinity gradients. It would play a similar role to PRO, although PRO could deliver pressure energy directly. RED has a potential role in recovering energy from natural salinity gradients or from those based on SWRO brines and other water streams.

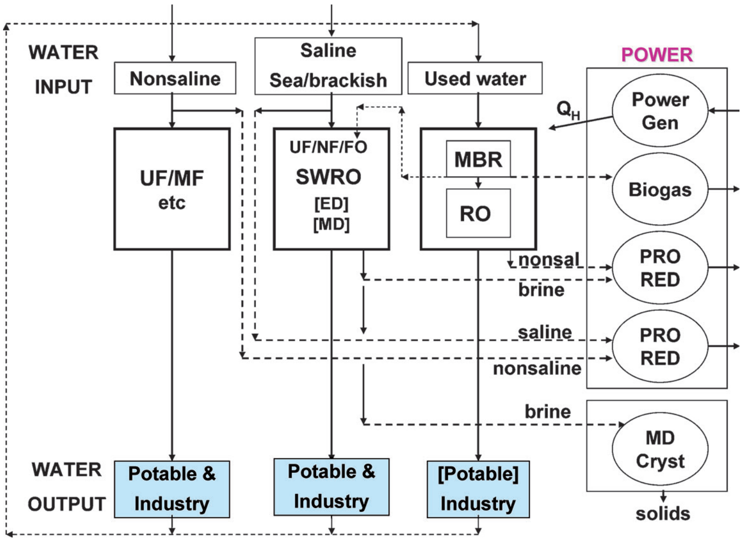


Figure 7. Membranes and the water domain.

4.7. Membrane Contactors

Membrane contactors can be used for gas/liquid contacting,[151] using hydrophobic microporous membranes, similar to MD. A potential application exists in the recovery of dissolved methane from AnMBR permeate streams; methane is relatively soluble in water. Further a membrane contactor absorber could be used to preferentially remove CO_2 from AnMBR biogas to improve the calorific value of the gas.[152] These applications depend on the adoption of the AnMBR, which appears to have a strong future prospect.

5. Conclusions: Membranes and the Water Domain

Figure 7 provides an overview of most of the current and future applications of membranes in the water domain. Future growth is assured due to impending water scarcity. There may be uncertainties around the uptake of PRO and RED for energy recovery and MD crystallization for brine processing. However RO membranes will continue to be the work horse for both saline and used water processing. ED could play a bigger role and MD a minor niche role. The demands of future decarbonization of energy and economic factors provide strong incentives for advances in material science and engineering for membranes in the water domain.

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