Critical Aspects of RO Desalination: A Combination Strategy

by

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Abstract

Due to a significant drop in the energy needed for RO desalination from 12 kWh/m³ to ~2 kWh/m³ over the past 20 years, which is close to 1 kWh/m³, the theoretical minimum for recovering salt-free water from seawater, the focus here is on the critical aspects that offer opportunities to further reduce costs. These include pre- and post-treatment; and analysis and optimization of the performance of RO systems, such as selectivity, capacity, and flux decline. Flux decline includes concentration polarization and fouling from inorganic, organic, biological constituents. We call these the “three legs” that undergird all membrane processes. The approach here is quantitative and includes detailed fluid mechanics and associated mass transfer of RO systems for optimizing performance.

1. Introduction

Greater than 1 billion people worldwide lack access to potable water, and almost 2 million children die each year for lack of clean water and adequate sanitation [1]. The need for potable water is becoming acute in many places including California, Israel, the Gulf region and other arid regions, especially as global warming continues to effect climate and sea levels. Worldwide, consumption of water for municipal, industrial and agricultural uses is expected to increase substantially and aggravate this situation. Creating new sources of high-quality water through reclaiming, recycling, and reusing water will address these challenges [2].

To expand water supply, the National Academy of Engineering (NAE) recommends that engineers and scientists develop new and better ways to desalt seawater, and purify low-quality water, including brackish groundwater, storm water, grey water, and wastewater. Membrane processes offer a promising route to meet these challenges. Forty years ago, the performance of pressure-driven membrane processes yielded high salt rejection, but extremely low permeation fluxes with high energy consumption. This situation has improved markedly over the past several decades and current large scale seawater reverse osmosis (SWRO) plants are able to produce clean water for ~\$0.50/m³ [3]. Most technologies (and users) are moving away from thermal processes such as multi-stage flash and multi-effect distillation, where possible, resulting in the increased demand for faster more energy-efficient processes, such as membranes. The minimum theoretical energy required to separate 35,000 ppm salt (seawater) at 50% recovery is ~1.06 kWh/m³ [4], while the actual energy required for the RO membrane step is now just below ~ 2 kWh/m³.

As a result of improvements in efficiency and cost, membranes now comprise about 65% of the total global desalination capacity of ~100 M m³/day [3, 5, 6], while 31% is from thermal processes. Currently, the water sources for desalination comprise seawater, surface water and saline wastewater at 59%, 21% and 20%, respectively, while annual growth for desalination with membranes is ~ 55%. The total market for membrane desalination technology was ~\$30 billion for 2015, with SWRO plants making up 50% [7]. Although the economics of desalination has

improved dramatically over the past three decades with improvements in energy recovery and membrane process technology [4], further efficiency gains by desalination technology and systems are needed, which will save energy and reduce environmental impact in the US and elsewhere in the future. To determine where such gains may be possible, here we consider the “three legs”, or major parameters, that govern all membrane processes: (i) selectivity, (ii) permeability, and (iii) concentration polarization and fouling. Whether designing a new membrane process or choosing an existing one, one must address all “three legs”.

RO performance is usually characterized first by selectivity and then by permeation flux as a function of time or accumulated volume collected (preferred) on the permeate side of the membrane [8]. Seawater (32,000 ppm) desalination membranes require >99.5% salt rejection in order to attain potable water standards. Other source waters (e.g., brackish groundwater) require lower salt rejection but may require greater selectivity among components (e.g., dissolved metals and boron). Once this rejection is reached, a high flux is desirable in order to render the process economical. A minimum flux of ~40 LMH (~24 GFD) is required to meet current industry standards for desalinating seawater. Membranes with higher permeability (permeate flux/unit applied pressure), but with similar selectivity or salt rejection, are desired to reduce capital costs by lowering membrane area or operating costs by lowering applied pressure requirements.

To maintain desirable performance (salt rejection and an economically acceptable permeation flux with accumulated volume), two different mass transfer limitations have to be minimized. They include concentration polarization (CP), which is the result of the retention of non-interacting species, and membrane fouling. The interaction between CP and fouling is also of great concern, as each phenomenon can worsen the other. CP is caused by the accumulation of rejected salt species during RO desalination, and leads to an increase in osmotic pressure opposing the flow. The driving force for transporting essentially salt-free permeate through a membrane comprises the applied pressure minus the osmotic pressure difference between the permeate and feed. [9-11]. The magnitude of this effect is inversely proportional to the size of the species (i.e. smaller species, like ions, have a larger effect than larger species, such as colloids). Typically, RO modules are arranged in series. This requires the pressure of the feed in the first module to be greater than the osmotic pressure of the concentrate (at the brine side membrane interface) in the last module. The second mass transfer limitation is due to fouling. Fouling is the irreversible build-up of interacting species on the surface or in the membrane pores. This is considered the Achilles’ heel of membrane processes because it can lead to a decrease and ultimate failure of a membrane process. Membrane fouling occurs for all pressure-driven membrane processes and negatively affects RO through organic (biofilm formation) and inorganic (mineral scaling) deposition onto and into the membrane causing performance decline with time. The value of ~2 kWh/m³ required for desalination quoted above excludes the energy required for intake, pretreatment, post-treatment, and brine discharge – this is where many future

cost improvements will likely take place. Thus, cost reductions in both pre- and post-treatment will be critical.

This paper investigates how the future goals for RO desalination technology and processing can be met, by reducing energy consumption; increasing permeability while maintaining desired selectivity and accounting for concentration polarization and fouling; and reducing the cost for intake, pretreatment, post-treatment, and brine discharge. In this paper, we discuss critical aspects of RO desalination, and focus on mitigating strategies of fouling and fouling analytics in RO. This approach relies on a combination strategy of membrane modification and module design (fluid mechanics), process optimization (pretreatment, periodic cleaning) and modeling. Pretreatment, cleaning and other mitigation strategies are used to address fouling and then discussed in detail. Other recent reviews have focused on fundamental transport properties [12, 13], energy requirements [14, 15], life cycle assessments [16], graphene based materials [17, 18], forward and pressure retarded osmosis [19, 20], and the overall RO process [21-23].

2. High flux selective membranes

Increasing permeation flux while maintaining selectivity is the holy grail of membrane science and technology [24-28]. So, it seems reasonable that new methods to form high-flux ultra-thin membranes be sought. Phase inversion and interfacial polymerization have been the dominant methods of preparing asymmetric polymer membranes for pressure-driven liquid separations for the past 40 years [29-32]. According to Kurihara [33], the interfacial polymerization method, which is widely used to prepare selective membranes and forms complex undefined rough surface morphology, needs to be replaced. Although others have recently shown that adding particles (e.g., titanium oxide, silver or zeolites) to a casting solution during interfacial polymerization can increase separation efficiency [34-37], none of these approaches, to our knowledge, have smoothed the surface on a molecular scale. Livingston et al. recently reported the successful addition of metal organic frameworks (MOFs) and nanoparticles (NPs) to synthetic membranes, an active area of chemistry and materials research [38].

If nature has optimized desalination, then we should learn nature's rules on how the aquaporin channel transports water selectively across the biological membrane. It comprises a ~ 3 Å diameter channel with mostly hydrophobic amino acids lining the walls [39]. Recent calculations show that desalination is possible at ~ 7 Å in hydrophobic channels like carbon nanotubes [40]. Conceptually, water flows through carbon or hydrophobic tubes with little or no resistance since water does not hydrogen bond to the walls [41]. Others have suggested that graphene, which is one atom thick, will offer the highest permeation flux possible for a desalination barrier when punched with 3-7 Å holes [42]. When oxidized to graphene oxide (GO) and laid as flakes onto each other on a porous support, it was shown that the tortuous paths exhibited extremely high water transport rates [43].

In **Fig. 1**, the current state-of-the-art of hydrophilic commercial and hydrophobic laboratory membrane performances are summarized. The former exhibits excellent selectivity ($>98\%$ salt rejection) with relatively low permeability ($2 \times 10^{-12} - 5 \times 10^{-12}$ for seawater and $6 \times 10^{-12} - 2 \times 10^{-11}$ $\text{m Pa}^{-1} \text{s}^{-1}$ for brackish water), while the latter shows very high permeability (2×10^{-10} $\text{m Pa}^{-1} \text{s}^{-1}$) with poor selectivity (50-60% salt rejection).

Fig. 1. Comparison of permeability and salt rejection of commercial RO membranes and nanostructured membranes reported in literature. Open symbols represent seawater/high salinity conditions while closed symbols represent brackish/low salinity conditions. Regions enclosed by dashed lines represent commercially available membranes. AP-B: aromatic polyamide (brackish); AP-S: aromatic polyamide (seawater); CA: cellulose acetate (brackish); CNT: carbon nanotube (brackish); Z-DG: zeolite, direct growth method (brackish); Z-IE: zeolite, interfacially embedded (brackish). The ideal RO membrane characteristics are indicated by the orange region (goal). A magnified view of the outlined box is shown to the right. Used with permission from Humplik et al., 2011 [23].

It is important to consider the implications of membrane surface chemistry and flux on membrane fouling. Hydrophobic membranes appear to offer high permeability, but may not sustain initially high values in the presence of organics in the feed that have high affinity for such surfaces. This is in contrast to more hydrophilic membranes, which generally exhibit less severe organic fouling. High flux membranes will inevitably lead to increased concentration polarization and fouling, which will ultimately limit the process. This is an example of how one must achieve a balance among the performance of all “three legs” of synthetic pressure driven membrane processes to achieve optimized membrane filtration and successful implementation at industrial scale.

3. Types of RO Fouling

i. General membrane fouling

Flux decline occurs during membrane filtration because species in the feed stream are rejected and accumulate on (or in) the membrane as filtration proceeds. As previously discussed, flux decline can occur as a result of concentration polarization phenomena through osmotic effects, which is reversible, and can be reduced by decreasing flux, increasing mass transfer thereby reducing the build-up of solute near the membrane, or both. In contrast, fouling phenomena involves physical and chemical interactions between the feed components and the membrane surface, which may lead to adsorption or adhesion. Such fouling is difficult to eliminate, but may be minimized by pretreatment to remove foulants from the feed; judicious selection or design of membrane properties (hydrophobicity, charge density, surface roughness); control of solution pH, ionic strength and hardness; and optimization of fluid mechanics including solution flux and surface shear. Restoring flux after fouling often requires cleaning with chemicals (acids, bases, detergents), and in some cases it may be irreversible.

The impact of fouling and the ability to restore flux depends in part on whether the foulant species are sufficiently small to penetrate into the pore structure, in part because the surface area within the porous structure can be much greater than the area of the membrane-feed interface (top face of the membrane), and because interactions with the porous support may be different. For example, Robertson and Zydney [44] found that albumin uptake in the substructure and matrix of asymmetric ultrafiltration membranes caused greater reduction in hydraulic permeability when the membrane molecular weight cutoff (MWCO) was large, because protein could gain access to the porous structure and sorption reached monolayer coverage.

ii. Biological Fouling

Mechanisms. Biological fouling was defined by Matin et al. [45] as the unwanted deposition and growth of biofilms. IUPAC defines biofilms as an “aggregate of microorganisms in which cells that are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS) adhere to each other and/or to a surface” [46]. EPS is composed of extracellular biopolymers having various structural forms, rich in 10 to 30 kDa heteropolysaccharides such as bacterial alginate [47]. Biofouling can increase transmembrane resistance, increase osmotic pressure due to hindered mass transfer away from the membrane surface, and increase axial friction losses and pressure drop in the feed channel, due to membrane fouling, spacer fouling, or both [48].

The progression of membrane biofouling has been characterized as: 1) initial attachment of planktonic cells, during which bacteria and nutrients present in the feed solution are transported to the surface; 2) colonization of the surface and formation of a biofilm structure, and, 3) subsequent increase in pressure drop, permeate flux reduction, and deterioration of

product quality [49]. Biofilm formation is perhaps the most problematic, as it can exacerbate pressure drop, lead to biocide resistance, and is difficult to remove, making biofouling a constant operational challenge [50].

A precursor to biofilm formation is the adsorption of humic substances, polysaccharides and proteins that “condition” the surface, changing surface properties and presenting binding sites for bacterial cells [45]. Then, bacterial cells are transported to the surface via permeation drag, where some adhere strongly, possibly as an adaptive response to low nutrient availability [51]. Subsequent EPS production, stimulated by cell-to-cell signaling, stress, or limited nutrient availability, physically stabilizes the bacterial community, forming a three-dimensional matrix that is often irreversible [51]. Finally, as the biofilm ages and is subjected to shear forces, portions of it may detach [52].

The biofilm that initially forms in feed channels and on membrane surfaces creates a hydraulic resistance that depends on biofilm composition, with EPS considered a major contributor to flux decline [49]. The volume of bacterial cells within a biofilm may be quite small; Dreszer et al. [48] reported a value of less than 0.5% of the biofilm volume. Biofilm composition may change in response to nutrients, temperature, redox potential, pH, age, and cleaning history [53, 54]. Since they can affect mass transfer, biofilms can promote precipitation of inorganics in systems that would otherwise be understaturated [53]. McDonogh et al. [55] reported that various cleaners could change the permeability of biofilms, in some cases increasing it by a factor of 8 without removing a significant portion of the biomass.

Desalination membrane modules are typically designed using either spiral-wound or hollow fiber configurations [56]; Khan et al. [54] report that cellulose triacetate membranes are available as fine hollow fibers. For both configurations, increased feed channel and transmembrane pressure drop and decreased salt rejection are potential indicators of biofouling [45]. Dreszer et al. [48] measured biofilm resistance of $6 \times 10^{12} \text{ m}^{-1}$ in short term (4 d) experiments employing transmembrane flux of $20 \text{ L m}^{-2} \text{ h}^{-1}$; this resistance is relatively small compared with the typical resistance of NF ($2 \times 10^{13} \text{ m}^{-1}$) and RO ($9 \times 10^{13} \text{ m}^{-1}$) membranes. The biofilm resistance was about an order of magnitude higher ($5 \times 10^{13} \text{ m}^{-1}$), approaching that of RO membranes, when the transmembrane flux increased to $100 \text{ L m}^{-2} \text{ h}^{-1}$. This resistance has been explained by a gel-like diffusion layer [49] or a tortuous matrix [48]. Zdrorow et al. [57] found that biofilms formed during desalination of Long Island Sound seawater pretreated by microfiltration. The biofilms, which consisted of a homogeneous microbial mat, caused a 5 to 7% decline in transmembrane flux over the course of the 4-d experiment; greater fouling was seen in colder weather, possibly due to greater EPS formation. A strong selection away from the bacteria naturally abundant in the seawater was observed; however, bacteria concentrations were stable, indicating succession. At high RO pressures, biofilm compression may also be important.

Vrouwenvelder et al. [58] examined biofouling of RO and NF membranes filtering groundwater pretreated with UF. They concluded that biofouling is mainly a feed spacer channel problem, because although the feed channel pressure drop increased substantially, the transmembrane pressure drop was relatively constant over 146 d. Consistent with the work of Dreszer et al. [48], the biofilm resistance was small compared to NF and RO membrane resistance. The increase in feed channel pressure drop, biomass ATP, and transmembrane pressure drop did not depend on whether there was permeate production ($J_v = 20 \text{ L m}^{-2} \text{ h}^{-1}$) or not ($J_v = 0$).

Role of anti-scalants. Antiscalants are used to inhibit the formation and precipitation of crystallized mineral salts. Most antiscalants are proprietary polymers or mixtures of polymers made from polyacrylic acids, polymaleic acids, organophosphates, polyphosphates, phosphonates, or other anionic polymers. The molecular weight of antiscalants is reported to range from 2 to 10 kDa. Anti-scalants used during pretreatment can introduce nutrients and substrate that promote biofouling [59]. Vrouwenvelder et al. [60] found that biofouling in pilot scale RO modules correlated with the ATP production of bacteria grown in batch tests using anti-scalant polymers as substrate. Biofouling also correlated with the organic carbon content of the anti-scalants that could be used by microbes as substrate (the assimilable organic carbon, AOC) even though the AOC values (4 to 112 $\mu\text{g C/l}$) were small, and significantly lower than the background dissolved organic carbon content (on the order of a few mg/L). Therefore, they recommend anti-scalants having negligible AOC values.

Sweity et al. [61] found that polyacrylate-based anti-scalants promoted biofouling by altering the hydrophobicity and surface charge of RO membrane surfaces. Polyphosphonate-based anti-scalants also contributed to biofouling by providing a source of phosphorous in otherwise phosphorous-limited conditions typical in seawater desalination [61]. More recently, the effects of different anti-scalants during brackish water desalination were investigated using microscopy techniques. Contact angle measurements increased from $21 \pm 5.8^\circ$ for a pristine membrane to $48 \pm 4.9^\circ$ and $49 \pm 1.3^\circ$ after addition of polyacrylate and polyphosphonate-based anti-scalants, respectively. The initial rate of flux decline during brackish water desalination was similar for both types of anti-scalants, but eventually reached a 30% lower permeate flux for polyacrylate-based anti-scalants [61]. Addition of a polyphosphonate-based anti-scalant showed higher uptake rates of oxygen, nitrogen and phosphorous but a smaller effect on salt rejection when compared to polyacrylate-based anti-scalant. A pilot-scale study showed larger amounts of EPS on fouled membrane samples that received dosages of polyacrylate-based anti-scalant, attributed to the nutritional stress given by phosphorous-limiting conditions that in turn lead to more EPS secretion. This stress behavior was further confirmed with confocal laser scanning microscopy (CLSM) and SEM images that show a thicker biofilm on the surface of membranes supplemented with polyacrylate-based anti-scalants. As a result, polyacrylate-based anti-scalants resulted in higher flux decline effects and more pronounced bacterial adhesion rates than

polyphosphonate anti-scalants. The use of anti-scalants in NF and RO processes is essential to prevent membrane deterioration and achieve optimal operating conditions. However, their use should be controlled and monitored to minimize biofouling effects; research is needed to develop alternatives that promote stable membrane performance [62].

Diagnosis of biofouling. There are two main goals for quantifying biofouling: (1) early detection for prevention of irreversible biofouling and (2) assessing post-mortem extent of biofouling to create fouling models for prediction and prevention. In either case, biological parameters of feed water are quantified by microbial analysis, which includes heterotrophic plate counts, total direct cell counts, ATP concentration, and assimilable organic carbon (AOC) concentration. When early detection is the goal, non-disruptive, and inexpensive measurement techniques can be used in the field to help assess whether a membrane needs to be cleaned to prevent irreversible fouling. Normalized Pressure Drop (NPD) is a widely used indicator to monitor fouling, by tracking the pressure needed to maintain constant flux operation, and defining a threshold to indicate when cleaning is needed to avoid operational problems [63]. However, NPD lacks the specificity needed to differentiate biofouling from other fouling sources, and is relatively insensitive to the onset of irreversible fouling.

Another non-invasive method uses the membrane fouling simulator (MFS) [64]. MFSs are small membrane cells equipped with a sensor for sensitive monitoring of pressure drop, and with a glass window that allows non-destructive visual monitoring. The membrane can be removed from the cell for destructive membrane testing and to obtain information about the physical and chemical characteristics of the biofouling layer [63]. MFSs have been used to measure biofilm oxygen consumption and conduct real time fluorescence imaging [65]. They have also been used to evaluate different pressure drop detectors [66]. MFSs are limited in that they only monitor feed channel pressure drop; however, these devices hold promise to help optimize cleaning strategies in NF and RO membranes.

Assessing biofouling at a level of detail sufficient to support model development requires examining the behavior and distribution of microbes on the surface of the membrane. Indirect measurements of biological activity include uptake of substrate, oxygen, nitrogen and phosphorus. Bacteria can be imaged with electron microscopy, and fluorescent staining in combination with confocal laser scanning microscopy and in-situ hybridization can localize type of microbes on surfaces and distribution of polysaccharides, lipids, and proteins. Data from such experiments can help elucidate mechanisms and key players in biofouling, which can inform models for biofilm growth. Such models can be helpful to identify and test methods to inhibit biofilm growth. The goal is to develop techniques to monitor membrane biofouling in real time, non-destructively, in- situ, accurately and reproducibly to track factors that promote biofilm growth [67].

4. Fouling Mitigation Strategies

i. Pretreatment

Pretreatment is a critically important step in effective desalination of seawater. It also offers the opportunity to reduce the total production cost of desalinated water. The raw seawater feed must first be treated in order to remove a large extent of the foulants before reaching the RO membrane. Physical pretreatment, including conventional filtration and MF/UF, can be used to reduce fouling, silt density index, and turbidity of the feed seawater. Physical pretreatment includes filtration through screens, sedimentation, cartridge filters, sand filters, and MF/UF membrane filtration [68]. Chemical pretreatment is also commonly used to reduce scale formation and coagulants as well as disinfect the water. Chemical pretreatment uses additional chemicals such as FeCl_3 and FeSO_4 as coagulants in addition to disinfectants and anti-scaling agents [77, 88]. Chemical pretreatment has proven to be effective; however, since chemicals are being introduced into the feed stream, they must be removed later on in the process. It is undesirable to add new species to the feed stream if possible, although some plants combine physical and chemical pretreatment. Several factors are involved when choosing the appropriate type of pretreatment. These include quality and consistency of the feed seawater, capacity of the system and available footprint for the equipment, cleaning and maintenance costs, and capital and operating costs [69]. Pretreatment steps are dependent upon the quality of the seawater, except for UF which is largely independent of the incoming water quality [70]. The methods currently employed have not changed much over the years, so newer technologies are needed. Desirable improvements include longer lifetime of UF membranes, alternative technologies that require lower pressure, and better chemical treatment options.

Physical pretreatment is less expensive than traditional chemical pretreatment since no additional chemicals need to be added, this includes the additional costs of the UF membranes [71]. Hollow fiber UF technology has increasingly gained acceptance as a viable alternative for seawater pretreatment [72-74]. Reasons for the increasing interest in UF pretreatment over conventional approaches include superior and more consistent filtrate water quality, ability to cope with variable feed water quality, lower plant footprint, and competitive cost [72]. UF membranes with a pore size of $0.02\ \mu\text{m}$ have been the most effective for removing silt, algae, bacteria, and large molecular weight organics [70]. For example, Hong et al. [74] demonstrated that the UF pretreatment achieved 1.96-log removal of bacterial cells. The permeate stream must have a turbidity below 0.1 NTU and a 15 min. silt density index (SDI_{15}) less than 2.5 [70]. The SDI_{15} is measured by monitoring the flux decline over 15 min. when the feed is continuously filtered through a $0.45\ \mu\text{m}$ membrane at a TMP of 30 psi. UF is able to achieve an SDI less than 1 starting from a feed with an SDI_{15} of 13-25, whereas conventional pretreatment is unable to reach below 2.5 [75]. Reducing the SDI further below 2.5 is not required, but the lower the SDI the lower the frequency of cleaning of the RO membrane. Conventional pretreatment involves coagulation and a two stage sand filtration, which requires the RO membrane be cleaned 4-12

times per year [76]. Typical lifetime of this system is 20-30 years. Using UF, the RO cleaning frequency is only 1-2 times per year. Typical lifetime of the UF membranes is 5-10 years [77]. An advantage of UF is that it is relatively independent of the feed water composition [70]. In order to prevent the UF membrane from being damaged, a fine screen of 80-120 μm must be used before the UF step [78, 79]. This will prevent tearing or other damage to the membrane from glass, shells, or other contaminants.

There are several other unique advantages to UF pretreatment. UF membranes are reliable and have been shown to maintain permeate turbidity over at least six months, even with high turbidity feed water [80-82]. They also have a small footprint and remove the cost of additional chemicals and disposal of those chemicals as hazardous waste. For instance, coagulants, such as ferric chloride, are no longer needed and the RO membrane cleaning frequency is reduced [78]. UF membranes require lower energy [84] and they reduce the environmental impact of the process by more than 30% since they have a smaller footprint, require fewer materials, and have low energy consumption [70, 85]. UF membranes are better at removing solids and are simpler to operate than chemical pretreatment methods. These membranes can also be embedded with metal nanoparticles, such as TiO_2 , to increase their anti-biofouling effects [86, 87]. These membranes are typically made of stable polymers with high glass transition temperatures, such as poly(ether sulfone) (PES) or polysulfone (PSf). A process diagram of traditional UF pre-treatment is shown in Fig. 2 [83]; for purposes of illustration, several examples will serve to illustrate important operational details.

Fig. 2. Process diagram of a conventional integrated UF-RO system design that utilizes an intermediate UF filtrate storage tank for UF backwash water, UF backwash pump, and RO booster pump. Used with permission from Gao et al., 2016 [83].

The Maspalomas-I Desalination Plant, located in the island of Gran Canaria, Spain, produces 14,500 m^3/d . Hollow fiber PVDF UF membranes (Dow 0.03 μm pore size) are used for RO pretreatment [3]. The UF system operates in dead-end mode at fluxes ranging from 65–80

LMH, depending on demand, with 60 min filtration cycles before backwashing with ultrafiltrate water. Air scour at the feed side of the fibers aids backwashing. Chemically enhanced backwash (CEB) is carried out using 200 mg/L sodium hypochlorite at intervals of 24 to 48 h for organic fouling control and disinfection. Hong et al. [3] found that CEB removed sulfate-reducing bacteria from UF membranes, preventing sulfate reduction and hydrogen sulfide production by *Pseudomonas* in coexistence with *Desulfovibrio*, thus mitigating corrosion problems and ensuring membrane integrity. An acid CEB with HCl at pH 2.0 to 2.2 is executed every 72 h as maintenance cleaning to prevent inorganic scale accumulation. In addition, the plant has capability for offline intensive cleaning via a clean in place (CIP) system using heated RO permeate; however, this has not been needed after almost one year of operation. To minimize the chlorine residual downstream of the UF membranes, a thorough rinse via backwash is carried out after CEB, and the initial ultrafiltrate volume after rinsing is wasted to drain until the residual chlorine is below 0.20 ppm. In addition, sodium bisulfite (SBS) is dosed temporarily at the UF product tank inlet. Sodium bisulfite dosing at the RO feed is also done after disinfection of the UF product tank.

The Adelaide Desalination plant has a 30,000 m³/d capacity, and employs Memcor submerged PVDF UF membranes for RO pretreatment. Membranes operated at a flux of 53 LMH during pilot testing, and 44 LMH during commissioning. Dixon et al. [1] describe UF cleaning trials at pilot scale and full scale commissioning at 1/10 capacity. The system design incorporates a UF product tank, and cartridge filters downstream of the feed tank and directly upstream of the RO membranes. Optimization of the UF cleaning regime included intake disinfection (shock dosing), maintenance washes, and CIP protocols to reduce energy and chemical consumption. The design UF backwashing interval was 30 min, but it found that a 70 min interval was sufficient. Shock dosing of the feed using 15 mg/L sodium hypochlorite was found to be an effective tool to control biogrowth in the UF system. Maintenance washes to control biological accumulation consisted of dosing 300 mg/L sodium hypochlorite at 4-d intervals. Less frequent (two week intervals) washes with sulfuric acid (pH 2 to 4) were also recommended. A two-stage CIP protocol consisted of 4 hr soak and filtration cycles using 500mg/L sodium hypochlorite followed by 0.25% citric acid, adjusted to pH 2.0 using sulfuric acid. The authors recommend a heating system heating to ensure a cleaning recirculation temperature range of 20–25 °C, but did not recommend a specific interval for this protocol. Sodium metabisulfite was used to neutralize free chlorine residual prior to the RO to prevent membrane oxidation. The best placement of the metabisulfite feed was directly upstream of the RO membranes, and downstream of the cartridge filters, to include the cartridge filtration in the shock chlorination pathway.

Cohen et al. have made several recent advancements in this field by directly integrating the UF and RO steps, without using an intermediate filtrate storage tank, and backwashing the UF membranes with the RO concentrate [83]. A schematic of this process is shown in **Fig. 3** [83].

Fig. 3. Process diagram of a directly integrated UF–RO system. Flow rate (Q) and pressure (P) at the UF–RO system interface are maintained by a control system. Used with permission from Gao et al., 2016 [83].

Both physical and chemical pretreatment have drawbacks. UF pretreatment includes cleaning costs, replacement membranes, and cartridge disposal. The waste is typically sent for land disposal. Cleaning, disposal, and replacement of membrane cartridges increases the cost to make the product water [77]. In fact, the cleaning cost of the UF membranes is more than the cleaning cost for the RO membranes [89]. Chemical pretreatment includes pre-treated sludge disposal, high chemical usage, and sludge production. The waste is typically deposited into a landfill. Transportation of the sludge represents 18.4% and disposal represents 78.3% of the cost of sludge removal, increasing capital costs by up to 25% [77]. Therefore, reducing the amount of sludge produced would significantly reduce the costs associated with chemical pretreatment. The areas that require the most improvement in the pretreatment process are corrosion of piping and other equipment, brine and sludge concentrate disposal, and boron and bromide level management in the water [77].

ii. Biocide treatment

The use of chlorine as a biocide is not always successful and in some cases has been known to worsen biofouling [53]. It is possible that chlorine promotes EPS formation by stressed organisms that survive the treatment, and those that do not survive may serve as a nutrient source for remaining organisms. In addition, chlorine may oxidize other organics (such as humic substances), making them more bioavailable as a carbon source [53]. Kahn et al. [54] demonstrated that chlorination could not prevent biofouling of hollow fiber SWRO membranes and concluded that chlorine failed to access all regions of the modules. They also cited the possibility that bacterial populations developed resistance to chlorine over time.

iii. Periodic cleaning

Another method used to mitigate fouling is periodic cleaning of the membranes. Clearly there is a trade-off between cleaning intensity and frequency and pretreatment. Since all membranes will inevitably foul, they usually need to be cleaned periodically. Membranes are typically cleaned when their performance falls below a certain threshold, usually after a decrease in permeate flux of 10% or a pressure increase of 15-20% [90, 91]. Cleaning represents approximately 5-20% of the overall cost of the RO process [92]. There are three different types of cleaning methods: physical, chemical, and biological. Of these, chemical cleaning methods are the most common. The chemicals used are chosen based on the membrane material and the solubility of the foulants. Additionally, the water used in the cleaning process must be of high quality, in order to avoid introducing more foulants into the system [93]. High quality water should be used, but additives such as ethylene diamine tetra-acetic acid (EDTA) and polyphosphates can also be used to increase the solubility of metal ions that are present on the membrane (Ca, Mg, Mn, Fe) [94]. These impurities can reduce the cleaning efficiency, especially chlorine. Species such as sodium, nitrates, and sulfates have been shown to increase the efficiency of the process (flux recovery) [93]. Common strategies for cleaning membranes include: 0.1 M sodium hypochlorite at 50°C for 30-60 min. (not compatible with stainless steel equipment over long periods), 0.1-0.5 M NaOH at 50°C for 30-60 min. (store membranes in 0.1 M NaOH), 0.1 M phosphoric acid at 50°C for 30-60 min. (used to dissolve residual minerals that may plug pores), and 1 M salt solutions (NaCl) for 30-60 min. (decreases the Debye length around proteins and the membrane surface causing the proteins to lift off the surface due to reduced electrostatic interactions) [95]. When choosing a cleaning method, there are several parameters to consider, such as pH, concentration, washing time, crossflow velocity, pressure, temperature, and chemical [96-98]. Physical methods, such as backpulsing have also been successful in cleaning the membranes after fouling [99-101].

Biofilm formation is particularly difficult to remove and is usually cleaned using a two-step process. First, the biofilm matrix is weakened using chemicals that interfere with bonding and second, shear forces are used to remove the biofilm from the surface [102]. Commonly used chemicals include alkalis, acids, metal chelating agents, surfactants, oxidation agents, and enzymes [103, 104]. For spiral wound cellulose acetate RO membranes, enzyme anti-precipitant-dispersants and bacterial agents with an anionic detergent were found to be the most effective ways to remove biofilms [105, 106].

The pore structure of the membranes is often altered due to fouling. In a paper by Roth et al. these changes were monitored by tracking salt concentration [107]. Before fouling, the salt concentration distribution was unimodal, but after fouling it was multimodal. It is believed that these effects could be due to an enlarged pore size. Additionally, chlorine is able to degrade many different types of membranes and therefore should be minimized or removed before reaching the membranes. The RO membranes are sometimes made of cellulose acetate, which

can be degraded by chlorine ions. One way to counter this is to add ammonia to the feed, forming ammonium chloride [108]. For polyamide membranes, chelating agents and surfactants with alkali were able to clean the membranes better than just acids and alkalis alone [106].

Backpulsing, reversing the flow direction, can be used to help dislodge foulants and increase the time between cleaning; it is also an effective method for reducing biofilm formation. Results have shown that backpulsing can increase the net flux by two-fold and four-fold for 0.2 μm Anopore and cellulose acetate, respectively, when fouled with 0.05 g L^{-1} yeast cells [99]. However, weaker backpulses were unable to dislodge strongly bound foulants and increasing the duration of the pulses only lead to an increase in fluid loss. Semi-empirical modeling the effectiveness of back-pulsing is also available [101].

iv. Chemical modification

Chemical modification of the UF and RO membranes is also an effective method for mitigating fouling. Current modification techniques include polymer grafting by chemical treatment (UV and plasma), thin-film coating, and layer-by-layer assembly. Belfort et al. have developed a high throughput screening platform that utilizes free radical polymerization to graft and screen hundreds of different surfaces per day [109-113]. Radicals can be induced on PES membranes using UV light (no initiator required) or atmospheric pressure plasma, thereby activating them and allowing them to react with a library of many different monomers each containing different functional groups and properties. One is able to vary the grafting density, monomer concentration, plasma power, exposure time, plasma distance from sample, and residence time of the plasma exposure. This method is also amenable to grafting newly synthesized monomers and screening them for the best performing modification. This allows one to tune the surface chemistry for a specific process or a specific step of a process. PEGs, zwitterions, amides, and amines have been shown to be anti-protein fouling, which can be useful for the UF pretreatment step to prevent biofilm formation due to polysaccharide and protein secretions. In particular, (N-isopropylacrylamide), diacetone acrylamide, 2-(dimethylamino) ethyl methacrylate) exhibited protein resistance [114]. This will increase the lifetime of the UF membranes and increase the time between cleaning. This platform was developed for UF PES membranes, but has been applied to MF and NF membranes as well and can be applied to RO.

Since polyamide membranes are typically negatively charged due to unreacted carboxylic and amino groups present on the surface, this leaves them open for reaction or non-covalent attachment, such as surface coating. Surface coating is typically a two-step process, first the membrane is soaked in a polymer coating solution and then the solvent is evaporated leaving a thin coating layer [115]. The membranes can be coated with various different polymers, such as PEG, polydopamine, zwitterions, and chlorine resistant coatings, in order to increase performance during desalination.

PEGs have long flexible chains with a large excluded volume and a repeating unit of $-(CH_2CH_2O)_n-$. PEGs have a Flory-Huggins interaction parameter of 0.4-0.5 [116]. Water molecules have been shown to create a hydration shell and lower the polymer-water interfacial energy, which reduces cell adhesion [117-119]. PEGs are known to be hydrophilic and reduce adhesion of bacteria and proteins [115]. Additionally, they can be cross-linked to form a hyper branched polymer which can prevent biofilm formation. Polydopamine coatings do not have a significant effect on permeability and can be used as an immobilization platform for covalently attaching PEG and other molecules of interest [120, 121].

Zwitterionic coatings are able to bind water more strongly than other materials due to electrostatically induced hydration [122, 123]. Chlorine resistant coatings are extremely useful since the membranes used in RO desalination are susceptible to degradation by chlorine. Meta-phenylene diamine (MPD) groups contain electron donating groups, such as $-CH_3$ and $-OCH_3$, that have high chlorine resistance [124-126]. Positively charged and neutral surfaces are believed to be more chlorine resistant than negatively charged surfaces. However, the addition of MPD makes the RO membranes less hydrophilic.

Layer-by-layer (LbL) assembly is another method that can be used to change the surface properties of a membrane. LbL was developed by Gero Decher and involves dipping the substrate in alternating solutions of polycations and polyanions with DI water washing in between [127, 128]. LbL assembly can use electrostatic interactions, hydrogen bonding, or covalent bonding to attach the layers to the surface. The film properties are a function of polyelectrolytes used, pH, and deposition time. The two types of polyelectrolytes are strong (e.g. poly(diallyl dimethyl ammonium chloride) and weak (e.g. poly allylamine hydrochloride) [129-132]. Since the layers are on the nanoscale in thickness, permeability is high and high charge density increases rejection [133]. Nanofiltration membranes with LbL deposition are able to retain ions for desalination [134, 135]. They have been able to achieve up to 96% salt rejection of SO_4^{2-} with a Cl^-/SO_4^{2-} selectivity of ~ 2.7 using 60 layers of deposition, although the fluxes were very low. LbL NF membranes were also able to remove F^- with high flux based on size exclusion (not charge) [136].

A study by Tieke et al. deposited 60 bilayers of polyvinyl alcohol (PVA) and polyvinyl sulfate (PVS) on a PAN/PET support and tested the assembly in a high pressure desalination test cell [137, 138]. The results showed up to 93.5% NaCl rejection at 40 bar. When a non-diluted salt system was used, 56.6% rejection at 20 bar and 74.5% rejection at 40 bar were achieved for NaCl. Rejection for divalent ions was greater than 95% at 40 bar. These lower rejections were due to concentration polarization and the inability of these LbL membranes to achieve high rejection at high salt concentration. However, as the number of layers increased, the permeability decreased by up to 2000 times the unmodified substrate. The flux can be increased using a more porous support layer. Another study by Park et al. used PAA and PAH to form nano-thin films on a PSf support to reject saltwater with a concentration of 2000 ppm [139]. The layers were

cross-linked via thermal annealing at 180°C for 1 hr. A rejection of 81% was achieved using 20 bilayers and up to 99% rejection was achieved when the dilute permeate was recycled.

LbL deposited layers are able to reduce the flux decline over time since they are more anti-fouling and reduce concentration polarization [140, 141]. This is advantageous even though the initial pressure requirement is higher than conventional RO. The biggest drawback of LbL is the added thickness, which leads to a decrease in flux by increasing the resistance. Additionally, non-covalent LbL attachments are likely unsuitable for water desalination applications. This is due to the fact that certain species (e.g. PEG) are water soluble and will dissolve into the feed stream over time [115]. This renders the LbL modification ineffective; therefore, covalent attachment is required. LbL is not able to achieve a high enough salt rejection to compete with current technology. In order to increase the rejection to current standards, either an excessive number of bilayers must be used or the layers need to be highly cross-linked. Since these changes will increase the resistance, the required operating pressure will increase. Dutta et al reported that LbL layers when neutralized become stiff and this could also affect performance [142].

v. Fluid mechanics

Introduction to the need for fluid flow: Fluid mechanics, with regard to synthetic membrane operation and performance, is intimately involved with the *transport of mass* of fluid and dissolved and suspended components in the fluid towards and away from the membrane. For desalination of sea- and brackish-waters by reverse osmosis (RO), water needs to be transported to the membrane so it can pass through the membrane while retaining the salt and other solutes on the feed or brine side. The difference between membrane ultrafiltration for bioprocessing and potable water reclamation with RO is that in bioprocessing the solutes, such as proteins, are the desired product. For potable water RO filtration, on the other hand, the carrier fluid (water) is the product. Consequently, pretreatment (to remove foulants) and fluid management (to control concentration polarization, CP) is important for RO, while fluid management is critical for ultrafiltration since the solids are retained and desired.

Feed fluid can flow directly toward the membrane and this is called normal or “dead-ended” flow. It is mainly used in small laboratory applications. For large-scale laboratory and commercial plants, the feed fluid moves across or tangentially along the membrane and is called tangential or crossflow filtration. The reason for this has to do with removing part of the buildup of retained species (salt, precipitate, organics, cells and other debris) at the solution-membrane interface. Since most other solutes besides salts are mostly removed through pretreatment for RO, only CP and fouling of salts that precipitate like CaCO_3 or silica are mainly of concern.

Laminar and turbulent crossflow: Most RO plants operate in crossflow or tangential mode in the laminar regime. The reason for this is most easily seen through the Fanning friction factor for flow in a tube of radius R and length L .

$$f = \frac{-\Delta p_{tc}}{\frac{\rho}{2} \bar{u}_0^2} = \frac{\text{axial pressure drop}}{\text{kinetic energy consumption}} \quad (1)$$

where Δp is the time-smoothed pressure drop down the channel of length, L , and $\bar{u}$ is the mean axial flow rate. In **Fig. 4**, f is plotted against the axial Reynolds number, $Re=(2UR/v)$, where v is the kinematic viscosity [143].

Fig. 4. Experimental dimensionless trans-cartridge pressure drop as a function of feed Reynolds number (Re_F) for different wall Reynolds number (Re_w). R is the volumetric recovery ratio. Used with permission from Mellis et al., 1993 [143].

For laminar and turbulent flow Δp is approximately proportional to $\bar{u}$ and $\bar{u}^2$, so that $f \sim 1/\bar{u}$ and a constant, respectively. Hence using less energy to pump the fluid across the membrane in the laminar regime is preferred in RO and other membrane systems in spite of increased mass transfer in the turbulent regime. With a permeable tube with wall flux, the effect is mostly observed in the transition and low turbulent regime and is proportional to the wall Reynolds number, $Re_w=(2V_wR/v)$, where V_w is the mean permeation wall flux.

Fluid flow in membrane slits and tubes: Berman (1956) and Yuan and Finkelstein (1956) using regular perturbation methods, solved the laminar flow fields in a porous slit (2-D) and a porous tube (3-D), respectively. The latter are given below for axial, u , and transverse, v , velocity:

$$\frac{u}{u_0} = \left[\frac{1}{0.7854 + \frac{0.8437}{\lambda}} + \frac{4\lambda x}{ReR} \right] \left[\frac{\pi}{4} \cos \frac{\pi}{2} \eta + \frac{f_1'}{\lambda} + \dots \right] \quad (2)$$

and

$$\frac{v}{u_0} = -\frac{2\lambda}{Re\sqrt{\eta}} \left[\frac{1}{2} \sin \frac{\pi}{2} \eta + \frac{1}{\lambda} f_1 + \dots \right] \quad (3)$$

where $\lambda = Re_w$, $u_0 = u(v=0)$ and $\eta = (r/R)^2$ and f_1 and f_1' are integral functions from Yuan and Finkelstein (1956). Berman's equations for flow in a slit are similar and simpler (1956).

Fluid mass balance in a membrane tube: Belfort (1981) has shown that for the tangential fluid velocity in the z-direction and r as the radial coordinate measured from the center-line, $v_z(r,z)$ (units: L/T), and inlet flow rate $Q_{in}(r,z=0)$ (units: L³/T), with Poiseuille parabolic flow are given by:

$$v_z(r, z) = v_z(0, z) \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (4)$$

and

$$Q_{in}(r, 0) = Q_0 = Q_{out}(r, z) + Q_{wall}(R, z) \quad (5)$$

where on substituting for $Q_{wall}=2\pi RzV_w$ for a length in the tube of z, and knowing that $v_z(0,z)= 2U$, we get a mass balance for flow in equals flow out plus flow through the walls:

$$v_z^{max,entrance} = v_z(0,0) = 2U = \frac{2Q^{exit}}{\pi R^2} + \frac{4zV_w}{R} \quad (6)$$

Thus for the case with flow leaving the exit, the length of the tube, z, cannot be too large.

Particle transport in laminar flow: Particles are thought to move in laminar flow in a cross flow membrane duct via Brownian motion (B), shear induced diffusion (SID) and inertial lift (IL) (**Fig. 5**) [144]. Clearly, these phenomena are important for different size ranges of particles of diameter 2a. Also, increasing axial velocity or Reynolds number increases the wall

shear rate, $\dot{\gamma}$, and hence the permeation flux, J , to the power of 1/3, 1 and 2 for B, SID and IL, respectively. Increasing particle radius, a , increases the permeation flux, J , to the power of -2/3, 4/3 and 3 for B, SID and IL, respectively.

Fig. 5. Experimental dimensionless trans-cartridge pressure drop as a function of feed Reynolds number (Re_F) for different wall Reynolds number (Re_w). R is the volumetric recovery ratio. Adapted from Belfort et al., 1994 [144].

Self-cleaning fluid mechanics: In 1928, Dean showed that fluid flowing around a curve produces vortices in a controlled manner [145]. Belfort has adapted this technology to synthetic membranes and shown that these vortices can be used to self-clean membranes from foulants like yeast cells and debris producing permeation flux improvements of over 400% in some cases [143, 146-153]. Advantages beside performance enhancement include scalable design, no moving parts or sealing problems, possible to backwash, no heating, no holdup on screens and easy to drain. However, more energy is needed to produce these self-cleaning vortices and this could exclude them from RO and water treatment due their low cost of product. An example is shown in **Fig. 6** for yeast ultrafiltration [154].

vi. CFD modeling of spacer-filled membrane modules

The use of Computational Fluid Dynamics (CFD) software has significantly aided the design of modules for membrane separations. CFD has been performed to analyze feed spacer performance [155-162], biofouling [163], mineral scaling [164] and particulate flow [165] in membrane modules. Development and verification of a particular model for momentum, species and energy conservation through comparison with experimental data are the critical first steps in the modeling of membrane systems. Subsequently, the verified model can be used to analyze different experimental conditions and module designs, drastically reducing the number of experiments needed to obtain an optimum design.

Fig. 6. Comparison of permeate flux while filtering yeast for a linear and a helical tube. Note that the linear tube is the same length as the coiled tube. Adapted from Luque et al., 1999 [154].

Fluid mechanics at membrane surfaces significantly influences the mass transfer characteristics of the separation process [166]. The mass transfer coefficient is a function of the Reynolds number of the fluid flow [167]. Spacers in membrane modules, which are primarily used to create channels for the feed flow by separating the membranes, also affect the flow pattern inside the module. Since spacers directly influence the fluid dynamics in the module, the mass transfer characteristics of the module are also affected. Introduction of spacers creates flow instabilities and turbulence, which reduce the effects of the mass transfer boundary layer at the membrane surface [162, 168]. Flow instabilities enhance mass transfer by reducing the effect of concentration polarization [169]. 2D modeling is often inadequate to describe the mass transfer characteristics in spiral wound modules since the flow field is 3D in nature [169]. Fimbres-Weihs et al. modeled spacers with orientations of 45° and 90° relative to the direction of the incoming feed flow [169]. The 45° spacer orientation exhibited increased mass transfer compared to the 90° spacer orientation. It was found that form drag was the main factor resulting in pressure drop in the module. Certain types of form drag, however, were shown to be beneficial to the separation process through the formation of vortices [169]. The vortices promote flow separation and reattachment at the membrane surface, which greatly facilitates mass transfer since the fluid near the membrane surface is replenished more frequently [169]. In contrast, viscous drag facilitates mass transfer by forcing a reduction in the thickness of the mass concentration boundary layer [169]. The use of spacers increases the pressure drop in the module, and therefore the energy input required for the separation. The challenge is to create the optimum spacer design which increases the mass transfer through the membrane as much as possible while requiring only minimal increases in energy input.

A major advantage of CFD is that the results may be much more accurate if the Navier-Stokes equations are solved directly without utilizing a model for turbulence [162]. Turbulence models are generally employed to obtain average values of the fluctuating components of the Navier-Stokes equations [162]. Santos et al. performed a CFD analysis of flow aligned spacers with an easily machined geometry for facile experimental comparison [162]. The cross section of the module studied was approximated as a rectangle since curvature was not expected to be practically significant due to the small height of the channel. Membrane permeation was not considered in the CFD modeling since the permeation velocity does not have a significant effect on the flow structure in the dense membranes used in RO. The no-slip boundary condition was used for both the channel and filament (i.e. spacer) surfaces. Twelve different spacer geometries were created by varying the distance between the centerline of the transverse spacers and by changing the number of longitudinal spacers. Fig. 7 shows close-up images of spacers used in RO modules in the desalination industry today.

Fig. 7. Photographs of spacers used in the desalination industry. A) Close-up of membrane spacer and B) cross section of spiral wound membrane module with a spacer in between each membrane leaf (samples courtesy of Caleb Funk, Dow Water & Process Solutions).

The mass transfer simulation results were only valid for the first geometrical unit that is repeated to construct the entire spacer structure, since at low Re a concentration boundary layer develops on the top surface. This boundary layer develops because the flow pattern is not disrupted along the top surface. The result is that subsequent repetitions of the geometrical unit are different than the first due to this growing boundary layer effect. The bottom surface, however, has its boundary layer periodically disrupted due to the flow over the transverse filaments, so the results for the bottom wall were expected to be representative of the entire module. A modified friction factor, f , was used to incorporate the spatial average of shear stress at the wall. The friction factor is defined as $f = \left(\frac{\Delta P}{l}\right) \left(\frac{h}{\rho U_0^2}\right)$, where ΔP is the pressure drop, l is the length of the channel, h is the channel height, ρ is the fluid density, and U_0 is the average channel fluid velocity. This expression differs from equation 1 through a factor of $-\left(\frac{h}{2l}\right)$. The modified friction factor at the wall was defined as $f_{wall,i} = \tau_{wall,i}(h^2 \rho / \mu^2)$, where $\tau_{wall,i}$ is the shear stress evaluated at the wall. The power number, Pn , for crossflow in the module was defined as $Pn = fRe^3$. Two

cases were studied: one with the channel height used as the characteristic dimension and the other which used the hydraulic diameter of the channel as the characteristic dimension, which takes the spacers into account.

Santos et al. used OpenFOAM CFD software to discretize the momentum and mass conservation equations [162]. To ensure simulation accuracy, a Courant number (Co) less than one was required, where the Courant number was defined as $Co = \frac{U_o \delta t}{\delta x}$. δt was defined as the time step and δx was the mesh cell size in the direction of the fluid velocity. Simulations were performed with water at 25°C and a kinematic viscosity of $8.93 \times 10^{-7} \text{ m}^2/\text{s}$. Crossflow velocities studied in the module were 0.03-0.15 m/s, corresponding to Re from 67-336. A Schmidt number, which is the ratio of momentum diffusivity to mass diffusivity, of 600 was used (typical of a dilute NaCl solution). Simulation results showed that there are two regions in the friction factor vs. Re plots: one region at low Re due to laminar flow and another due to a transitional flow regime at higher Re . The friction factor decreases with increased transverse spacer distance and increases with increased number of longitudinal units. This is logical because head loss is expected to increase as more transverse filaments per unit length are encountered in the flow path.

Asymptotic relations in the form of $f = aRe^b$ were fit to the data to determine parameters that fit the low Re and high Re cases. The values of a and b were different for each of the spacer geometries investigated and were determined through fitting the asymptotic relations to the data. The intersection of these asymptotes was used to define a critical value, Re_c , for the onset of flow instability. As transverse filament distance decreased, the flow was stabilized and the critical Re number increased to higher values. For a given transverse spacer distance, increasing the number of longitudinal spacers did not change the critical Re number significantly. This was likely due to using the channel height as the characteristic dimension. When the channel hydraulic diameter was used instead, the dispersion of the critical Re numbers was reduced by 30%, but did not yield constant critical Re number for all cases. The CFD model showed very good agreement with experimental results, indicating the model with periodic geometrical elements and cyclic boundary conditions hold. After the CFD model was verified, further CFD simulations were run. It was shown in the time-averaged velocity plot that circulation was induced at the corner of the upstream transverse filament for the spacer configuration with the largest distance between transverse filaments and without any longitudinal filaments. The circulation was due to boundary layer separation as the fluid could not maintain perfect contact with the filament. The size of this circulation zone increases with increasing Re until the critical Re is reached, when higher velocity fluctuations are observed by analyzing the magnitude of the Reynolds stresses. The velocity fluctuations are more significant in the bottom section of the channel between transverse filaments. Since filaments are not present in the top section, velocity fluctuations are damped out. It is evident from **Fig. 8** that increasing the

transverse spacer distance increases velocity fluctuations especially in the bottom section of the channel.

Fig. 8. CFD analysis of the S1L0, S2L0, and S3L0 spacers for $Re = 336$: a) time-averaged velocity profile and b) magnitude of Reynolds stress tensor. Used with permission from Santos et al., 2007 [162].

The time average shear stress fluctuations are higher on the bottom wall. This is due to vortex shedding and transient flow. The number of longitudinal filaments does not seem to influence the flow profile or transition from laminar to transitional flow for a particular inter-transverse filament distance. A linear relation was observed between the modified friction factor (which was defined above) and the mean Sherwood number in the channel. The Sherwood number used here is defined as $Sh = \frac{k_c h}{D_{AB}}$, where k_c is the local mass transfer coefficient and D_{AB} is the mass diffusion coefficient. Depending on the location of the membrane, the optimal geometry for enhanced mass transfer will be different. This allows the modified friction factor to be used to predict the optimum mass transfer efficiency. Using only the modified friction factor would result in less experimental/computational work to determine the ideal spacer geometry for the application.

Subramani et al. performed CFD simulations of open channel flow and compared the results with flow around cavity, submerged and zigzag type filaments [170]. A cross-section view of simulation results for these three different spacer designs are shown in **Fig. 9.** The cross-section is taken in a vertical plane parallel to the flow to show the effect of the spacers on the flow pattern. The membrane is located on the top surface in **Fig. 9**, orthogonal to the plane of the paper. The cavity geometry includes spacers that lie at the bottom surface of the channel. The submerged geometry contains spacers that are completely immersed in the flow and do not touch the channel top or bottom. The zig zag geometry employs spacers which alternate from being attached to the top and bottom surfaces, causing the fluid to flow in a zigzag type pattern. Under the conditions studied, the zigzag configuration had larger stagnant zones (**Fig. 9(C)**) due to the changing direction of fluid flow that increased concentration polarization, making it the least effective spacer orientation. The other geometries have faster moving fluid near the

membrane surface, reducing the boundary layer thickness. Similar to the work performed by Santos et al. discussed previously, there will be a trade-off between the increased mass transfer due to the addition of spacers and increased energy cost due to the higher pressure drop. Therefore, careful optimization must be performed to determine the most efficient operating point.

Fig. 9. Side-view illustrations of fluid flow through short sections of spacer-filled channels with: (A) cavity, (B) submerged, and (C) zigzag spacer configurations. Flow is from left to right, as shown by the arrows, and the membrane is located above the spacers and orthogonal to the plane of the paper. Used with permission from Subramani et al., 2006 [170].

It has been shown that CFD is a useful tool to predict optimum spacer geometry and design, as well as effects of fouling on the flow patterns in a module. Using CFD can drastically reduce the number of experiments needed to find an optimum spacer design to increase mass transfer while keeping power requirements at a minimum.

vii. Particle deposition

Lyster et al. monitored the scaling of an RO membrane surface with gypsum in an optically transparent plate-and-frame RO cell and compared the results with a 3D hydrodynamics and mass transfer model [164]. The gypsum scaling was found to be non-uniform on the membrane surface, with increased scaling observed as the fluid moves from the entrance to the exit of the RO cell. Near the concentrate exit from the module, the highest scaling was observed due to large recirculation zones which reduce mass transfer from the membrane surface. To describe particulate flow in curved ducts, Prashant et al used multi field CFD [165].

5. Fouling Analytics of Pre-treatment

i. 3D Modeling

Experimentally, Belfort and Guter (1972) were the first to measure the effect of plastic spacer design on fluid flow and mass transfer to a membrane surface using developer and photographic film [168]. Vrouwenvelder et al. used CFD to model the biofouling of RO membranes with and without spacers [163]. Two types of pressure drop are important in membrane processes: transmembrane pressure drop (i.e. pressure difference between feed and permeate) and feed spacer channel pressure (FCP) drop (i.e. pressure difference between feed and concentrate lines). Both pressure drops vary with axial distance along the membrane.

As time increases, channeling develops on the surface of the spacer, resulting in regions with poor flow and regions with higher flow. This qualitatively confirms the model as it predicts the fouling behavior with time. **Fig. 10** compares the flow patterns near the membrane surface with and without feed spacers. Feed spacer fouling has a much stronger impact on the velocity profile than membrane fouling only. Therefore, models that describe fouling should also include fouling of the spacer geometry as well as that of the membrane surface. Biofouling in RO modules is an FCP drop dominated problem, even when the feed to the module is pre-treated.

Fig. 10. Calculated flow velocity field at different times with (A-C) and without (D-F) feed spacer, presented in sections at $z = 585 \text{ um}$ (75% of the feed channel height). The times are: (A and D) 6h, (B and E) 42h, and (C and F) 80h. Used with permission from Vrouwenvelder, et al., 2010 [163].

ii. Quantitative analysis and membrane performance comparison

Since desalination plants have used ultrafiltration as a pretreatment method, it is important to predict and understand their fouling performance. Most previous work that focused on understanding membrane fouling involved experiments. Particle trajectory analysis is an exception to this rule [165, 171-177]. Another exception is the global model and algorithm that predicts the performance of crossflow during MF and UF in the laminar flow regime [178]. A typical algorithm is shown in **Fig. 11** that simulates and optimizes an ultrafiltration process. The model accounts for solute polydispersity, ionic environment, electrostatics, membrane properties and operating conditions. Computer programs were written for different versions of the model algorithm that can optimize MF/UF processes rapidly in terms of yield, purity, selectivity, or processing time.

Fig. 11. Flow sheet of the algorithm used in the global MF/UF model to determine the maximum selectivity between hemoglobin and bovine serum albumin in a batch ultrafiltration mode. Figure used with permission from Baruah et al., *Biotechnol. Prog.* 2005, 21, 1013-1025 [178].

This model and algorithm is an invaluable technique to rapidly design new or optimize existing MF and UF processes separately or in combination in both pressure-dependent and pressure-independent regimes. Its predictive capabilities for variations in solution conditions (pH and ionic strength), membrane properties (mean pore size and permeation flux) and fluid mechanical conditions (shear rate) are demonstrated with details of the model by Baruah et al. (2005) [178].

iii. Fouling models and adaptation to crossflow

Fouling models: Membrane fouling phenomena may involve pore (or surface) blockage, pore constriction, and cake formation, shown schematically in **Fig. 12**. These so-called “classical” fouling mechanisms act to reduce the accessible number of pores, reduce the effective pore cross sectional area, or introduce a resistance in addition to the membrane resistance,

respectively. As implied in the figure, the mechanisms that occur depend on the membrane pore size distribution relative to the size distribution of feed components, and multiple mechanisms may occur. One approach to model fouling is to incorporate resistances, in addition to the membrane resistance, into the flux equation.

$$J_v = \frac{\Delta P - \sigma_o \Delta \pi}{\mu (R_m + \sum R_i)} \quad (7)$$

The result is the resistance-in-series model, where R_i represents additional resistances caused by fouling; this approach is typically used to incorporate the additional resistance, R_c , due to cake formation. The assumptions inherent in different fouling models will be briefly reviewed; mechanisms and flux equations are summarized in Table 1.

Fig. 12. Schematic depictions of the classical fouling mechanisms. Note the distribution of feed component sizes and membrane pore sizes.

During cake formation, it is assumed that the time rate of change in flux is proportional to the change in cake layer resistance, R_c , expressed as the product of specific resistance, α_c , [$\text{m}^{-1} \text{kg}^{-1}$] and cake mass, m_c . The buildup of cake mass is then assumed to be proportional to the rate of advective transport to the membrane surface, $J_v C_b$.

The effects of pore blockage and pore constriction on membrane properties are introduced by first expressing membrane resistance in terms of the Hagen-Poiseuille equation for laminar flow. When pore blockage is the operative fouling mechanism, prior to the establishment of a cake layer, the time rate of change in flux is proportional to the rate of change in the number of accessible pores (or pore area, $A_{p,T}$). The change in pore area is assumed to be proportional to the advective transport of solute to the membrane surface. The complete pore blockage parameter, α_{cb} , is equal to the area of pores blocked per unit mass of solute transferred to the surface [$\text{m}^2 \text{kg}^{-1}$].

The intermediate pore blockage model is similar to the complete pore blockage model, but allows particles to deposit onto previously deposited particles. There is an equal probability for particles to deposit on previously deposited particles (in which case they do not reduce flux further) or on the unfouled membrane surface, where they completely block pores and contribute to further flux decline. Therefore, the rate of pore blockage is assumed to be proportional to the ratio of the unblocked area to the total area. Xu and Chellam [179] found that initial flux decline due to deposition of rod-shaped bacteria (*Brevundimonas diminuta* and *Serratia marcescens*), prior to the secretion of new extracellular polymeric substances, was quantitatively described the intermediate blocking law before transitioning to cake filtration at later times. Empirical deposition factors were introduced to account for the morphology of bacterial deposits.

When pore constriction (aka standard blocking) is the operative fouling mechanism, the time rate of change in flux is proportional to the rate of change in the pore radius. The change in pore volume is assumed to be proportional to the rate of advective transport of solute to the membrane surface. The pore constriction parameter, α_{pc} , is equal to the volume of pores blocked per unit mass of solute transferred to the surface [$\text{m}^3 \text{kg}^{-1}$]. Table 1 summarizes classical fouling mechanisms and models.

Table 1. Classical Fouling Mechanisms and Models

Constant Pressure	Mechanism	Flux Equation	Rate Constant
Cake Formation	$\frac{dR_c}{dt} = \alpha_c J_v A_m C_b$	$J_v = J_{v,o} [1 + k_c t]^{-1/2}$	$k_c = \frac{2\alpha_c A_m C_b J_{v,o}}{R_m}$
Pore blockage	$\frac{dA_{pore,T}}{dt} = -\alpha_b J_v A_m C_b$	$J_v = J_{v,o} \exp[-k_b t]$	$k_b = \frac{J_{v,o} \alpha_b C_b}{N_o \pi r_p^2}$
Intermediate blocking	$\frac{dA_{pore,T}}{dt} = -\alpha_{int} J_v A_m C_b \frac{A_{pore,T}}{A_{pore,o}}$	$J_v = \left[\frac{1}{J_{v,o}} - k_{int} t \right]^{-1}$	$k_{int} = \frac{\alpha_{int} C_b}{\pi N_o r_p^2}$
Pore constriction	$\frac{d}{dt} (\pi r_p^2 \delta_m) = -\alpha_{pc} J_v A_m C_b$	$J_v = J_{v,o} [1 + k_{pc} t]^{-2}$	$k_{pc} = \frac{J_{v,o} \alpha_{pc} A_m C_b}{\pi \delta_m r_o^2}$

Features of the flux versus time plots vary subtly for different mechanisms, making it difficult to distinguish among them from such plots. A better approach is to use the relationship between flux and volume filtered, $J_v A dt = dV$, to develop analogous analytical relationships between flux and filtration volume, and filtration volume versus time. Linear forms of these models can be used to graphically assess the fouling mechanism. Such “characteristic coordinates” include J_v versus V for the complete blockage model, t/V versus t for the pore

constriction model, and t/V versus V for the cake formation model. Differences in fouling mechanisms can become clearer when the data is plotted on coordinates that linearize the data for one of the models. For example, when data is plotted on t/V versus t coordinates, the pore constriction model plots as a straight line whereas the complete blockage model is concave upward and the cake formation model is concave downward, clearly illustrating different behavior for the three models.

For dead-end filtration under constant applied pressure, the differential rate laws corresponding to pore blockage, pore constriction, and cake formation can all be formulated as a single equation as proposed by Hermia [180]:

$$\frac{dJ_v}{dt} = kJ_v (J_v)^{2-n} \text{ or } \frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (8)$$

where k is a rate constant or “fouling coefficient”, with units that depend on the value of n , n is a dimensionless filtration constant, and V is the total volume (or mass) filtered [m^3]. The term dt/dV is equal to $1/JA_m$, which is the differential time needed to collect a unit volume of permeate, i.e., $\mu R_T / \Delta P A_m$. The fouling mode is reflected in the value of the filtration constant: i) cake formation corresponds to $n = 0$; ii) pore constriction (standard blocking) corresponds to $n = 1.5$; and, iii) complete pore blocking corresponds to $n = 2$. Taniguchi et al. [181] used this approach to determine the causes of fouling during UF treatment lake water containing humic substances (natural organic matter), and found that pore blockage was the cause of flux decline during the initial period of filtration, but over time cake formation became most important.

Membrane comparison: In many membrane research and engineering applications it is necessary to compare the performance of different membranes, to identify the best selection to meet process goals, which usually include optimizing permeability, rejection characteristics, and flux decline due to fouling. A widely employed approach is to compare flux versus time curves for different membranes; experiments are often designed such that the initial flux is the same for all experiments, to assure that the convective transport of foulants to the membrane is similar. Membranes having smaller flux decline are generally considered as having lower fouling potential and hence higher performance. However, as we will show, flux decline curves often depend on membrane hydraulic permeability, which is often not accounted for in many of the fouling studies that appear in the literature.

Comparisons based on flux decline can be misleading when membranes having different inherent (initial) permeability are evaluated. Consider the resistances in series model, Eq. 7, incorporating membrane resistance and a fouling resistance R_F that depends on time (or volume throughput); the sum of membrane and fouling resistance is the total resistance, R_T . As discussed above, and as idealized by the Hagen-Poiseuille equation, the membrane resistance is related to membrane properties such as thickness, pore density, and pore radius. The time rate of change in flux due to fouling exhibits an inverse dependence in the membrane resistance:

$$\frac{dJ_v}{dt} = -\frac{\Delta P}{\mu} \frac{1}{(R_m + R_F)^2} \frac{dR_F}{dt} \quad (9)$$

In addition, the time rate of change in fouling resistance, dR_F/dt , also may depend on membrane properties. Therefore, the rate of flux decline is smaller for membranes having greater resistance, other factors, such as membrane-foulant interactions, being equal. Ideally, we wish to compare the fouling potential of different membranes independent of membrane resistance (or permeability). Classical fouling models can be employed to identify whether this is possible, and which approaches are best. In this analysis, we assume two different membranes have the same pore size and porosity, but different thickness, and hence different resistance. We assume the membranes have the same surface chemistry, and hence the same affinity for foulants in the feed, as reflected in the same fouling rate constants (α_c , α_{cb} , α_{ib} , or α_{pc} , values). They are operated at the same initial flux (hence different transmembrane pressure values) and the feed concentration is also the same.

When pore blockage is the operative mechanism, two membranes having different resistances can be compared on either flux vs time or volume throughput vs time coordinates. That is, as long as the fouling rate constant is the same, the same curve is found, regardless of the membrane resistance. Therefore, differences in the flux vs time curve will be due to differences in fouling potential, not membrane properties.

When cake formation is the operative mechanism, two membranes having different resistances cannot be compared on either flux vs time or volume throughput vs time coordinates. That is, even though the fouling rate constant is the same, the rate of flux decline is lower for the membrane having the higher resistance; therefore, differences in the flux vs time curve will be due to differences in membrane properties, not fouling potential. However, because fouling resistance depends only on cake formation, not membrane properties, it is possible to evaluate fouling potential independent of membrane resistance by plotting fouling resistance, R_F , vs volume throughput; this is illustrated in **Fig. 13**. When pore constriction (standard blocking) is the operative mechanism, the fouling potential of two membranes having different resistances cannot be compared independently from the resistance. As with cake formation above, even though the fouling rate constant is the same, the rate of flux decline is lower for the membrane having the higher resistance; therefore, differences in the flux vs time curve will be due to differences in membrane properties, not fouling potential. Unfortunately, there is no set of coordinates that can be used to isolate the fouling potential of the different membranes independent of resistance. To overcome this limitation, and to provide a more general basis for comparing membrane performance regardless of the fouling mechanism, we recommend employing an energy criterion:

$$\text{Energy} = \int J_v(t) A_m \Delta P dt = V(t) \Delta P \quad (10)$$

Fig. 13. Two membranes having the same fouling potential (cake specific resistance) but different resistance values cannot be compared on flux vs time coordinates; the membrane having the higher resistance appears superior, but only because it has a higher resistance (Plate A). Fouling potential can be examined independent from membrane resistance by plotting fouling resistance vs. volume throughput (Plate B).

The advantage of the energy criterion is that it accounts for the effects of both flux decline, and initial resistance. Membranes having high initial resistance require greater transmembrane pressure drop to yield the same starting flux as a low resistance membrane, thus negating and apparent benefit of a slower rate of flux decline when process cost (energy consumption) is considered. This is illustrated in **Fig. 14**, where fouling is by the pore constriction mechanism, and the two membranes compared have the same fouling rate constant. Although the membrane having the higher resistance exhibits slower flux decline, it is apparent that the performance of the membrane is not superior when energy consumption is taken into account.

Effects of crossflow: Crossflow can enhance mass transfer processes that induce back transport from the membrane surface, reducing the net flux of foulant to the membrane surface. Such back transport can result from diffusion, inertial lift and shear forces. In terms of classical fouling models shown in Table 1, the net advective transport of solute to the membrane surface is now proportional to $J_v - J^*$, where J^* can be thought of as an effective velocity associated with mass transfer away from the membrane surface [182] or a critical flux [183, 184].

Fig. 14. Two membranes having the same fouling potential (pore constriction) but different resistance values cannot be compared on flux vs time coordinates; the membrane having the higher resistance appears superior, but only because it has a higher resistance (Plate A). Membrane performance can best be assessed by considering energy consumption (Plate B) which shows that when fouling potential is the same, the lower resistance membrane is superior, even though it exhibits greater flux decline.

iv. Models using 3 mechanisms

Combined mechanisms: Ho and Zydney [185] developed a model that combines pore blockage and cake filtration modes of fouling, and later Duclos-Orsello and Ho [186] developed a model that incorporates all three classical fouling mechanisms. Bolton et al. [187] also present models based on different combinations of classical fouling models. In both the pore blockage and cake filtration model, and the three mechanism model, which also incorporates pore constriction, total flow through the membrane, $Q_T [\text{m}^3 \text{s}^{-1}]$, is the sum of flow through unblocked pores and through “blocked” pores:

$$Q_T = J_v A_T = Q_{\text{unblocked}} + Q_{\text{blocked}} = J_{\text{unblocked}} A_{\text{unblocked}} + J_{\text{blocked}} (A_T - A_{\text{unblocked}}) \quad (11)$$

where $A_T = A_{\text{unblocked}} + A_{\text{blocked}}$. Consistent with the pore blockage model, the rate of pore coverage (the rate of loss of open area) is assumed to be proportional to the advective transport of solute, leading to an exponential decrease in open area with time. In the three-mechanism model, flux through unblocked pores is given by the pore constriction model. Flow through the blocked region is assumed to be described by the resistance in series model discussed above.

When only pore blockage and cake formation are considered, resistance due to pore constriction is neglected, whereas it is included in the three-mechanism model.

In the three mechanism model, initially pore constriction occurs through all the open pores while the membrane surface is blocked gradually by deposited solute to form an inhomogeneous blocked area. Once a pore is blocked by an aggregate deposited on the surface, no further pore constriction can occur, but as in the two-mechanism model, a cake layer subsequently will build up over the blocked area. These models have been used to successfully describe protein filtration [185], filtration of natural colloids [181] and have been shown to converge towards the correct single mechanism when experimental conditions were designed to make that mechanism dominate the fouling process [186].

The above discussion of fouling models has focused on constant pressure operation, i.e., ΔP was treated as a constant, and flux declined with time as fouling occurred. In many large-scale applications, constant flux operation is preferred, especially in the biotechnology industry. All of the above fouling relationships have analogies for constant flux operation [188-190]. In addition, the solute deposits in the above discussion were treated as incompressible. Xu and Chellam [190] confirmed that colloidal silica formed incompressible cakes whereas bacteria and natural colloids formed cakes that were compressible. Bacteria compressed in a straight-line manner whereas power-law compressibility was observed for coagulated natural colloids during constant pressure MF. The resistance of colloidal cakes was dominated by morphology, not the mode of deposition, confirming that the cake permeability was determined by the instantaneous pressure.

v. Biofouling models

Chellam and Cogan [189, 191] have presented a resistance in series model to account for fouling (flux decline in constant pressure or pressure increase during constant flux filtration) that results from bacterial deposition and subsequent EPS production. Resistances include contributions from the membrane, R_m , bacteria, R_a , and EPS, R_e . Resistance from deposited bacteria is assumed to follow a saturation model

$$R_a = \frac{\mu_a B}{K + B} \quad (12)$$

Where B is the bacterial population and μ_a and K are rate parameters. The rate of deposition depends on the open membrane area A_{open} , which declines exponentially. A unique feature of this model is the incorporation of EPS production; resistance due to EPS is proportional to the EPS concentration, (E) , $R_e = \kappa_1 E$. The production of EPS is assumed to be controlled by a quorum sensing “switch”, whereby production is low until bacteria reach a threshold density, B^* , after which it increases rapidly. This phenomenological behavior is captured qualitatively by a production law, G :

$$\frac{dE}{dt} = \kappa_1 G(B, E) \text{ where } G = \frac{\kappa_1 [1 + \tanh(\gamma(B - B^*))]}{2(1 + E)} \quad (13)$$

This unified model was applied to single-species bacterial cultures in constant flux, dead-end microfiltration. The model was able to predict experimental pressure data well, using parameters calibrated previously in constant pressure filtration. This finding also confirms that hydraulic resistance is determined by instantaneous pressure, not operating mode. The authors also fit experimental data with conventional blocking law models. Both traditional blocking law models, which employed a linear compressible cake blocking law, and the unified model provided good fits to the data, except at low fluxes, where the blocking law models provided better fits. The authors proposed that a limitation of the unified model may be in how bacterial deposition and changes in open area are modeled. Still, the model showed promise of predicting filtration dynamics with few a priori adjustments once parameters are determined from the type of bacteria, membrane, and operating parameters.

Lapidou et al. [192] advocate modeling as a platform to integrate experimental observations of biofilms and physical, chemical and biological processes (e.g., community structure) occurring at different spatial and temporal scales. Models of increased complexity are developed to accommodate multiple biomass species and multiple biomass types (active biomass, inert biomass and extracellular polymeric substances (EPS)); the physical structure of a biofilm in two or three dimensions; and how biomass density varies throughout the biofilm. Biofilm structure is important because there is a feedback between the effect of the biofilm on the surrounding fluid, and the effects of the fluid (forces that act on the biofilm and cause detachment) on the biofilm. Advances in microscopy have revealed that biofilms do not grow in flat layers, but have channels and pores, and mushroom like protrusions into the fluid, depending on conditions [193].

The way a model captures such features depends on how biofilm growth proceeds, i.e., the rules – the system of logic and assumptions - that govern how biomass is distributed. Two approaches have received the greatest attention; Lapidou et al. [192] review the advantages of using cellular-automata (CA) and individual-based (IbM) models to simulate biofilm growth on RO membranes.

Cellular automata models employ an array of compartments that are allowed to populate with bacterial cells to a predetermined capacity. In the Unified Multi-Component Cellular Automaton (UMCCA) model by Lapidou and Rittmann, biomass grows at a rate defined by the substrate concentration and the microbial kinetic rate parameters for substrate uptake, metabolism, maintenance, and death. When a compartment reaches capacity, the biomass is subdivided to simulate cell division. The new growth causes biomass to be “pushed” along the shortest path to a nearby unoccupied cell chosen randomly from among all equidistant nearest-neighbors. Active biomass produces inert biomass and EPS, but these components do not move;

this is consistent with the role of EPS as a structural component of biofilms, and with inert biomass acting as a byproduct of active growth.

In individual-based models, the microbial processes discussed in cellular automata models are treated at the individual cell level, and not with a predefined grid. Tracking individual cells is more computationally intensive than cellular automata models. Growth patterns (e.g. exponential growth) emerge only as a result of the substrate uptake, metabolism and maintenance of individual cells. One approach is to represent the biofilm structure by a collection of non-overlapping hard biomass spheres, which could represent single bacteria or a micro-colonies. When spheres reach a defined density, they divide and disperse in random directions; biomass spreading then occurs by minimizing the overlap of spheres.

The need to define a lattice in cellular automata models presents limitations, because biomass can only move in a finite number directions defined by how the lattice is arranged, and different lattice systems can influence the resulting biofilm structure even for the same propagation rules. As a result of the stochastic rules for biomass redistribution, a high degree of internal mixing of multiple species may occur within a colony. However, as biomass decays, compartments can empty leaving on the EPS structure, and thus simulating changes in porosity observed experimentally in aged biofilms. Also, it is possible to incorporate biofilm consolidation into cellular automata models, allowing biofilm density to change over time.

Individual based models idealization of biomass as hard spheres is unrealistic, but these models offer greater flexibility because there is no lattice to constrain the movement of biomass. Model parameters define the spacing among biomass particles, biomass packing, and hence biofilm porosity; varying the density in space or time can prove difficult. This may prove superior for young biofilms with no cavities, whereas the cellular automata models may be better for aged biofilms. Incorporating cell to cell signaling via molecular exchange (e.g., quorum sensing) remains a challenge for both types of models.

Radu et al. [194] developed a two-dimensional model that incorporates fluid dynamics, mass transfer, biofilm properties, and geometric characteristics of a spiral-wound RO membrane. They attempted to incorporate interactions between fluid flow, biofilm growth, feed composition, and system configuration. Fluid flow was modeled using the Navier-Stokes equation while advection dispersion relationships determined the transport of solute and substrate compounds. Monod kinetics were employed for biofilm growth, and biomass accumulation, transport and sloughing were modeled using a cellular automata algorithm. Their model provided a reasonable approximation of the effects of biofouling on flux loss, pressure drop increase over time, and decline in salt rejection. The model was able to corroborate previous data on the effects of spacer geometry in laminar flow, and flux decline due to biofilm-enhanced concentration polarization during desalination of brackish water.

Numerical and mathematical models have helped reveal details about the underlying mechanisms of biofouling. For example, increasing feed salinity generally leads to more pronounced concentration polarization effects, but associated changes in biofilm permeability can result in negligible drop in permeate flux [195]. Three-dimensional models can also be constructed for a more explicit representation of biofilm growth inside membrane modules [196]. Lastly, combined fouling models may become particularly useful because biofouling may occur in parallel with scaling and may enhance mineral precipitation [197].

6. Post Treatment

Reverse osmosis permeate is generally slightly acidic, has low alkalinity and buffering capacity, and has low concentration of hardness minerals calcium and magnesium [198]. Post-treatment is needed to protect human health, protect downstream infrastructure, and support downstream uses; specifically to 1) disinfect the water and maintain a disinfectant residual; 2) reduce the aggressiveness of the produced water relative to metal corrosion and concrete dissolution; 3) provide sufficient mineral content (calcium and magnesium) to protect human health, and to sustain agriculture and horticultural uses; and, 4) provide sufficient alkalinity to support downstream wastewater treatment [198]. Removal of boron may be addressed through plants design [199, 200]. (e.g., membrane selection, multiple passes with pH adjustment) or through post treatment.

RO permeate is readily disinfected because they contain a low microbial load, low total organic carbon concentration, and low particle content [201]. Turbidity of RO permeate is low, and inorganic turbidity introduced by remineralization does not interfere with disinfection by chlorine [201]. Although potential passage of viruses through some RO membranes may be a consideration, viruses can be readily inactivated using low doses of chlorine and short contact times ($C \times t$ values). The aggressiveness of RO permeate is reduced primarily through pH adjustment, alkalinity addition, and adjusting the water chemistry through remineralization so there is a tendency to precipitate calcium chloride [199, 202]. Based on a review of the literature, utility surveys, and case study reviews, Duranceau et al. [203] recommended the goals presented in Table 2, including a pH range of 6.5 to 9.5 for seawater RO permeate.

Table 2. Desalination Post Treatment Water Quality Goals. Used with permission from [203].

Parameter	Seawater	Brackish water
pH	6.5–9.5	7.5–8.4
Alkalinity (mg/L as CaCO_3)	50–125	75–150
Hardness (mg/L as CaCO_3)	50–85	75–110
Calcium concentration (mg/L)	50–75	60–100
TDS (mg/L)	100–500	85–350
Sulfate to chloride ratio	1–1.3	0.5–1
Turbidity (NTU)	0.6–3	0.2–2
Boron	0.5–1	NA

The State of Israel requires a narrower range, 7.5 to 8.3 for desalinated water, and the World Health Organization recommends $\text{pH} < 8$ because higher values reduce the efficiency of

chlorine disinfection [201]. Several researchers have found that corrosion and release of corrosion products can be reduced by maintaining sufficient alkalinity. Alkalinity is measured as the titration of basic species to the carbonic acid endpoint (about pH 4.5). In terms of carbonate species, which are usually predominant, it is defined as:

$$\text{Alkalinity \{meq/L\}} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (38)$$

Carbonate alkalinity is an important component of buffer capacity or intensity, β , which quantifies the relationship between the change in pH and the change in concentration of strong acid or base, C_b :

$$\beta = \frac{dC_b}{dpH} = \frac{2.3C_T K_{a1} [\text{H}^+]}{(K_{a1} + [\text{H}^+])^2} + \frac{2.3C_T K_{a2} [\text{H}^+]}{(K_{a2} + [\text{H}^+])^2} + 2.3([\text{H}^+] + [\text{OH}^-]) \quad (39)$$

Where C_T is the total concentration of carbonate species, which can be estimated from measurements of alkalinity and pH, and K_a values are the acid dissociation constants for carbonic acid (H_2CO_3^* , K_{a1}) and bicarbonate (HCO_3^- , K_{a2}). A buffer intensity greater than 0.5 milliequivalents per pH unit has been cited as indicative of a balanced, stabilized source water [203]. Alkalinity and resulting buffer capacity resist pH changes during subsequent treatment, blending, and distribution. Examples of processes that can potentially affect pH values include fluoridation with fluorosilicic acid (H_2SiF_6) and chlorination by chlorine gas:

Imran et al. [204] found that release of corrosion products from unlined cast iron and galvanized iron pipes (red water release) had a strong negative correlation with alkalinity, except when water was high in chloride and sulfate. A similar correlation with both Fe and Mn was found for UK waters [205]. As a result, Imran et al. [204] recommend maintaining alkalinity concentrations above 80 mg/L of CaCO_3 , a value that is reflected in the State of Israel Public Health Regulations [206].

Sonthheimer et al. [207] proposed a Siderite model for the formation of corrosion resistant scales. Dense protective layers and low corrosion rates resulted when buffer intensity was high and $\text{pH} < 8.5$, conditions that favored the reaction of corrosion product Fe^{2+} and carbonate, CO_3^{2-} , to form Siderite, over the direct oxidation of Fe^{2+} to ferric oxides. However, Siderite was not required to be a constituent of the protective layer, which may form from subsequent Siderite oxidation to, e.g., Magnetite (Fe_3O_4 (s)). Also, the presence of calcium and the formation of some calcite was necessary, so it is likely that the protective scale was a mixed precipitate.

Alkalinity may also be required for downstream processes, such as wastewater treatment or water reclamation. For example, when biological ammonia nitrification is required, alkalinity is consumed [208]:

McNeill and Edwards note that precipitation of a thin layer of calcium carbonate (calcite) was the earliest proposed method to control iron corrosion [209], and Delion et al. [199] recommend that to protect distribution networks and equipment, water should be slightly scale forming to create a protective coat on internal surfaces. For this reason, many different indices related to calcium carbonate stability have been developed and promoted [199]. Although still used [202], the Langlier Index does not provide an effective means of controlling iron corrosion, and other calcite indices have only limited use in corrosion control [209]. Still, Birnhack et al. [198] recommend the calcium carbonate precipitation potential (CCPP, mg/L as CaCO_3) as a quantitative and unambiguous parameter; values $3 < \text{CCPP} < 10$ are recommended to decrease the rate of corrosion and reduce red water events, as reflected in the State of Israel Health Regulations.

The World Health Organization (WHO) has recommended that remineralizing RO permeate with calcium and magnesium salts should be considered from a strictly health point of view in some cases, especially where there is evidence of a dietary deficiency of calcium and magnesium, and where a supply is moving from a source that has significant levels of calcium and magnesium to low-mineral desalinated water [201]. This relates primarily to the potentially beneficial effects of magnesium in preventing some types of heart disease, association between magnesium deficiency and metabolic syndrome, indicating a pre-diabetic condition, and beneficial effects of calcium in reducing osteoporosis risk.

Insufficient calcium and magnesium concentrations can result in downstream reclaimed water that is high in sodium and not suitable for agricultural purposes, especially in arid regions where precipitation is low and reclaimed water makes up a high fraction of the total water supply. The sodium hazard associated with an irrigation water supply is quantified by the sodium absorption ratio, given as

$$\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}} \quad (43)$$

Where species in brackets indicate molar concentrations. Irrigation waters having high SAR levels can lead to the build-up of high sodium levels and displacement of calcium and magnesium, leading to soil dispersion, a loss of soil structure, lowering of infiltration and percolation rates, soil crusting, poor seedling emergence, and poor aeration [210].

Polyphosphate offers benefits for preventing scaling and precipitation of iron or manganese and facilitating certain types of iron corrosion control, but is not recommended for lead corrosion control [211]. Utilities were advised to determine the minimum polyphosphate dose that achieves iron corrosion control, in order to minimize residual polyphosphate. This is because the maximum soluble lead concentrations in pipes during stagnation are proportional to this residual value.

7. Conclusions and Future Prospects

Although reverse osmosis is now the method of choice for desalination of seawater to portable water, its application has been mainly in arid regions (e.g., Israel and the Gulf) due to its relatively high cost. We demonstrate in this review that opportunities exist to reduce the cost of RO desalination by emphasizing pretreatment, fouling and post treatment. Recent focus on the RO process and associated equipment have reduced the energy consumption from 15 to ~ 2 kWh/m³ over the past 25 years. This excludes the energy required for intake, pretreatment, post-treatment and brine discharge. Clearly reducing this energy consumption further will require enormous effort. Several mitigating strategies to reduce fouling are reviewed, especially in light of the 'three legs', or major parameters that govern all membrane processes: (i) selectivity, (ii) permeability, and (iii) concentration polarization and fouling. These include operational and membrane module-related approaches. Thus, pretreatment and cleaning is essential for mainlining high performance, while surface chemical modification, module design for optimal fluid mechanics and mass transfer offer orthogonal ways to reduce fouling. New computational methods, such as molecular simulation of fouling, and for seeking optimal fluid mechanics and mass transfer, inter membrane spacer design and its effects on reducing fouling, and particle trajectory analysis for predicting and reducing fouling.

Further technical advances will require a deeper understanding of the fundamental science underlying pretreatment, fouling and post-treatment. Extensive use of fouling models will help identify the likely type and cause of fouling.

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