A Review: The Operational and Environmental Challenges of Reverse Osmosis Desalination

Alexander Eik*

October 11 2021

Abstract

In the coming future, water security will be an issue that many nations face. As reverse osmosis (RO) further expands in market share, efforts to improve its efficiency and sustainability will grow. In this review, RO is discussed in the context of its operational and environmental challenges. These include the tradeoffs between selectivity and permeance, membrane fouling, brine disposal and more. Each challenge is reviewed in its current state, with future solutions examined. In particular, optimization in the RO process, membrane modification and the Zero-Liquid-Discharge approach play a huge role in the future of RO desalination. The pros and cons of each challenge and solution are weighed, with a final recommendation on the ideal improvements to strive for. Overall, membrane technology has matured as the vast improvements in RO have mainly come from enhanced membranes. Now, greater focus in membrane fouling and brine management are required as they pose the largest obstacles to the operation and sustainable functioning of RO desalination.

^{*}Mentored by: Dr. Nikzad Falahati

Contents

1	Inti	Introduction				
2	Background Information					
	2.1	Theor	retical Background	4		
		2.1.1	Reverse Osmosis	4		
		2.1.2	Water Recovery	4		
		2.1.3	Mathematical Foundation	5		
	2.2	Funda	amental Flaws of Reverse Osmosis	7		
3	Оре	eration	nal Challenges and Solutions	10		
	3.1^{-2}		orane Technology: Selectivity Vs. Permeance	10		
	3.2		orane Fouling	13		
		3.2.1	Pretreatment	13		
		3.2.2	Membrane Modification	15		
4	Environmental Concerns of Brine					
	4.1 Current Brine Management					
		4.1.1	Surface Discharge	18		
		4.1.2	Municipal Water Treatment	18		
		4.1.3	Deep Well Injection	19		
		4.1.4	Evaporation Ponds	19		
	4.2					
		charge				
		4.2.1	Reverse Osmosis in ZLD	20		
		4.2.2	Forward Osmosis in ZLD	21		
		4.2.3	Wind-Aided Intensified eVaporation in ZLD	22		
		4.2.4	Membrane Distillation	23		
		4.2.5	Brine Concentrators	23		
		4.2.6	Multi-Stage Flash Distillation	23		
5	Dis	Discussion and Evaluation				
6	Conclusions and Outlook			26		
7	Future Research Needs			27		

1 Introduction

Despite water being an abundant resource, with two-thirds of the planet covered in water, large portions of this resource is not suitable for human consumption. At current estimates, 20% of the world's population is facing water insecurity. By 2030, water shortages are expected to affect up to 40% of world inhabitants. The growing scarcity of water is through various factors, including as an exponentially increasing population, increased industrialization and agriculture, and climate issues. Therefore, finding sources of freshwater is a top priority for many governments and research agencies as water scarcity affects the well-being and prosperity of many countries [ea18a].

To meet this need, many countries have turned to the most abundant source of water on Earth: seawater. Desalination of seawater has the potential to provide an unlimited source of pure water and is naturally advantageous, as seawater is readily available in arid coastal areas [Pri09]. Desalination involves the removal of the salts, minerals and other contaminants from either seawater or brackish water (freshwater mixed with seawater) in order to produce clean water [Qas19].

Historically, desalination involved thermal phase change processes to extract pure water from seawater through evaporation and condensation. At present, thermal desalination processes include multi-stage flash evaporation (MSF), multiple-effect distillation (MED), and thermal vapor compression (TVC) [Ali18] However, thermal desalination is inherently energy-intensive in nature as it relies on the inefficient conversion of energy from fossil fuels. Thermal processes require 10-15 kWh/ m^3 of pure water recovery, which is 4 to 5 times as much as a conventional reverse osmosis process [Cip09].

With increasing developments in membrane technology and energy efficiency, membrane-based processes are now the main method in desalination, with reverse osmosis taking 65% of the industry [Saa21]. Furthermore, membrane-based processes have many benefits, including a low spatial requirement, operational simplicity, and ease of automation [Qas18].

Within the various membrane-based processes, the most widely used techniques in desalination are reverse osmosis (RO), membrane distillation (MD) and nanofiltration (NF). From these, RO remains the most popular as it is highly reliable, has a high salt rejection rate, and can be used in a wide range of salinity. NF, however, requires very exact processes that make it operationally unfeasible. Lastly, MD is more energy efficient and safer than reverse osmosis as the applied pressure requirement is lower, but it suffers from low product recovery [Alt14].

Since the 1950s and the introduction of inefficient cellulose derived mem-

branes, the overall efficiency and utilization of RO has increased rapidly. With the development of polyamide membranes, salt rejection and flux rate both increased, allowing for the decrease in overall costs for RO [She15]. As it currently stands, RO requires 2-4 kWh/ m^3 of pure water recovery, which is much higher than the theoretical minimum of 1kWh/ m^3 [Kim19].

Thus, this paper aims to review the current challenges facing RO desalination and the efforts aimed at improving productivity and sustainability. The operational and environmental challenges of RO will both be discussed, where improvements and potential solutions to such challenges are subsequently discussed.

2 Background Information

2.1 Theoretical Background

2.1.1 Reverse Osmosis

Osmosis is defined as a natural process in which water molecules spontaneously move from a solution of low solute concentration (low osmotic pressure) to a solution of high solute concentration (high osmotic pressure) via a semi-permeable membrane. The semi-permeable membrane rejects the solutes and other contaminants, preferentially selecting water molecules to pass through. Osmosis continues until osmotic equilibrium is reached, where the water potentials on both sides of the membrane are balanced. For reverse osmosis, a pressure higher than the osmotic pressure is applied, forcing water molecules through the semi-permeable membrane from a solution of high solute concentration to a solution of low solute concentration [Qas19].

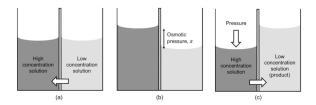


Figure 1: Schematic of (a) osmosis, (b) osmotic equilibrium, and (c) reverse osmosis [Qas19]

2.1.2 Water Recovery

The basics of water recovery in RO involves passing the feed through an RO membrane module. This results in 2 streams of water, the permeate stream and the rejection stream. In the permeate stream, uncontaminated water is

collected after the membrane has filtered out solutes and other particles from the feed stream. The concentration of solute in the permeate stream is much lower compared to the feed. The rejection stream involves the production of brine. Rejected solutes and contaminants continue to follow along with the remaining feed, increasing the resultant solute concentration of the water in this stream. In RO, a key term, recovery (r), is determined as the percentage of permeate water that is recovered from the feed water [Qas19]:

$$r = 100\% \times \frac{Q_p}{Q_F}$$

Figure 2: [Qas19]

Qp is the permeate flow rate while Qf is the feed flow rate as seen in Figure 2. In modern RO systems, recovery is an important criterion that needs to be managed in order to maintain high volumes of flux without compromising the salt rejection rate. Generally, having minimal increments in the salt rejection rate drastically reduces the permeate production rate [Lee11]. Thus, a careful balance needs to be found to maintain the economic feasibility of RO desalination.

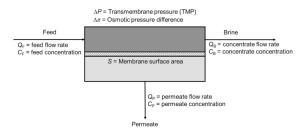


Figure 3: A schematic of a cross-filtration and continuous RO process [Qas19]

2.1.3 Mathematical Foundation

The energy usage of desalination varies from process to process. The energy requirement depends on each plants' individual separation process, technology level and equipment. Nevertheless, regardless of the separation method, thermal or RO, the theoretical minimum energy of desalination can be determined.

It is only by determining the theoretical minimum energy that the energy

efficiency of current desalination methods can be investigated. By establishing the theoretical minimum, there is a marker to guide the industry's efficiency targets. The method of calculation requires the Gibbs free energy of mixing [Par20]:

$$E_{min} = \int -d(\Delta G_{mix}) = \int -RTlna_{w}dn_{w} = \int \prod_{s} \overline{V}_{w}dn$$

 $\triangle G_{mix}$, R, T, a_w , n_w , \prod_s and V_w refers to the Gibbs free energy of mixing (kJ/mol), gas constant (J/K•mol), temperature (Kelvin), activity of water, moles of water, osmotic pressure of seawater(atm), and molar volume of water respectively.

This equation involves the integration of the Gibbs free energy of mixing, where the energy required to separate a mixture or solution is the same but opposite in sign to the energy required to combine the components [Shr15]. The theoretical minimum energy of seawater desalination at a salinity level of 35 g/L and a temperature of 25 °C is $1.07 \text{ kWh/}m^3$ for 50% recovery, which has already been demonstrated by many researchers [Par20]. However, the practical energy usage of RO desalination is higher than the minimum energy due to the numerous non-ideal conditions. The practical minimum is estimated to be around $1.6 \text{ kWh/}m^3$ when energy consumption from the whole process is considered [Coh17]. Nevertheless, there is still room for improvement in reducing the overall energy consumption in RO desalination.

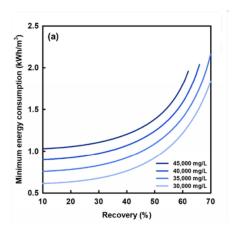


Figure 4: Theoretical minimum energy consumption at different levels of recovery and salinity at $25^o\mathrm{C}$ [Coh17]

2.2 Fundamental Flaws of Reverse Osmosis

One issue that arises in RO is concentration polarization (CP). When solutes from the feed stream flow towards the membrane, the solute concentration of the stream increases closer towards the membrane. This results from the rejected salts and contaminants temporarily increasing the concentration of solute at the membrane surface, creating a boundary layer of high solute concentration. This allows the solutes to diffuse away from the membrane surface back to the bulk feed. However, the rate of back-diffusion is lower than the build-up of solute concentration, resulting in a permanent boundary layer with a higher concentration of solutes than the bulk feed (Chen et al., 2010).

CP is an unwanted outcome of RO as the membrane surfaces are exposed to feeds with increased solute concentration, which significantly hampers the efficiency of RO desalination. Primarily, the increased solute concentration increases the counteractive osmotic pressure of the feed stream, thereby reducing the overall driving force pressure. Furthermore, a result of the highly saline boundary layer is a secondary effect where there is a risk of salt precipitation on the membrane surface. This aggravates the probability of scaling, where supersaturation of solutes builds a thin film on the membrane. (Sutzkover et al., 2000 and Fritzmann et al., 2007).

Moreover, the boundary layer at the membrane results in increased solute flux across the membrane and cake formation. Cake formation is especially harmful to RO membranes as they further hinder the diffusional back-transport of solutes away from the boundary layer, causing cake-enhanced concentration-polarization, an enhanced version of CP (Gutman and Herzberg, 2013). Ultimately, this deteriorates overall membrane solute rejection and thus membrane efficacy (Fritzmann et al., 2007).

While the effects of CP are deleterious, CP is reversible and can be controlled in a membrane module by means of velocity adjustment, pulsation, ultrasound, or an electric field (Sablani et al., 2001). Newer technologies such feed spacers or micro-mixing can be employed to further curb this issue (Haidari et al., 2018 and Guha et al., 2017).

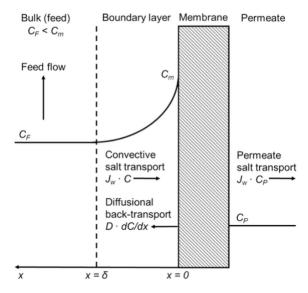


Figure 5: Schematic of a concentration gradient formed from CP, where C_f , C_m , J_w , D, and C_p refer to the concentration of the feed stream, membrane boundary layer, water flux rate, salt back-transport rate, and concentration of the permeate respectively. [Qas19]

Membrane fouling is another technical issue that reverse osmosis faces. Membrane fouling is the condition in which the membrane undergoes plugging or coating by some element in the feed stream such that the permeate flux rate is reduced [Jam04]. As an unavoidable issue, it is one of the most challenging operational and economic aspects of RO desalination, requiring the industry upwards of USD \$15 billion in mitigation cost [Fil15].

Fouling is divided into two categories: internal or surface. Internal fouling involves the clogging of pores and pore adsorption, while surface fouling involves the accumulation of impurities on the membrane surface. For RO, surface fouling is more prevalent due to the low pore volume of the membrane [Jia17]. The deposits on membrane surface or within the pores caused by membrane fouling reduces the overall flux rate by increasing pressure requirements. Membrane fouling poses a serious concern to both the productivity of RO, but also the costs of the process. Increased maintenance costs, pressure requirements, system downtimes and cleaning requirements are resultant consequences of employing RO in desalination [Guo12].

Furthermore, different fouling types can be observed. This depends on both the foulants in the feed stream and can be categorized as biological, organic, colloidal or inorganic fouling [Sim18].

Biofouling occurs when microorganisms found in the feed stream adhere to the membrane surface then proliferate, forming biofilms [Fle97]. Biofilms involve the colonization of the membrane surface by microorganisms. To survive in the high-pressure and high shear forces environment, bacteria secrete an extracellular polymeric substance (EPS) which binds the microorganisms together and protects the colony. As such, dealing with biofouling is a very complex issue as bacterial communities are highly diversified and EPS are composed of different types of organic molecules [Yu16].

Organic fouling is another difficult type of fouling to deal with. There are three main types of organic matter: natural organic matter (NOM); algal organic matter (AOM) that is made up of extracellular and intracellular macromolecules; and wastewater effluent organic matter that consists of background NOM plus soluble microbial products. Organic fouling is the formation of biofilm through the aggregation of organic debris and other microbial particles [Amy08]. For RO fouling specifically, natural organic matter contributes the most. NOM is found in both terrestrial water and seawater, and consists of humic substances, which are the byproducts of chemical and biological degradation of organic residues [Dal00]. Moreover, another major contributor to organic fouling is AOM fouling. Certain AOM known as transparent exopolymer particles were found to stick onto membrane surfaces, forming a foundational layer for bacterial attachment to occur and thus promoting further fouling of RO membranes [Vil09].

Colloids are another major problem for RO desalination. Being small particles, they are not able to be filtered by pretreatment processes. However, they are large enough to concentrate on the RO membrane surface to cause fouling. These foulants include silicates, clay, oxides and organic macromolecules [Gre09]. Fouling caused by colloids occurs when such particles accumulate on the membrane surface, forming a cake layer. As previously discussed, the cake layer exacerbates concentration polarization and leads to cake-enhanced osmotic pressure (CEOP). CEOP also promotes the permeation of solutes from the feed into the membrane, gradually lowering salt rejection and clogging the pores. CEOP actually results in more productivity loss than the cake-layer formation itself [Hoe03].

Inorganic fouling, also known as scaling, is the precipitation of minerals from the feed on the membrane surface [Sim18]. In a salt-rejection membrane system, the solute concentration of the boundary layer resulting from concentration polarization can be up to 10 times the original feed solution, depending on membrane efficiency and salt rejection rate. As such, the solute concentration of many molecules can exceed their solubility limit, resulting in their precipitation and thus leading to scale formation. Scaling foulants include many low solubility compounds such as calcium carbonate, barium sulphate, silica and calcium phosphate [Lis00].

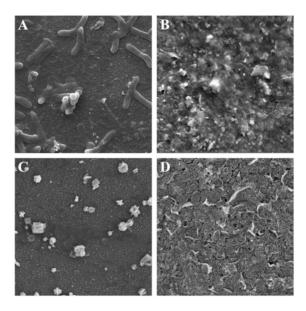


Figure 6: SEM of four types of membrane fouling: (A) Biological, (B) Organic, (C) Inorganic, and Colloidal [Jia17]

3 Operational Challenges and Solutions

While the energy consumption of RO desalination is much lower than thermal desalination processes, the overall energy consumption is still high. The specific energy consumption (SEC) of RO desalination was reduced from 20 kWh/ m^3 in 1970 to 2.5 kWh/ m^3 in 2010 [Par20]. This was achieved through the significant improvements in membrane technology, energy recovery, and plant efficiency [Coh17]. Nevertheless, there are still opportunities to reduce the energy consumption of RO desalination even further. As discussed previously, the theoretical minimum energy is $1 \text{kWh}/m^3$ at 50% recovery, whilst a practical minimum is closer to 1.6 kWh/ m^3 . Given the world's focus on lowering energy consumption and achieving carbon-neutral or green industries, improving RO desalination further could help greatly. Notably, various ways to reduce the energy consumption of RO desalination can be classified into two broad categories: improvement in the RO membrane technology and reductions in membrane fouling.

3.1 Membrane Technology: Selectivity Vs. Permeance

In the development of modern desalination plants, the main technologies leading to the reduction of energy consumption are the improvements in membrane performance. Better membranes led to improved flux rates and salt rejections at lower pressure requirements. Reducing the pressure requirements significantly impacts both the energy consumption of RO and the cost of water production. The global average energy required to reach the operating pressure of up to 85 bar is 65-85% of the total energy consumption, directly costing US\$0.11-0.24/ m^3 when producing water [Liy13].

Currently, modern RO desalination plants utilize polyamide thin-film composite (TFC) membranes that are produced through interfacial polymerization (IP). IP was developed in the 1980s by Cadotte et. al [Pur18], and involves reacting trimesoyl chloride (TMC) and m-phenylenediamine (MPD) directly upon a polysulfone support to form a thin polyamide layer [Lu21].

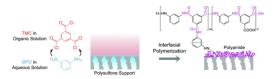


Figure 7: Schematic representing the typical interfacial polymerization process in the production of TFC RO membranes. TMC and MPD react at the surface of the polysulfone support to form a thin polyamide layer [Lu21]

The mechanism that controls the separation of water and solutes in the feed stream is known as the solution-diffusion model. Water and solutes separate into the polyamide layer, then diffuse through the membrane and desorb into the permeate. The difference in permeabilities between the water and solutes through the membrane allows for the subsequent separation.

The equation for water flux, Jw, is expressed below:
$$J_w = A(\triangle P - \triangle \pi)$$

where A is the water permeability coefficient and $\triangle P$ and $\triangle \pi$ are the applied pressure and osmotic pressure differences across the active layer, respectively [Lu21]. A key issue is considering the tradeoff between water permeability and salt rejection. Current membranes have to sacrifice either high flux rates or salt rejection rates [Lee11]. Ideally, membranes should have both high water permeance and high salt rejection. However, this is difficult to achieve.

To work towards this ideal, recent studies have proposed prioritizing salt rejection over water permeability as a measure to improve RO efficiency. After analyzing the desalination process and modelling changes to output, it was demonstrated by Werber et. al that further improvements to water permeability would have minimal effects on the energy efficiency of RO. For example, when specifically applied to RO desalination, increasing water permeability of TFC

membranes by 5-fold would lead to an insignificant 3.7% reduction in energy consumption [Wer16]. Therefore, devoting significant attention to membrane permeability may be inefficient in its own right.

On the other hand, focusing on improving membrane selectivity is crucial due to the poor rejection of small molecules, such as boron and chlorine byproducts, that current RO membranes exhibit [Hai20]. As such, costly post-treatment processes are required for their removal to purify the permeate further. Therefore, improving the selectivity of RO membranes is a more effective strategy to attain improvements in operational efficiency and water quality.

The mechanisms that control the levels of membrane selectivity are steric hindrance, Donnan exclusion, and dielectric effect [Zho20]. Steric hindrance is based on membrane pore volume, where spatial constraints directly affect the permeance of certain molecules based on size. For Donnan Exclusion, positively-charged functional groups in the membrane matrix form a stable electric field termed Donnan potential, which inhibits transfer of positively charged species [Zen19]. Finally, dielectric effect refers to the loss of energy that an ion faces when it moves from a solvent with a high dielectric constant to a medium with a low dielectric constant (water to polymer membrane). This penalty subsequently restricts the diffusion of ions across the membrane.

All three of the rejection mechanisms originate from the molecular structure of polyamide membranes. Theoretically, the polyamide membrane forms a crosslinked structure where MPD and TMC conjoin in a 3:2 monomer ratio. Practically, some linear segments are formed instead with a monomer ratio of 1:1. When this happens, unreacted acyl chloride groups undergo hydrolysis to form carboxylic groups, thus creating a negatively-charged membrane surface. Crosslinked segments resist swelling due to the formation of chain linkages between polyamide backbones, helping to increase the selectivity of the membrane. On the other hand, linear segments undergo more swelling, which facilitates ion movement within the polymer matrix. With a greater frequency of cross linkages, the membrane's selectivity increases [Lu21].

Solutions include utilizing nanoscale materials during the IP process. For example, Kim et. al developed a carbon nanotube(CNT)-polyamide nanocomposite membrane that improves the membrane productivity. The resultant formation of a nanocomposite structure increased the compactness and stability of the membrane matrix, helping to drastically boost selectivity with negligible effects on permeance, diminishing the tradeoff between permeance and selectivity [Kim14]. More recent work includes the embedding of graphene oxide quantum dots (GOQD) in RO membranes, where the GOQD improved the internal polarity of the matrix, facilitating a 3-fold increase in salt rejection with little change in flux [She20]. The introduction of nanoparticles and nanotechnology, which modify the configuration and hydrophilicity of membrane matrices,

appears to be a promising area to improve membrane performance. As for the cost of this technology, carbon nanotubes can be produced and treated cheaply, with a rough cost of US\$100-200/kg of nanotubes [Uni18].

Surface morphology, in terms of ridge-valley structures, also plays a role in membrane performance. The polyamide rejection layer formed through IP, creates a "ridge-and-valley" structure, where the increase in surface roughness leads to a greater membrane area which improves overall water permeability [Lau12]. Specifically, nanovoids (>100nm in size) created by CO2 effervescence during IP, are the main component of ridge-and-valleys [Ma18]. At the same time, high levels of surface conformity are contributors to membrane fouling, as the ridges allow foulants greater adsorption and adhesion [Son19]. Careful tuning of surface morphology along with antifouling properties need to be considered with this particular property. Overall, a wide variety of material characteristics, beyond what was discussed, play a part in membrane selectivity. As such, more research into the relationships between membrane structure and selection need to be investigated to find the optimal balance between salt selectivity and water permeance.

3.2 Membrane Fouling

As discussed in the theoretical background, membrane fouling is the accumulation of foulants or impurities on the membrane surface or within the membrane pores. Fouling is a serious problem for RO desalination, affecting flux rate, product quality, and salt rejection. It also increases the operational cost of RO and shortens membrane lifespan. Fouling is both reversible and irreversible, where the latter is more harmful to RO operations as flux rate is lowered in the long run and entire membrane modules have to be replaced. Given its unavoidable nature, a variety of techniques must be used to combat its deleterious effects.

In summary, there are two main routes to combat membrane fouling: pretreatment of the feed solution and membrane modifications to increase fouling resistance. Of the four types of fouling discussed, the effects of organic, colloidal and inorganic fouling can be significantly curtailed using pretreatment methods to decrease the amount of foulant in the feed. In contrast, pretreatment alone is ineffective against biofouling as bacterial proliferation can occur with the presence of tiny numbers of bacteria [Goh18].

3.2.1 Pretreatment

Pretreatment involves the additional removal of impurities from the feed before it undergoes RO using methods such as chlorination, ozonation, and ultrafiltration.

Traditionally, RO desalination plants employ chlorination followed by coagulation-flocculation processes and extensive filtration to remove macromolecules [Wil01].

The common chemicals that are used in such pretreatment solutions are ferric chlorides or sulfates, cationic polymers, polyelectrolyte polymer blends, sulfuric or hydrochloric acid, and chlorine. They are used in coagulation, flocculation, scaling inhibition, improving coagulation, and bacterial inhibition respectively [Cot10]. Coagulants and flocculants allow suspended solids and impurities to settle in the filtration process, effectively removing such foulants from the feed. Scaling inhibitors are used to enhance the solubility of calcium carbonate and magnesium sulfate, which are added to curb the extent of scaling. Lastly, chlorine is an oxidising agent that aims to limit the effects of biofouling by reducing the proliferation of microorganisms. However, this does not come without drawbacks, as chlorine-based treatments in the form of Cl_2 or NaOCl produce hypochlorous acid that degrades PA-based membranes. Aromatic groups and amides on the surface of RO membranes are especially affected by attacks by free chlorine [Gla94]. As a result of chlorine attacks, the polyamide layer suffers structural changes that lead to a loss of cross linkages, worsening salt rejection rates. Upon further investigation on the mechanisms of chlorine on membrane performance, membranes that have chlorine resistance have been developed to protect against membrane degradation [Kwo12].

Ozonation is a wastewater process that has been widely researched, and determined to have extremely powerful oxidation capabilities that can degrade organic macromolecules. In other studies, ozonation pretreatment was found to eliminate the detrimental effects of humic acid fouling. Humic acid makes up almost 50% of organic foulant, and often aggregates in the presence of Ca^{2+} ions to foul membranes. However, ozonation was able to cleave the aromatic rings on humic structures, degrading the harmful Ca-humic complexes [Zha19]. Ozonation has also seen success where Yin et. al restored membranes of upto 95% of its original performance when fouled by biopolymers such as bovine serum albumin and sodium alginate [Yin20]. However, ozonation is not an ideal technique. It is an unstable chemical that has to be produced on site and can lead to the production of carcinogenic bromates [Ngu12].

Compared to the previous methods, additional membrane filtration through UF is considered an unconventional technique, where many initially doubted the role and efficacy of UF as a pretreatment method. However, UF has seen widespread success in filtering foulants with negligible increases in operational cost when applied in RO desalination [Lau14]. At this moment, many UF-RO integrated desalination plants are under construction. An advantage of UF pretreatment is its ability to effectively deal with extremely turbid feed water with high silt density indices (SDI). This supplies the RO process with much purer water, minimizing the extent and rate of fouling in RO modules. UF, which has pore sizes between MF and NF, adequately encapsulates a large portion of the foulants (bacteria, silt, algae, and organic macromolecules) found in feed streams and is able to filter them out at low pressures (2-3.5 bar) [Lau14].

Industry-wise, desalination plants aim to produce feed solutions with an SDI of 4 to 5, which is often achievable through conventional techniques [Gre09]. However, UF is even more effective at lowering the SDI to even below a value of 3, allowing for the production of feed water with significantly lower fouling propensity [Kre98]. While UF is effective at removing organic molecules, colloids, bacteria and other macromolecules for the RO process, UF itself is affected by the particles in which it filters, as these also easily foul UF membranes via surface adsorption [Pea07]. To further mitigate such issues, conventional pretreatments can be combined with UF-RO to lower the fouling material in the general feed stream by up to 70%, thereby reducing the frequency of cleaning [Tan11]. Comparing UF to conventional pretreatment techniques, UF has lower spatial requirements and is more efficient at removing foulants, leading to 30% operational cost reduction [Pea04].

3.2.2 Membrane Modification

Membrane modification refers to the changing of chemical and physical characteristics of the selective or support layer. Factors such as hydrophilicity, surface charge, and surface roughness can all be altered as they contribute to membrane fouling propensity [Hai20]. A few membrane modification methods, such as surface modification, nanomaterial enhancement and component modification will be discussed below.

Significant attention has been given to creating antifouling membrane properties as a way to improve the efficiency of RO desalination. One of the main methods to confer antifouling properties to the membrane is modifying the membrane surface, altering the chemistry of the surface monomers or substrates. By controlling the chemical structure of the membrane components as well as changing the IP reaction process, researchers are able to fine-tune the surface [Gho09].

To improve antifouling properties, improving hydrophilicity has been demonstrated to be a suitable method. Higher hydrophilicity improves surface wettability, resulting in greater permeability as well as fouling resistance. The specific mechanism involves the reduction in electrostatic forces of attraction between foulant and surface. Hydrophilic surfaces repel the often-hydrophobic foulants, conferring fouling resistance [Wu15]. By modifying the surface charge of membranes to match the charge of foulants, the subsequent repulsion forces inhibit the initial adsorption of foulant, slowing down the fouling process [Zha15].

Surface morphology is another factor that has a significant effect on the antifouling properties of membranes. While researchers may aim to increase surface roughness to increase the membrane surface area and thus its permeability, increased roughness is also correlated to an increase in fouling area. The ideal antifouling surface is a smooth but hydrophilic membrane with a relatively more positive charge. Wu et. al demonstrated through the immobilization of

poly(N-vinylpyrrolidone) on a membrane surface that a smooth and hydrophilic membrane surface was able to reduce the effects of membrane fouling by 25%, whilst having a base permeability similar to or higher than normal membranes, allaying the potential conflict of deciding between permeability and fouling resistance [Wu15].

Current research has also concentrated on using modern nanomaterials to produce nano-enhanced membranes (NEM) with improved levels of hydrophilicity and other fouling resistant properties. Such nanomaterials include nanoparticles or tubes, such as the quantum dots and carbon nanotubes (CNT) mentioned previously. Other than improving water permeability and selectivity, these nanomaterials are also used to improve fouling resistance. When added to membranes, CNTs and MWCNTs drastically improve membranes' fouling resistance by creating hydrophilic mechanically strong surfaces without sacrificing water transport abilities [Liu17]. Other researchers have demonstrated similar behaviors with their membranes, as seen when Zhao et al. demonstrated that MWCNTs could increase the water flux of the RO membrane by 2-fold while decreasing its fouling propensity significantly [Zha14].

Other types of nanotubes have been explored, especially hallowsite nanotubes (HNT). HNTs are made of clay silicate minerals with hollow nanotubular structures. Traditionally studied to be used as adsorbents for dyes and heavy metals, HNTs have drawn interest from researchers in the membrane industry as they contain many hydrophilic hydroxyl surface groups and have a large specific surface area [Zen17]. This gives HNT-modified membrane fouling resistance as well as increased permeability. Furthermore, when coupled with 3aminopropyltriethoxysilane (APTES), the interfacial interactions between the membrane and HNT are strengthened. This enhances the smoothing effect that HNTs induce, helping to improve a membrane's antifouling properties [Zen16]. The hydrophilicity of HNTs were further enhanced when dextran, a hydrophilic polysaccharide, was grafted into HNTs before implantation into RO membranes. Water-contact angle of the HNT-dextran membrane was decreased by more than 30 degrees compared with the control membrane, demonstrating its improved hydrophilicity. These membranes also showed 46% less fouling compared to the control. By incorporating these HNT nanotubes, SEM displayed decreased roughness, which also helps to explain the antifouling properties of HNT-dextran membranes [Yu14].

Finally, recent efforts have been aimed at developing new types of nanotubes, such as titanate nanotubes (TNT). Similar to HNTs, TNTs take advantage of the hydrophilic properties and large specific surface area of titanium oxide, helping construct an efficient and highly performative membrane. The TNT structure also helps increase membrane permeability, where the hollow structure of the tubes forces gaps in the membrane. However, by increasing the concentration of TNTs above a certain limit, this actually decreases the salt

rejection rate of the membrane. Overall, TNTs create hydrophilic membrane surfaces that increase the fouling resistance by 50% and improve the effects of membrane cleaning by over 10%, showing promise as a potential membrane component [Ema15].

Instead of adding new components to the membrane, the development of new membrane materials has been explored as a potential addition or replacement of polyamides. One such material is poly(ethylene glycol) (PEG). The material is hydrophilic in nature as it is able to form hydrogen bonds with water molecules. As such, this decreases the frequency and extent of unwanted interactions between the foulant and the membrane [Gol14]. Gol and Jewrajka used IP to cross link TMC and a variety of PEGylated molecules (MPD + MPDPEG and PEGylated melamine). When put through IP, the resultant membranes have superior hydrophilicity and stability. Moreover, the improved fouling resistance does not require the sacrifice of lower flux rates. Other innate properties of PEG confer further fouling resistance, such as the ability of PEG chains to repel proteins and lower protein adhesion. Bera et. al developed a unique PA membrane with PEGvlated melamine and triazine rings included. The PEG in the melamine helped to lower bacterial adhesion, while the triazine rings demonstrated biocidal properties, lowering the levels of fouling even further. This membrane demonstrated a denser, smoother and more hydrophilic surface, which are characteristic of antifouling membranes [Ber15].

4 Environmental Concerns of Brine

There are many environmental challenges for RO desalination, at every part of the process. However, the primary concern that faces desalination currently is the issue of brine management and its environmentally-friendly disposal.

4.1 Current Brine Management

While desalination is touted as a viable path to address water scarcity, desalination processes also lead to environmental issues. In desalination, RO separates the impure feed stream into pure water as the permeate and brine as the waste product. Currently, global desalination capacity is over 100 million m^3/day . With an average recovery rate of 50%, millions of cubic meters of brine are produced daily [Pan19]. However, brine disposal methods currently harm the environment. These methods commonly include surface water discharge, sewer discharge, deep-well injection, and evaporation ponds [Mic18]. Furthermore, brine is not just extremely concentrated salt water, but also contains harmful chemicals, organic compounds and heavy metals added during the pretreatment process.

Multiple researchers ranging from Lattemann and Höpner, Missimer and Maliva, Frank et al., have all investigated the possible environmental conse-

quences of brine ejection into marine and terrestrial ecosystems. The major consequences of brine disposal include increased salinity of ecosystems, imbalances caused by total dissolved solid content, presence of pretreatment chemicals and metals.

In particular, brine is roughly 1.6-2 times higher in salt content, while being around 1.5 times warmer than surface temperatures of the sea (22°C) [Cam17] [Mis18]. While individual brine ejection from single desalination plants would not cause major damage to the environment, multiple plants carrying out desalination in the same area over long periods of time will. Even by increasing marine salinity slightly, the disruptions to the osmotic balance of marine species can occur, leading to cell dehydration and a higher mortality rate in the long run [Bel17]. Moreover, Petersen et al. recognized that increasing ocean salinity by 10% above the normal 35g/L caused negative effects to the physiology and visual appearance of coral in the Gulf of Agaba. Corals play important roles as fish nurseries and ecological diverse habitats, where their destruction is accelerated by desalination processes [Pet18]. For the effects of increased temperature, Li et al., demonstrated how the release rates of heavy metals were correlated with an increase in temperature, with the rates increasing two-fold [Li13]. This is in line with a contemporary study, where the effects of heavy metal concentration in the brine disposal areas of Persian Gulf desalination plants were investigated, with increased copper iron and chromium levels reported [Als16].

4.1.1 Surface Discharge

Surface water discharge is a brine disposal method that directly ejects brine into open waterways. This brine disposal method is the most common, with around 90% of desalination plants employing it [Pan19]. This will negatively impact the marine environment as the brine is more concentrated than seawater and pollutants from the RO process may harm marine life.

Nevertheless, potential solutions to this problem have been researched. Bleninger and Jirka suggests that submerging the disposal pipe at lower depths and ejecting the brine at angles of 30-60 degrees will improve the dilution rates of brine by two- to four-fold, thus reducing the impact of salinity [Ble08]. Furthermore, relatively cheap predisposal treatment methods can also be employed, such as dilution with regular seawater or municipal wastewater to decrease the salinity. By doing so, the impacts on ecological systems have been found to be greatly reduced, at a cost of $0.05-0.30/m^3$ [Ara17].

4.1.2 Municipal Water Treatment

For smaller-scale inland desalination plants processing brackish water, the brine can be processed by nearby municipal wastewater facilities. This is specific to brackish water, as overly concentrated levels of TDS in seawater brine may negatively impact wastewater treatment facilities. Municipal wastewater facilities

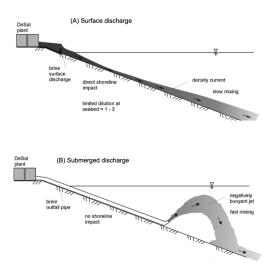


Figure 8: Schematic of brine discharge methods: (a) shoreline discharge and (b) submerged discharge [Ble08]

have TDS limits of 3g/L, while seawater brine is usually found at 55g/L [Val14]. As such, this disposal method is typically used by brackish water plants, with costs of disposal ranging from $$0.32 - 0.66/m^3$$ of brine [Ara17].

4.1.3 Deep Well Injection

Another commonly used brine disposal method is deep-well injection, where brine is forced into designated underground aquifers. These are separated from normal groundwater aquifers that are usually drawn from for freshwater processing. Again, this method is employed by brackish water desalination plants, as their brine concentrations are sufficiently low. These designated deep-wells are surrounded by layers of clay and impermeable rock formations that hinder the movement of saline water [Per15]. These containment aquifers are placed at depths of 500 to 1500 meters, and have a lifespan of 25-30 years. However, the primary concern of this brine disposal method is the potential leakage of the deep-wells and subsequent contamination of freshwater aquifers. As such, costly hydrogeological surveys, drill testings, and pilot tests have to be conducted to ascertain the suitability of deep-well sites. Thus, the cost of this disposal method skyrockets, ranging from \$0.54 to $2.65/m^3$ of brine [Ara17].

4.1.4 Evaporation Ponds

Through the creation of shallow basins, brine is exposed to sunlight where the solar energy slowly evaporates the brine. This method results in the precipitation of salt crystals, which are harvested and further processed. Evaporation is

a common method for many desalination plants that are located in arid regions given the availability of solar energy [Rod12]. One drawback of this method is that these evaporation ponds need to be adequately lined and isolated from groundwater reserves to prevent contamination of freshwater sources. To abide by environmental regulations, these ponds need to be double-coated with impervious linings to prevent leaking of brine and trace heavy metals [Roy14]. As such, given the stringent environmental requirements and spatial inefficiencies of this disposal method, the cost is drastically higher at a range of \$3.28 to $$10.04/m^3$ [Ara17].

Method	Origins of Brine	Cost (US\$) (Arafat, 2017)
Surface Discharge	Seawater	0.05 - 0.30
Municipal Water Treatment	Brackish Water	0.32 - 0.66
Deep-Well Injection	Brackish Water	0.54 - 2.65
Evaporation Ponds	Seawater	3.28 - 10.04

Figure 9: Table showing methods of conventional brine disposal and their respective costs [Ara17]

4.2 Environmentally Friendly Brine Management: Zero Liquid Discharge

While some solutions such as submerged discharge help to reduce the environmental impacts of brine through rapid dilution, marine ecosystems will still face contamination. Any ejection of anthropogenic waste will ultimately impact our environment. Thus, Zero-Liquid-Discharge (ZLD) is an approach to brine management that reduces environmental pollution.

As denoted by its name, ZLD involves the full extraction of water from waste brine to prevent any liquid ejection, helping to increase total water recovery and reduce pollution of marine ecosystems [Pan19]. The water recovery is at a rate of 95-99%, producing highly pure water, while the remaining salts are potentially valuable to other industrial processes [Xio17]. To achieve ZLD, each desalination plant requires a unique configuration of processing methods based on its location, quality of brine, and available technology. These range from membrane-based technologies to thermal technologies, with energy consumptions ranging between 0.6 to 73 kWh/ m^3 . Given society's goal to reduce energy consumption, a few energy-efficient techniques that help to achieve ZLD will be discussed.

4.2.1 Reverse Osmosis in ZLD

Reverse osmosis and high-pressure reverse osmosis is the most common technology used in desalination. By applying a pressure greater than the osmotic

pressure of the feed, saline water is filtered to produce pure water. Despite its success at filtering regular sea water or brackish water with concentrations below 35g/L, the extremely saline concentrations of brine limits the efficacy of RO. When the TDS of brine is increased, the osmotic pressure it exerts also increases. In particular, the osmotic pressure of NaCl ranges from 59-211 bar for salinities of 70g/L to 250g/L respectively. Currently, conventional TFC membranes can only cope with pressures up to 82 bar and salinities of up to 70g/L [Pan19]. Since the TDS of brine is often at 70g/L or greater, water recovery is energy intensive. At TDS of up to 85g/L, water recovery is only at 10% [Ain11]. Such pressure and TDS limits are overcome through the use of specially designed membranes that are able to handle pressures of up to 120 bar. However, flux rates are still extremely low, with water recovery at less than 8% [Sol20]. As such, given the safety concerns of high pressures, technical limitations of RO membranes, and the energy intensity of such high pressures (3-9 kWh/ m^3), RO is not a very efficient or sustainable way to recover water from brine for ZLD [Sch18].

4.2.2 Forward Osmosis in ZLD

Forward osmosis (FO) is another membrane technology that relies on osmotic pressures. Rather than applying an external hydraulic pressure, forward osmosis relies on using a "draw solution" that has a higher TDS concentration than the concentrated brine, allowing water molecules to diffuse down a water potential gradient through a membrane. This water is then extracted from the draw solution [Amj18]. Compared to RO, FO excluding the energy consumption of draw solution recovery is much more energy efficient since there are no high-pressure requirements. The draw solution is the main feature of FO. Ideally, the draw solution should be readily available, relatively low cost, non-toxic and have low fouling propensity [Zha16]. There are currently a variety of draw solutions, each made using a different solute, ranging from organic solutes to inorganic salts, nanoparticles, and more.

These solutions range from NH3/CO2 solutions to hyperconcentrated brine. For the NH3/CO2 solution, a satisfactory water recovery rate of 64% was observed for a brine solution with a TDS of 73g/L. Despite its good flux rate, ammonia is a toxic chemical that makes this solution non-ideal, as potential reverse solute diffusion may occur, contaminating the feed [McG13]. Hyperconcentrated brine solutions with TDS levels of 100-200g/L used as draw solutions were able to achieve reasonable flux rates of $3.5\text{L}/m^2h$ when used on brine with a TDS of 41g/L [Eus16].

Draw solutions have their pros and cons based on what system they are used in, with the membrane it is used in conjunction with and other processes playing a factor in the efficacy of draw solutions. This creates a situation where there is no ideal or universal FO draw solution, adding complexity to this method. Furthermore, the energy consumption of the draw solution recovery and the concentration polarizations on both sides of the membrane disadvantages this method [Gao14]. To alleviate the issues above, recent studies have investigated the modification of TFC membranes to improve the antifouling properties of FO membranes and reduce the effects of CP. Through the use of nanosheets and quantum dots, several researchers have created more efficient FO membranes [Guo18] and [Xu19].

At this moment, FO is still a novel method, with few avenues available for energy efficient water recovery. Compared to RO, the energy consumption of FO excluding the draw solution recovery ranges from $0.1\text{-}0.85~\text{kWh}/m^3$, showing promise as a sustainable method of water recovery, especially for high-TDS brine. However, when including the recovery stage, the energy consumption jumps as high as $13\text{kWh}/m^3$ (Kolliopoulos et al., 2018).

4.2.3 Wind-Aided Intensified eVaporation in ZLD

Wind-Aided Intensified eVaporation (WAIV) is a thermal-based process that reduces the volume of brine in an effort to achieve ZLD. Specifically, towers of vertically-stretched wetted surfaces use wind energy and power to expedite the evaporation process. These surfaces, usually made of woven nettings or textiles, are soaked with brine through a distribution system.

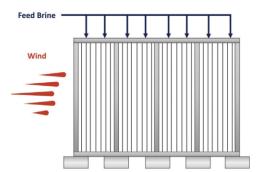


Figure 10: Schematic of WAIV unit [Pan19]

So far, there is minimal literature on WAIV as a salt recovery method. For the available research, Oren et al. showed that WAIV was capable of concentrating brine upwards of 300g/L from RO brine [Ore10]). Moreover, Macedonio et al. integrated WAIV modules with membrane crystallizers to achieve water recovery of 88.9% [Mac11]. Recently, a full-scale pilot in Queensland Australia demonstrated that the WAIV was able to achieve an evaporation performance 24 times that of a similarly sized evaporation pond [Mur15]. In conjunction with its low cost of $\$0.83/m^3$, WAIV is a very economical method [Mac11]. It is also

energy efficient and sustainable, with a consumption of $0.6\text{-}1\text{kWh}/m^3$ [Pan19]. Furthermore, renewable wind energy is used for evaporation, improving the promise of WAIV as a sustainable method to achieve ZLD.

4.2.4 Membrane Distillation

Membrane distillation (MD) combines thermal energy with membrane based processes. Utilizing thermal energy, the feed undergoes a phase change and passes through a hydrophobic microporous membrane, where it condenses into the permeate. The hydrophobic membrane inhibits the movement of liquid molecules while permitting vapour molecules, achieving a high flux rate $(30L/m^2h)$ with salt rejection of over 99% [Ash16]. In MD, the brine being treated can be extremely saline, with TDS limits of 350g/L [Tun11]. The advantage of MD is its low temperature requirements of $40 - 80^{\circ}$ C [ea18b]. This lowers the energy requirements of the process, improving its sustainability aspect. However, some MD processes suffer from low flux rate and concentration polarization related issues. Recent developments have aimed to modify MD membranes to increase mechanical strength and thermal resistance. These include the modification of ceramic membranes by grafting hydrophobic agents such as aluminium oxide and titanium dioxide. Unlike RO, which improves in productivity with increased hydrophilicity, MD relies on increased hydrophobicity to increase vapour selectivity. Kujawa et. al utilized metal oxide grafts on ceramic membranes, increasing selectivity above 98% with flux rates of upto $4.8L/m^2h$ [Kuj17]. Overall, MD is still a thermally intensive process with low efficiency, resulting in energy consumptions ranging from 39-67 kWh/ m^3 [Pan19].

4.2.5 Brine Concentrators

Brine concentrators are a very common technique used to achieve ZLD. A Brine concentrator (BC) module is made up of a vertical tube that serves as an evaporator. The feed is heated up to boiling point then passed through a deaerator that extracts non-condensable gases. This brine is then mixed with a slurry and evaporated. The water in the brine is evaporated and recondensed while the metal sulphates in the slurry acts as crystal seed to recrystallize existing salts. As for the technical specifications of BC, the process has a TDS limit of 250 g/L with a 90-99% water recovery. For its energy specifications, BC requires $15\text{-}26\text{kWh/}m^3$, significantly more than membrane based processes [Pan19]. While it has good efficiency and high levels of water recovery, the capital costs of BC is high as these modules require high-end materials that can resist corrosion such as super duplex stainless steel or titanium [Sha13].

4.2.6 Multi-Stage Flash Distillation

Multi-Stage Flash distillation (MSF) is a leading thermal desalination method even in current times. Originally developed for desalination, it has also been used to recover water from brine. In MSF, brine is heated in a flash unit, reaching temperatures of $110-120^{\circ}\mathrm{C}$ where some water is evaporated and extracted.

The remaining vapours are then passed through successive units where the flash heating process is repeated until most of the water has been extracted [Mab15]. While MSF is still widely used in desalination, it has minimal literature as a ZLD method. Issues that arise from MSF include the corrosion that the system faces. MSF systems are made using normal-grade stainless steel, but corrode under the treatment of high-TDS brine [Dey19]. To build corrosion resistant systems, expensive materials such as super duplex stainless steel, titanium or high nickel alloys need to be used, raising the capital costs of MSF systems. Furthermore, the energy consumption of MSF is high, at $20\text{-}27 \text{ kWh}/m^3$ [AK13].

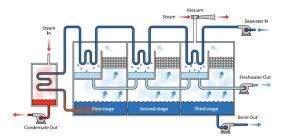


Figure 11: Schematic of MSF unit used in desalination. In a ZLD system, brine would replace seawater in the inlet [AK13].

5 Discussion and Evaluation

Overall, RO faces many challenges, with equally as many possible solutions being developed. While polyamide TFC membranes dominate the industry with their high selectivity, flux rates and overall stability, issues such as nonideal membranes and fouling pose as obstacles to RO. For the tradeoffs between membrane selectivity and permeance, membrane selectivity was discussed to be of greater importance than permeance. Werber et al. demonstrated that a fivefold increase in membrane permeance would only lead to a 3.7% reduction in energy consumption, while current membranes lack sufficient selectivity which prompts additional post-treatment processes. As such, selectivity is a factor that requires greater attention. Nanomaterials in particular have shown to improve selectivity, where carbon nanotubes or quantum dots enhance the selectivity with minimal impacts on flux rate. As mentioned in Section 3.1, nanomaterial technology is an economically viable strategy, with nanotubes costing US\$100-200/kg. While research has demonstrated the technical possibility of using nanotechnology in membranes, the issue is with the scalability of the technology. Daer et al. indicates how the alignment and dispersal of nanotubes is not yet optimized, increasing the production cost of large scale industrial projects [Dae15]. However, nanomaterials are still a promising option to improve RO productivity.

As for reducing membrane fouling, both pre-treatment and membrane modification techniques prove useful at achieving this goal. Conventional pre-treatment techniques such as chlorination and ozonation have been employed successfully in municipal freshwater treatment facilities, and are able to significantly reduce the effects of biological and organic fouling (Section 3.2.1). However, they introduce toxic chemicals to the feed stream, as seen when ozone forms carcinogenic bromate. Instead, UF is a membrane-based pretreatment technology that effectively filters out many foulants with no toxic byproducts. UF also has lower spatial requirements compared to conventional techniques. As Pearce et al. highlighted in an earlier report, the lower spatial requirements of UF would lead to cost reductions of 30%. Furthermore, the combination of both conventional methods and UF pre-treatment is a potential solution that reduces the amount of toxic chemicals required while lowering the total amount of foulant in terms of SDI.

To further reduce fouling propensity, RO membranes have been modified in many ways to increase their fouling resistance. Both surface modification and nanotube embedment are methods that increase fouling resistance and improve permeance. Immobilization of hydrophilic substances on membrane surfaces and embedment of hydrophilic nanomaterials both decreased the effects of fouling by more than 25%. For nanoenhanced membranes, the effect is even more pronounced, with up to 50% reductions in fouling ability (Section 3.2.2). However, surface modified membranes are prone to strong forces that will degrade the active layer, while nanotubes are mechanically and chemically resistant. Given their low material costs, nanoenhanced membranes are a viable option for producing anti-fouling membranes. Nevertheless, as mentioned above, more optimized production processes have to be developed before such membranes can be deployed in full-scale industry projects. As such, there is still no clear cut superior choice between the two membrane types due to their existing flaws.

A key environmental concern of RO desalination is the issue of clean brine management. Containing high levels of dissolved salts and toxic waste, brine has the ability to pollute the marine ecosystems where it is discharged. This is evident in the damage caused to coral reefs, which are especially sensitive to changes in the environment. Safer methods of disposal such as evaporation ponds or deep wells are not foolproof, with opportunities for leakage. Taking the ZLD approach to brine management is one of the key methods to preventing environmental pollution. RO and FO are both energy efficient membrane processes that can aid in water recovery, with energy consumptions of 3-13 kWh/ m^3 . However, RO cannot withstand high pressure necessitated by the high osmotic pressures of brine, while extracting water from the draw solution in FO uses 95% of the energy consumption. Thermal processes such as MD, BC and MSF (Section 4.2.4-6) are all technically viable strategies to reduce the overall amount of liquid discharge. Despite their technical efficacy, they all have extremely high energy consumptions of 15kWh/ m^3 and above, making them

unideal technologies to be employed in an energy conscious society. WAIV on the other hand shows promise as a ZLD process as it has remarkably low energy consumptions of $0.6 \text{kWh}/m^3$. However, this method has no water retention capability on its own, as water is lost in evaporation. It has to be combined with other energy-intensive techniques to achieve water recovery. Overall, ZLD is still an aspect of desalination that consumes high amounts of energy. This is an inherent aspect of the approach as the water recovery rates are expected to be above 95%, posing a large thermal or energy requirement. While energy requirements may be high, sustainable energy can be used to prevent the discharge of toxic liquid brine and subsequent pollution of our worsening environment.

6 Conclusions and Outlook

As water scarcity is exacerbated by growing anthropogenic activity, desalination will be a key factor in maintaining water security efficiently and sustainably. However, significant impediments such as membrane fouling and non-ideal membranes severely limit the productivity of reverse osmosis. These circumstances lower the total output while increasing energy consumptions and operational costs. Not only does reverse osmosis have technical obstacles, but its increase in popularity has also brought upon significant environmental pollution. Brine disposal and management remains a major issue in reverse osmosis desalination, with hyperconcentrated brine containing toxic chemicals and organic molecules that pollute marine ecosystems. With enhanced control measures based on the Zero-Liquid-Discharge approach, the negative impacts of brine disposal can be solved effectively. The water extraction or brine concentration methods such as membrane distillation or forward osmosis effectively reduce brine volume by up to 95-99%, improving total fresh water volume and decreasing toxic waste.

This review has discussed the various operational and environmental challenges found with reverse osmosis desalination, as well as current solutions in development. For operational challenges, newly explored methods such as new membrane production techniques and membrane modification are leading the charge. In particular, membrane modification using nanomaterials is an extremely promising option, so long as methods can be devised to scale the membranes up to industrial level systems. This will help to improve membrane selectivity, permeance, and improve fouling resistance, which are amongst the largest obstacles to reverse osmosis. On the environmental end, membrane and thermal technologies compete within the Zero-Liquid-Discharge approach. Ultimately, thermal technologies have the edge due to their ability to handle hyper concentrated brine, but improvements to membrane technology will drive these techniques given their inherent energy efficiencies. Overall, more efficient processes and less environmental pollution will assist in the longevity of desalination.

7 Future Research Needs

At present, RO in desalination is expected to rise in market dominance as communities transition away from inefficient thermal processes. While it is a welldeveloped technology that will solve our water insecurity, several key areas need to be addressed. Firstly, membrane fouling is the largest obstacle that RO faces. Experiments using larger nano-enhanced membranes can be conducted to observe the operational capabilities of the technology as it scales up to industrial levels. Furthermore, more experiments in the nano-membrane production process will allow for improved dispersal and alignment of nanomaterials within the membrane. Secondly, sustainable brine management methods need increased research. The ZLD approach, while being energy-intensive, is extremely vital for the preservation of the environment and marine ecosystems. Improving the permeance of high pressure RO membranes may increase the usage of these energy-efficient techniques. Moreover, experiments that combine WAIV technology with other ZLD methods can possibly lead to the optimization of WAIV technology for increased water recovery, leading to improved productivity of RO.

References

- [Ain11] Roger Aines. Fresh water generation from a quifer-pressured carbon storage: Feasibility of treating saline formation waters. Energy Procedia, 2011.
- [AK13] Ali Al-Karaghouli. Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes. Renewable and Sustainable Energy Reviews, 2013.
- [Ali18] Aamer Ali. Membrane technology in renewable-energy-driven desalination. *Renewable and Sustainable Energy Reviews*, 2018.
- [Als16] Fatimh Alshahri. Heavy metal contamination in sand and sediments near to disposal site of reject brine from desalination plant, arabian gulf: Assessment of environmental pollution. *Environmental Science and Pollution Research*, 2016.
- [Alt14] Ali Altaee. Comparison between forward osmosis-reverse osmosis and reverse osmosis processes for seawater desalination. *Desalination*, 2014.
- [Amj18] Muhammad Amjad. Novel draw solution for forward osmosis based solar desalination. *Applied Energy*, 2018.
- [Amy08] Gary Amy. Fundamental understanding of organic matter fouling of membranes. *Desalination*, 2008.
- [Ara17] Hassan Arafat. Desalination sustainability. Elsevier Gezondheidzorg, 2017.
- [Ash16] B.B. Ashoor. Principles and applications of direct contact membrane distillation (dcmd): A comprehensive review. *Desalination*, 2016.
- [Bel17] Natalia Belkin. The effect of coagulants and antiscalants discharged with seawater desalination brines on coastal microbial communities: A laboratory and in situ study from the southeastern mediterranean. Water Research. 2017.
- [Ber15] Anupam Bera. Pegylation and incorporation of triazine ring into thin film composite reverse osmosis membranes for enhancement of antiorganic and anti-biofouling properties. *Desalination*, 2015.
- [Ble08] Tobias Bleninger. Modelling and environmentally sound management of brine discharges from desalination plants. *Desalination*, 2008.
- [Cam17] M.L. Cambridge. Effects of high salinity from desalination brine on growth, photosynthesis, water relations and osmolyte concentrations of seagrass posidonia australis. *Marine Pollution Bulletin*, 2017.

- [Che10] Paul Jiaping Chen. Desalination of seawater by reverse osmosis. *Membrane and Desalination Technologies*, 2010.
- [Cip09] Andrea Cipollina. Seawater desalination: Conventional and renewable energy processes (green energy and technology). *Springer*, 2009.
- [Coh17] Yoram Cohen. A perspective on reverse osmosis water desalination: Quest for sustainability. AIChE, 2017.
- [Cot10] Joseph Cotruvo. Desalination technology. Van Haren Publishing, 2010.
- [Dae15] Sahar Daer. Recent applications of nanomaterials in water desalination: A critical review and future opportunities. *Desalination*, 2015.
- [Dal00] Abdul Ghani I. Dalvi. Studies on organic foulants in the seawater feed of reverse osmosis plants of swcc. *Desalination*, 2000.
- [Dey19] M.A. Deyab. Enhancement of corrosion resistance in msf desalination plants during acid cleaning operation by cationic surfactant. *Desalination*, 2019.
- [ea18a] Mohammad Ali Abdelkareem et. al. Recent progress in the use of renewable energy sources to power water desalination plants. Desalination, 2018.
- [ea18b] Sana Abdelkader et al. Direct contact membrane distillation applied to saline wastewater: Parameter optimization. Water Science and Technology, 2018.
- [Ema15] D. Emadzadeh. A novel thin film nanocomposite reverse osmosis membrane with superior anti-organic fouling affinity for water desalination. Desalination, 2015.
- [Eus16] Ramon Christian Eusebio. Optimization of forward osmosis system for the utilization of reverse osmosis brine. *Desalination and Water Treatment*, 2016.
- [Fil15] Emmanuelle Filloux. Biofouling and scaling control of reverse osmosis membrane using one-step cleaning-potential of acidified nitrite solution as an agent. *Journal of Membrane Science*, 2015.
- [Fle97] Hans-Curt Flemming. Reverse osmosis membrane biofouling. Experimental Thermal and Fluid Science, 1997.
- [Fra17] Hila Frank. Short-term effects of swro desalination brine on benthic heterotrophic microbial communities. *Desalination*, 2017.
- [Fri07] C. Fritzmann. State-of-the-art of reverse osmosis desalination. *Desalination*, 2007.

- [Gao14] Yiben Gao. Characterization of internal and external concentration polarizations during forward osmosis processes. *Desalination*, 2014.
- [Gho09] Asim K. Ghosh. Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes. *Journal of Membrane Science*, 2009.
- [Gla94] Julius Glater. The search for a chlorine-resistant reverse osmosis membrane. *Desalination*, 1994.
- [Goh18] P.S. Goh. Membrane fouling in desalination and its mitigation strategies. *Desalination*, 2018.
- [Gol14] Ravindra M. Gol. Facile in situ pegylation of polyamide thin film composite membranes for improving fouling resistance. *Journal of Membrane Science*, 2014.
- [Gre09] Lauren F. Greenlee. Reverse osmosis desalination: Water sources, technology, and today's challenges. Water Research, 2009.
- [Guh17] Rajarshi Guha. Reactive micromixing eliminates fouling and concentration polarization in reverse osmosis membranes. *Journal of Membrane Science*, 2017.
- [Guo12] Wenshan Guo. A mini-review on membrane fouling. Bioresource Technology, 2012.
- [Guo18] Hao Guo. Polydopamine coating on a thin film composite forward osmosis membrane for enhanced mass transport and antifouling performance. *Journal of Membrane Science*, 2018.
- [Gut13] Jenia Gutman. Cake/biofilm enhanced concentration polarization. Encyclopedia of Membrane Science and Technology, 2013.
- [Hai18] A.H. Haidari. Optimal design of spacers in reverse osmosis. Separation and Purification Technology, 2018.
- [Hai20] Ruth Hailemariam. Reverse osmosis membrane fabrication and modification technologies and future trends: A review. Advances in Colloid and Interface Science, 2020.
- [Hoe03] Eric M.V. Hoek. Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes. *Environmental Science & Technology*, 2003.
- [Jam04] K. Jamal. Mathematical modeling of reverse osmosis systems. *Desalination*, 2004.
- [Jia17] Shanxue Jiang. A review of reverse osmosis membrane fouling and control strategies. *Science of The Total Environment*, 2017.

- [Kim14] Hee Joong Kim. High-performance reverse osmosis cnt/polyamide nanocomposite membrane by controlled interfacial interactions. ACS Applied Materials & Interfaces, 2014.
- [Kim19] Jungbin Kim. A comprehensive review of energy consumption of seawater reverse osmosis desalination plants. *Applied Energy*, 2019.
- [Kol18] Georgios Kolliopoulos. Energy requirements in the separationregeneration step in forward osmosis using tma-co2-h2o as the draw solution. *Chemical Engineering Research and Design*, 2018.
- [Kre98] Seymour Kremen. Silt density indices (sdi), percent plugging factor: Their relation to actual foulant deposition. *Desalination*, 1998.
- [Kuj17] Joanna Kujawa. Hydrophobic ceramic membranes for water desalination. *Applied Sciences*, 2017.
- [Kwo12] Young-Nam Kwon. Surface modification of a polyamide reverse osmosis membrane for chlorine resistance improvement. *Journal of Membrane Science*, 2012.
- [Lat08] Sabine Lattemann. Environmental impact and impact assessment of seawater desalination. *Desalination*, 2008.
- [Lau12] W.J. Lau. A recent progress in thin film composite membrane: A review. *Desalination*, 2012.
- [Lau14] W.J. Lau. Ultrafiltration as a pretreatment for seawater desalination: A review. *Membrane Water Treatment*, 2014.
- [Lee11] Kah Peng Lee. A review of reverse osmosis membrane materials for desalination—development to date and future potential. *Journal of Membrane Science*, 2011.
- [Li13] Haiyan Li. Effect of ph, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. *Journal of Chemistry*, 2013.
- [Lis00] C.A.C Lisdonk. Monitoring scaling in nanofiltration and reverse osmosis membrane systems. *Desalination*, 2000.
- [Liu17] Yanan Liu. Synergy of the mechanical, antifouling and permeation properties of a carbon nanotube nanohybrid membrane for efficient oil/water separation. *Nanoscale*, 2017.
- [Liy13] S. Liyanaarachchi. Problems in seawater industrial desalination processes and potential sustainable solutions: A review. Reviews in Environmental Science and Bio/Technology, 2013.

- [Lu21] Xinglin Lu. Fabrication of desalination membranes by interfacial polymerization: History, current efforts, and future directions. *Chemical Society Reviews*, 2021.
- [Ma18] Xiao-Hua Ma. Nanofoaming of polyamide desalination membranes to tune permeability and selectivity. *Environmental Science & Technology Letters*, 2018.
- [Mab15] Abdel Nasser Mabrouk. Technoeconomic study of a novel integrated thermal msf-med desalination technology. *Desalination*, 2015.
- [Mac11] F. Macedonio. Wind-aided intensified evaporation (waiv) and membrane crystallizer (mcr) integrated brackish water desalination process: Advantages and drawbacks. *Desalination*, 2011.
- [McG13] Robert L. McGinnis. Pilot demonstration of the nh3/co2 forward osmosis desalination process on high salinity brines. *Desalination*, 2013.
- [Mic18] Michael Mickley. Updated and extended survey of us municipal desalination plants. *Reclamation: Managing Water in the West*, 2018.
- [Mis18] Thomas M. Missimer. Environmental issues in seawater reverse osmosis desalination: Intakes and outfalls. *Desalination*, 2018.
- [Mur15] Brendan Murray. Waiv technology: An alternative solution for brine management. Journal of the Australian Water Association, 2015.
- [Ngu12] Thang Nguyen. Biofouling of water treatment membranes: A review of the underlying causes, monitoring techniques and control measures. *Membranes*, 2012.
- [Ore10] Y. Oren. Pilot studies on high recovery bwro-edr for near zero liquid discharge approach. *Desalination*, 2010.
- [Pan19] Argyris Panagopoulos. Desalination brine disposal methods and treatment technologies a review. *Science of The Total Environment*, 2019.
- [Par20] Kiho Park. Towards a low-energy seawater reverse osmosis desalination plant: A review and theoretical analysis for future directions. *Journal of Membrane Science*, 2020.
- [Pea04] Graeme Pearce. Pretreatment options for large scale swro plants: Case studies of of trials at kindasa, saudi arabia, and conventional pretreatment in spain. *Desalination*, 2004.
- [Pea07] G.K. Pearce. The case for uf/mf pretreatment to ro in seawater applications. *Desalination*, 2007.

- [Per15] Putri Pertiwi. An environmental protection (zero discharge) utilizing idle wells to inject produced water for pressure maintenance using deep well injection method. *Proc. Indonesia Petrol Association*, 2015.
- [Pet18] Karen Petersen. Impact of brine and antiscalants on reef-building corals in the gulf of aqaba potential effects from desalination plants. Water Research, 2018.
- [Pri09] Noka Prihasto. Pre-treatment strategies for seawater desalination by reverse osmosis system. *Desalination*, 2009.
- [Pur18] Mihir Kumar Purkait. Introduction to membranes. *Interface Science and Technology*, 2018.
- [Qas18] M. Qasim. The use of ultrasound to mitigate membrane fouling in desalination and water treatment. *Desalination*, 2018.
- [Qas19] Muhammad Qasim. Reverse osmosis desalination: A state-of-the-art review. *Desalination*, 2019.
- [Rod12] Fernando A. Rodriguez. Comparison of evaporation rates for seawater and brine from reverse osmosis in traditional salt works: Empirical correlations. *Water Supply*, 2012.
- [Roy14] Alakendra N. Roychoudhury. Geochemical evaluation of soils and groundwater affected by infiltrating effluent from evaporation ponds of a heavy mineral processing facility, west coast, south africa. *Journal* of Geochemical Exploration, 2014.
- [Saa21] Aldo Saavedra. Comparative analysis of conventional and emerging technologies for seawater desalination: Northern chile as a case study. *Membranes*, 2021.
- [Sab01] S. Sablani. Concentration polarization in ultrafiltration and reverse osmosis: A critical review. *Desalination*, 2001.
- [Sch18] A. Benjamin Schantz. Emerging investigators series: Prospects and challenges for high-pressure reverse osmosis in minimizing concentrated waste streams. *Environmental Science: Water Research & Technology*, 2018.
- [Sha13] Devin Shaffer. Desalination and reuse of high-salinity shale gas produced water: Drivers, technologies, and future directions. *Environmental Science & Technology*, 2013.
- [She15] Seema Shenvi. A review on ro membrane technology: Developments and challenges. *Desalination*, 2015.

- [She20] Qin Shen. Engineering heterostructured thin-film nanocomposite membrane with functionalized graphene oxide quantum dots (goqd) for highly efficient reverse osmosis. ACS Applied Materials & Interfaces, 2020.
- [Shr15] Abhishek Shrivastava. Energy efficiency breakdown of reverse osmosis and its implications on future innovation roadmap for desalination. *Desalination*, 2015.
- [Sim18] Lee Nuang Sim. A review of fouling indices and monitoring techniques for reverse osmosis. *Desalination*, 2018.
- [Sol20] DuPont Water Solutions. Dupont xus180808 reverse osmosis element. www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/45-D01736-en.pdf., 2020.
- [Son19] Xiaoxiao Song. Confined nanobubbles shape the surface roughness structures of thin film composite polyamide desalination membranes. *Journal of Membrane Science*, 2019.
- [Sut00] Iris Sutzkover. Simple technique for measuring the concentration polarization level in a reverse osmosis system. *Desalination*, 2000.
- [Tan11] Chatkaew Tansakul. Adsorption combined with ultrafiltration to remove organic matter from seawater. Water Research, 2011.
- [Tun11] Chan Mya Tun. Sustainable integrated membrane contactor process for water reclamation, sodium sulfate salt and energy recovery from industrial effluent. *Desalination*, 2011.
- [Uni18] Vanderbilt University. Cheap, small carbon nanotubes. Science Daily, 2018.
- [Val14] Alireza Valipour. Performance of high-rate constructed phytoremediation process with attached growth for domestic wastewater treatment: Effect of high tds and cu. *Journal of Environmental Management*, 2014.
- [Vil09] Loreen Villacorte. The fate of transparent exopolymer particles (tep) in integrated membrane systems: Removal through pre-treatment processes and deposition on reverse osmosis membranes. Water Research, 2009.
- [Wer16] Jay R. Werber. The critical need for increased selectivity, not increased water permeability, for desalination membranes. *Environmental Science & Technology Letters*, 2016.
- [Wil01] Mark Wilf. Improved performance and cost reduction of ro seawater systems using uf pretreatment. *Desalination*, 2001.

- [Wu15] Junhui Wu. Improving the hydrophilicity and fouling resistance of ro membranes by surface immobilization of pvp based on a metal-polyphenol precursor layer. *Journal of Membrane Science*, 2015.
- [Xio17] Rihua Xiong. Current status and technology trends of zero liquid discharge at coal chemical industry in china. *Journal of Water Process Engineering*, 2017.
- [Xu19] Shengjie Xu. Novel graphene quantum dots (gqds)-incorporated thin film composite (tfc) membranes for forward osmosis (fo) desalination. Desalination, 2019.
- [Yin20] Zhonglong Yin. Alleviating reverse osmosis membrane fouling caused by biopolymers using pre-ozonation. *Journal of Membrane Science*, 2020.
- [Yu14] Haoxia Yu. Improving the antifouling property of polyethersulfone ultrafiltration membrane by incorporation of dextran grafted halloysite nanotubes. *Chemical Engineering Journal*, 2014.
- [Yu16] Wenzheng Yu. Evaluation of ferrate as a coagulant aid/oxidant pretreatment for mitigating submerged ultrafiltration membrane fouling in drinking water treatment. *Chemical Engineering Journal*, 2016.
- [Zen16] Guangyong Zeng. Novel polyvinylidene fluoride nanofiltration membrane blended with functionalized halloysite nanotubes for dye and heavy metal ions removal. *Journal of Hazardous Materials*, 2016.
- [Zen17] Guangyong Zeng. Application of dopamine-modified halloysite nanotubes/pvdf blend membranes for direct dyes removal from wastewater. Chemical Engineering Journal, 2017.
- [Zen19] L. Zeng. Anion exchange membranes for aqueous acid-based redox flow batteries: Current status and challenges. *Applied Energy*, 2019.
- [Zha14] Haiyang Zhao. Improving the performance of polyamide reverse osmosis membrane by incorporation of modified multi-walled carbon nanotubes. *Journal of Membrane Science*, 2014.
- [Zha15] Wenxiang Zhang. A review on flux decline control strategies in pressure-driven membrane processes. *Industrial & Engineering Chemistry Research*, 2015.
- [Zha16] Dieling Zhao. Multi-functional forward osmosis draw solutes for seawater desalination. *Chinese Journal of Chemical Engineering*, 2016.
- [Zha19] Xuehao Zhao. Ozonation as an efficient pretreatment method to alleviate reverse osmosis membrane fouling caused by complexes of humic acid and calcium ion. Frontiers of Environmental Science & Engineering, 2019.

 $[{\rm Zho20}] \quad {\rm Xuechen~Zhou.~Intrapore~energy~barriers~govern~ion~transport~and} \\ \quad {\rm selectivity~of~desalination~membranes.~} Science~Advances,~2020.$