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Review Desalination brine disposal methods and treatment technologies - A review

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Brine is the by-product of the desalination process.
- Disposal methods and treatment technologies are evaluated.
- Membrane- and thermal-based treatment technologies are analyzed.
- A brine treatment technology framework is introduced for Zero Liquid Discharge.
- Challenges and future prospects for ZLD treatment technologies are presented.

article info abstract

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Brine, also known as concentrate, is the by-product of the desalination process that has an adverse impact on the environment due to its high salinity. Hence, viable and cost-effective brine management systems are needed to reduce environmental pollution. Currently, various disposal methods have been practiced, including surface water discharge, sewer discharge, deep-well injection, evaporation ponds and land application. However, these brine disposal methods are unsustainable and restricted by high capital costs and non-universal application. Nowadays, brine treatment is considered one of the most promising alternatives to brine disposal, since treatment results in the reduction of environmental pollution, minimization of waste volume and production of freshwater with high recovery. This review article evaluates current practices in brine management, including disposal methods and treatment technologies. Based upon the side-by-side comparison of technologies, a brine treatment technology framework is introduced to outline the Zero Liquid Discharge (ZLD) approach through high freshwater recovery and wastewater volume minimization. Furthermore, an overview of brine characteristics and its sources, as well as its negative impact on the environment is discussed. Finally, the paper highlights future research areas for brine treatment technologies aiming to enhance the effectiveness and viability of desalination. © 2019 Elsevier B.V. All rights reserved.

Abbreviations: AEM, anion exchange membrane; AGMD, air gap membrane distillation; BC, brine concentrator; BCr, brine crystallizer; BW, brackish water; BWRO, brackish water reverse osmosis; CEM, cation exchange membrane; CF, concentration factor; CFRO, counterflow reverse osmosis; COMRO, cascading osmotically mediated reverse osmosis; DC, direct current; DCMD, direct contact membrane distillation; DT, disc tube; EC, eutectic concentration; ECP, external concentration polarization; ED, electrodialysis; EDM, electrodialysis metathesis; EDR, electrodialysis reversal; EFC, eutectic freeze crystallization; EP, eutectic point; ET, eutectic temperature; FO, forward osmosis; HPRO, high-pressure reverse osmosis; ICP, internal concentration polarization; MCr, membrane crystallization; MD, membrane distillation; MED, multi-effect distillation; MSF, multi-stage flash distillation; NF, nanofiltration; OARO, osmotically assisted reverse osmosis; PE, polyethylene; PP, polypropylene; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; RES, renewable energy sources; RO, reverse osmosis; SD, spray dryer; SEC, specific energy consumption; SGMD, sweeping gas membrane distillation; SW, seawater; SWRO, seawater reverse osmosis; TDS, total dissolved solids; VMD, vacuum membrane distillation; WAIV, wind-aided intensified evaporation; WWTP, wastewater treatment plant; ZLD, zero liquid discharge.

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Contents

1. Introduction

Water is unquestionably the source of life on our planet and the driving force of human progress. As the world's population is growing and the pollution of existing natural water resources is increasing, water scarcity has increased significantly in recent years. The world population is expected to increase from 7.7 billion in 2017 to 9.4–10.2 billion by 2050, with two-thirds of the population residing in cities. At the same time, it is estimated that $>50\%$ of the countries on our planet could address water stress or water shortage by 2025, while by 2050, as much as 75% of the world's population could address water scarcity [\(Liyanaarachchi et al., 2013;](#page-20-0) [UNESCO, 2017](#page-21-0)). Hence, the global scarcity of freshwater is a vital and serious humanitarian issue that has to be addressed. For this reason, most countries have been investigating alternatives to conventional water resources.

Desalination is perceived as a viable and feasible solution to address this worldwide problem. In the desalination, the feed water is separated into two streams, the product stream (freshwater) and the by-product stream (brine). At the end of 2017, there were 19,372 desalination plants worldwide with a total desalination capacity of roughly 99.8 mil-lion m³/day [\(IDA and GWI, 2017](#page-19-0)). Despite the fact that desalination produces freshwater, a crucial environmental issue is the brine coproduced from desalination processes [\(Sadhwani Alonso and Melián-](#page-21-0)[Martel, 2018\)](#page-21-0).

Brine is commonly disposed of in the environment with various methods, such as surface water discharge, sewer discharge, deep-well injection, evaporation ponds and land application [\(Mickley, 2018](#page-20-0)). Brine, except its high salinity, may contain dangerous pretreatment chemicals, organics and heavy metals. Numerous researchers investigated the negative environmental impact of brine disposal on the marine environment, groundwater and soil quality. Thus, potential environmental damage includes eutrophication, pH fluctuations, increase of heavy metals in marine environments, etc. ([Heck et al.,](#page-19-0) [2016;](#page-19-0) [Petersen et al., 2018;](#page-20-0) [Heck et al., 2018\)](#page-19-0).

Despite the fact that disposal methods have been widely used so far, the concern about a long-term impact on the environment and human health leads to the need for a different approach. To eliminate the demand for brine disposal, desalination brine can be treated using the Zero Liquid Discharge (ZLD) approach. ZLD effectively minimizes wastewater discharge and enables freshwater and salt to be recovered [\(Wenten et al., 2017\)](#page-22-0). ZLD can be achieved through various membrane-based and thermal-based technologies. Two technologies specifically developed for brine treatment, the brine concentrator and crystallizer, are currently being applied in full scale. To date, these technologies have very high capital and operating costs, so their adoption is limited ([Mansour et al., 2018\)](#page-20-0). Consequently, with the development of new emerging technologies and the enhancement of the existing commercial technologies, more effective ZLD systems can be available.

The main objective of this review is to analyze and evaluate the brine management practices, including disposal methods and treatment technologies. Initially, the characteristics of brine and its adverse environmental impacts are presented. Further, brine disposal methods and the need for a different beneficial approach are widely discussed. An analysis and a comparison of brine treatment technologies are

presented, while a brine treatment framework is introduced to achieve ZLD. Finally, future research areas for technology improvement and broader implementation of ZLD systems are presented.

2. Desalination brine and its environmental impacts

Brine, also known as concentrate or reject, is the highly concentrated saline water produced as a by-product in desalination processes. This liquid stream contains most of the dissolved solids of feed water in concentrated form, as well as some pretreatment chemicals (e.g., residual amounts of antiscalants, coagulants and flocculants) and microbial contaminants. Brine is a broad term used for the desalination by-product regardless of its salinity, however, this term is usually used for saline streams of >55,000 mg/L of total dissolved solids (TDS). In this approach, brine with a TDS concentration of >55,000 mg/L can be called 'high-TDS brine'. The quantity and quality of desalination brine depend on feed water quality, pretreatment, desalination process and water recovery rate ([Voutchkov, 2014;](#page-22-0) [Fatta-Kassinos et al., 2016](#page-19-0)).

2.1. Characteristics of brine

Brine quantity is a function of the desalination plant size and water recovery rate. Typically, water recovery rate (R) is expressed as the percentage (%) of the volume of freshwater produced (O_n) to the total volume of saline feed water (Q_f) ,

$$
R = \frac{Q_p}{Q_f} \cdot 100\% \tag{1}
$$

The water recovery rate of a desalination plant depends on the technology and salinity of the feed water. For example, seawater reverse osmosis (SWRO) plants usually have a water recovery rate of 40% to 55%, while brackish water reverse osmosis (BWRO) plants of 70% to 90% [\(Kim and Hong, 2018](#page-19-0); [Turek et al., 2017\)](#page-21-0). It is obvious that higher water recovery rates lead to smaller brine volumes with higher salinities and vice versa. However, as the water recovery rate increases, the concentration of dissolved solids in the brine stream may exceed the solubility of sparingly soluble salts, such as calcium carbonate $(CaCO₃)$, calcium sulfate (CaSO₄), barium sulfate (BaSO₄) and thus precipitation may occur. These precipitates, along with colloids, bacteria and organic matter, can foul membrane and system surfaces, decrease process performance and limit water recovery rate ([Mitrouli et al., 2016;](#page-20-0) [Warsinger et al., 2018](#page-22-0)). However, chemicals such as acids, scale inhibitors and disinfectants are added to the feed stream to reduce scaling and fouling and improve water recovery rate [\(Goh et al., 2018\)](#page-19-0).

The volume of brine produced by the desalination plant can be determined by the following equation,

$$
Q_b = Q_f - Q_p \tag{2}
$$

Brine quality depends on the feed's salinity, the salt rejection of the membranes (in the case of a membrane-based desalination plant) and the water recovery rate. The TDS of brine (TDS $_{\text{brine}}$) can be defined in terms of the feed and permeate TDS (TDS_{feed} and TDS_{permeate} , respectively) and the R:

$$
\text{TDS}_{\text{brine}} = \text{TDS}_{\text{feed}} \cdot \left(\frac{1}{1 - R}\right) + \frac{R \cdot \text{TDS}_{\text{permeate}}}{100 \cdot (1 - R)} \tag{3}
$$

By neglecting the TDS_{permeate} (usually \sim 1% in SWRO), the TDS_{brine} can be defined more simply as:

$$
\text{TDS}_{\text{brine}} = \text{TDS}_{\text{feed}} \cdot \left(\frac{1}{1 - R}\right) \tag{4}
$$

The concentration factor (CF) is then defined as:

$$
CF = \frac{Q_f}{Q_f - Q_p} = \frac{1}{1 - R}
$$
\n⁽⁵⁾

The concentration factor for SWRO plants is typically from 1.5 to 2 while for BWRO it is from 2.5 to 10 [\(Gude, 2016\)](#page-19-0). Overall, the correlation between water recovery rate and concentration factor is illustrated in [Fig. 1](#page-3-0). This figure shows that as water recovery rate approaches 100%, there is a sharp increase in the concentration factor. Meanwhile, the ratio of the brine volume to saline feed water volume is decreasing linearly. [Table 1](#page-3-0) presents the characteristics of brine obtained from different desalination plants. As shown in [Table 1,](#page-3-0) differences in the ion composition of the brine streams are observed. This was likely due to the variation in the feed water, chemicals and different operational conditions of the treatment processes used. Furthermore, it is noteworthy that brine from seawater (SW) desalination plants contains large amounts of Na⁺ and Cl[−], with other ions such as Ca^{2+} , Mg²⁺ and $SO₄²$, with small variances depending on the regional characteristics of the SW and plant recovery. On the contrary, brine from brackish water (BW) desalination plants has very different ion composition depending on the origin of the feed water, the concentration of salts and plant recovery.

2.2. Environmental impacts

Desalination brine has always been considered the by-product/ waste of the desalination process. Various research studies [\(Heck](#page-19-0) [et al., 2016;](#page-19-0) [Lattemann and Höpner, 2008](#page-20-0); [Petersen et al., 2018;](#page-20-0) [Missimer and Maliva, 2018](#page-20-0); [Frank et al., 2017](#page-19-0); [Benaissa et al., 2017;](#page-18-0) [Belatoui et al., 2017\)](#page-18-0) assessed the potential environmental impacts of brine disposal on the marine environment, groundwater and soil. The main environmental concerns associated with brine disposal are: increased salinity of receiving water bodies and soil, regional impacts of high-TDS brine on marine benthic communities near the discharge point, esthetic problems, disposal of pretreatment and membrane cleaning chemicals, disposal of corrosion metals such as copper (Cu), ferrous (Fe), nickel (Ni), molybdenum (Mo) and chromium (Cr).

Brine can be harmful to the environment due to its salinity, temperature and chemical substances. Both brine salinity and temperature depend on the production process. The brine salinity is 1.6–2 times higher than the seawater salinity (35 g/L). Regarding the temperature, the brine produced by membrane-based technologies is at ambient seawater temperature (22 °C), whereas the brine produced by thermal-based technologies is 1.37–1.82 times higher than 22 °C ([Cambridge et al.,](#page-18-0) [2017;](#page-18-0) [Missimer and Maliva, 2018\)](#page-20-0). As presented in [Table 2,](#page-4-0) different types of chemicals are used in the desalination processes for pretreatment operations.

Brine from only a single desalination plant would not adversely affect the marine environment, but brine from multiple plants operating in the same area for a long period of time could have adverse impacts on the marine environment. Numerous studies [\(Matsumoto and](#page-20-0) [Martin, 2008](#page-20-0); [Gacia et al., 2006](#page-19-0); [Cooley et al., 2013;](#page-18-0) [Brika et al., 2015;](#page-18-0) [de-la-Ossa-Carretero et al., 2016](#page-18-0); [Al-Shammari and Ali, 2018\)](#page-18-0) have shown that even a slight increase in salinity can be harmful to marine life as it disrupts the osmotic balance of marine species with their environment. This disruption leads to cell dehydration, a decrease in turgor pressure and may lead to the extinction of species in the long term [\(Einav et al., 2003](#page-18-0); [Belkin et al., 2017\)](#page-18-0). In the study by [Jenkins et al.](#page-19-0) [\(2012\),](#page-19-0) it was found that some marine species could be harmed by a change in salinity of only 2–3 parts per thousand, whereas other species are more tolerant to salinity changes. More recently, [Petersen et al.](#page-20-0) [\(2018\)](#page-20-0) observed that increased salinity (10% above ambient) significantly negatively altered the physiology and visual appearance of the coral. At the same time, the increased salinity combined with the

Fig. 1. Concentration factor (CF) as a function of water recovery rate (R).

addition of polyphosphate-based antiscalants had a greater influence on all coral species tested.

However, there have been examples, where ocean outfalls have been dimensioned appropriately in areas with abundant currents (e.g., Australia) and thus no negligible impacts have been observed on the marine flora and fauna species ([Sydney Water, 2005](#page-21-0); [Chevron](#page-18-0) [Australia, 2015\)](#page-18-0). Moreover, recent studies have suggested that the long-term impact of brine disposal in outfall areas could be mitigated by using multiport diffusers [\(Del-Pilar-Ruso et al., 2015;](#page-18-0) [Portillo et al.,](#page-21-0) [2012\)](#page-21-0).

Brine with a higher temperature (e.g., 30–40 °C) than ambient seawater temperature may have several harmful effects on marine life as the toxicity of metals and chemicals increases with temperature [\(Uddin, 2014;](#page-21-0) [Li et al., 2013\)](#page-20-0). Furthermore, various heavy metals, such as Cu and Ni, may become part of the brine stream when the Cu-Ni alloys used in heat exchangers begin to corrode during the desalination process. In a recent study, [Alshahri \(2016\)](#page-17-0) examined the heavy metal concentrations in the brine disposal area of desalination plants in the Arabian Gulf (also called 'Persian Gulf'). Results indicated that the Cu, Fe and Cr concentrations in sand and sediments are significantly higher than the concentrations in the shale due to anthropogenic pollution. Similarly, a research study on coastal sediments in the Al-Khafji region (Arabian Gulf) revealed that high levels of Cu in the northern coastline

Table 1

may have been caused by the brine disposal from the desalination plant along the coast ([Alharbi et al., 2017](#page-17-0)). Furthermore, soil deterioration and groundwater pollution are a major concern when brine is disposed of into unlined evaporation ponds ([Mohamed et al., 2005](#page-20-0); [Bhandary et al., 2018](#page-18-0)). The soil structure may deteriorate because of the high salinity of brine, as Ca^{2+} is replenished by Na⁺ in the exchangeable ion complex ([Heck et al., 2016;](#page-19-0) [Maliva and Missimer, 2012\)](#page-20-0).

3. Current brine disposal methods

Considering that desalination processes produce significant amounts of brine, different methods of brine disposal have been developed by the desalination industry. These methods include surface water discharge, sewer discharge, deep-well injection, evaporation ponds and land application. However, none of the previously listed disposal methods can be widely applied to any type and size of the desalination project. The choice of the most suitable brine disposal method depends on numerous factors. These factors are quantity, quality and composition of the brine; the geographical location of the disposal site; availability of receiving site; the permissibility of the option; public acceptance; capital and operating costs and the capacity of the facility for future expansion ([National Research Council, 2008;](#page-20-0) [Mickley, 2018](#page-20-0)). As far as cost is concerned, brine disposal cost varies from 5% to 33% of the total cost of

Table 2

Chemicals commonly used in desalination plants [\(Cooley et al., 2013;](#page-18-0) [Voutchkov, 2017](#page-22-0); [Azerrad et al., 2019\)](#page-18-0).

the processes and depends on the characteristics and volume of the brine, the level of pretreatment, means of disposal and the nature of the disposal environment [\(Eslamian, 2016](#page-19-0)). Fig. 2 illustrates the application of the different disposal methods in the United States and Australia ([Hoang et al., 2009](#page-19-0); [Mickley, 2018\)](#page-20-0).

3.1. Surface water discharge

Surface Water Discharge is a brine disposal method that includes the direct discharge of brine into oceans, rivers, bays, lakes and other open water bodies. The brine is transferred to the disposal site where it is discharged via an outfall structure into the receiving water body. This method is adopted by the majority of SW desalination plants $(>90\%)$ of global SW plants). In contrast, inland BW desalination plants are more limited as inland water bodies are usually of high quality and thus can be used as water sources. To this respect, disposal is only feasible if the composition of the brine is suitable for harmonization with the receiving water body ([Younos, 2005;](#page-22-0) [Ziolkowska, 2014](#page-22-0)).

As mentioned before, brine can be harmful to the marine environment either because of its higher than usual salinity or because of the presence of pollutants that would not exist differently in the receiving water body. With appropriate measures, however, brine disposal in surface water could remain a viable method for SW desalination plants [\(Shrivastava and Adams, 2018](#page-21-0)). For example, before discharge, the brine can be diluted with regular SW or municipal wastewater to decrease the salinity level ([Arafat, 2017](#page-18-0)). Research has found that there is an insignificant adverse impact by decreasing concentrations if dilution and rapid mixing are cautiously used

[\(Lattemann and Höpner, 2008](#page-20-0)). The cost of this disposal method ranges from US\$0.05/ m^3 to US\$0.30/ m^3 of brine rejected [\(Ziolkowska](#page-22-0) [and Reyes, 2016;](#page-22-0) [Arafat, 2017\)](#page-18-0).

3.2. Sewer discharge

Sewer Discharge is a brine disposal method that includes the discharge of brine into the nearby wastewater collection system. This method is broadly adopted by small-scale BW desalination plants due to the potential negative impact of the brine's high TDS content on the receiving wastewater treatment plant (WWTP) [\(Chang, 2015\)](#page-18-0). Generally, high salinity hinders the biological treatment process in a WWTP as the TDS concentration of the influent exceeds 3000 mg/L ([Valipour](#page-21-0) [et al., 2014](#page-21-0)). Considering that the SW brine TDS level can be higher than 55,000 mg/L, the WWTP capacity has to be at least 20 times higher than the daily volume of brine discharge to sustain the plant's influent TDS concentration lower than 3000 mg/L. Moreover, if the salinity of the final wastewater effluent becomes too high, environmental and regulatory issues may arise during final disposal. Besides, a basic pretreatment, such as pH neutralization or any other requirements can be imposed because brine may contain heavy metal traces. This ensures the infrastructure and treatment process as well as the quality of the final wastewater effluent ([Hobbs et al., 2016](#page-19-0)). Consequently, disposal in a sanitary sewer is mainly used by BW desalination plants and is rarely applied for SW desalination purposes. The cost of this disposal ranges from US\$0.32/ $m³$ to US\$0.66/ $m³$ of brine rejected ([Ziolkowska](#page-22-0) [and Reyes, 2016](#page-22-0); [Arafat, 2017\)](#page-18-0).

Fig. 2. Most common brine disposal methods in the United States and Australia.

3.3. Deep-well injection

Deep-Well Injection is a brine disposal method that includes the injection of brine into a defined deep underground aquifer, adequately isolated from water aquifers above it. This method is commonly used by BW desalination plants of all sizes. The brine is injected into a well that consists of many layers of casing and grouting. Then, porous rocks are used to contain the brine, while clay and other impermeable rock formations are used to hinder the water aquifers pollution ([Thomas](#page-21-0) [and Benson, 2015;](#page-21-0) [Maliva et al., 2011](#page-20-0); [Pertiwi, 2015](#page-20-0)). The depth of these wells normally varies between 500 m and 1500 m, depending on the site's geological conditions. Meanwhile, the receiving aquifer must be able to receive the brine produced over the life of the plant (25–30 years) [\(Gálvez et al., 2010;](#page-19-0) [Olabarria, 2015\)](#page-20-0).

The main environmental concern for deep-well injection is the potential pollution of nearby water aquifers that could be used be used as a source of drinking water [\(American Water Works Association,](#page-18-0) [2011\)](#page-18-0). Before constructing an injection well, detailed hydrogeological studies, drill testing holes, environmental overviews and pilot tests must be performed ([Mickley, 2018\)](#page-20-0). The capital cost of deep-well injection is higher than the two previous disposal methods. Therefore, this brine disposal method is usually considered in the absence of another viable alternative. The cost of this disposal method ranges from US $$0.54/m³$ to US\$2.65/m³ of brine rejected [\(Ziolkowska and Reyes,](#page-22-0) [2016;](#page-22-0) [Arafat, 2017](#page-18-0)).

3.4. Evaporation ponds

Evaporation ponds are a brine disposal method that includes shallow, lined earthen basins in which brine slowly evaporates via direct solar energy. Once the freshwater has evaporated, the minerals in the brine are precipitated into salt crystals, which are periodically harvested and disposed of off-site. Evaporation ponds have been broadly adopted for brine disposal in many dry and semi-dry areas due to the source of solar energy ([Rodríguez et al., 2012](#page-21-0)).

This method has to be accurately designed and operated to reduce environmental concerns regarding groundwater pollution. Generally, environmental regulations oblige the evaporation ponds to be constructed with impervious lining to protect underlying aquifers. If the brine has high levels of trace metals, a double-lined pond must be constructed. Furthermore, if the ponds are not lined or the point liner is corrupted, a part of the brine may percolate to the water aquifer underneath the pond and decay its water quality [\(Roychoudhury and](#page-21-0) [Petersen, 2014](#page-21-0)). The choice of this method depends on various factors including climate conditions, availability and cost of land, water quality of the underlying groundwater aquifers. The cost of this disposal method ranges from US\$3.28/ $m³$ to US\$10.04/ $m³$ of brine rejected, making it the most expensive method ([Ziolkowska and Reyes, 2016](#page-22-0); [Arafat, 2017\)](#page-18-0).

3.5. Land application

Land application is a brine disposal method that includes spray irrigation of brine on salt-tolerant plants and grasses (e.g., grasses used in parks, lawns and golf courses). This disposal method is mainly used for low volumes of BW brine and its full-scale application is restricted by climatic conditions, seasonal demand as well as the availability of suitable land and groundwater conditions [\(Ladewig and Asquith,](#page-20-0) [2011\)](#page-20-0). Since each plant has a different salinity tolerance, the quantity of brine that can be used depends on the plant species, soil and brine characteristics. Nearly all plants can tolerate TDS concentrations of b500 mg/L. However, only high-salinity tolerant plants (called 'halophytes') can be irrigated with a brine with TDS higher than 2000 mg/L [\(Panta et al., 2016\)](#page-20-0).

Irrigation may have a negative impact on the groundwater aquifer below the irrigated area. The salinity of the shallow groundwater aquifers is usually less than the salinity of the brine and therefore the surface runoff and ground percolation of the brine can increase the aquifer salinity. Exceptions, however, are the shallow saline coastal aquifers or deep confined aquifers which are isolated from direct or indirect interaction with the brine. The choice of this method depends on various factors including climate, availability and cost of land, percolation rate, irrigation demands, water quality of the underlying groundwater aquifers, salinity tolerance of irrigated plants and the ability of the land application system to comply with regulatory requirements and groundwater quality standards. The cost of this disposal method ranges from US\$0.74/ $m³$ to US\$1.95/ $m³$ of brine rejected [\(Ziolkowska and](#page-22-0) [Reyes, 2016;](#page-22-0) [Arafat, 2017\)](#page-18-0).

3.6. Evaluation and comparison of brine disposal methods

[Table 3](#page-6-0) provides an overview of the disposal methods for desalination brine management and outlines their application areas and key advantages/disadvantages. Each method differs in complexity and costs. Surface water discharge is convenient for handling large brine volumes with low capital/operating costs and energy demands. It is both the cheapest and most widely adopted disposal method ([Fig. 2](#page-4-0)). However, this method may disturb the marine environment and result in an increase in the salinity of semi-closed seas such as the Mediterranean and the Red Sea ([Williams and Follows, 2011](#page-22-0)). To comply with regional environmental regulations and minimize environmental hazards, marine outfalls must be designed to dilute the brine as efficiently as possible. It has been reported that a dilution factor of 40-fold could be sufficient to protect 99% of marine species ([Falkenberg and Styan,](#page-19-0) [2015\)](#page-19-0). In contrast to semi-closed seas, in regions with abundant currents such as in Australia, appropriately dimensioned ocean outfalls can have a negligible environmental impact ([Chevron Australia, 2015\)](#page-18-0). If WWTP exists near the desalination plant, then sewer discharge could be an attractive option as it also has low capital and operating costs. Nevertheless, brine substances may hinder the biological processes of the WWTP when large volumes of brine are disposed of. It is noteworthy that costs for both surface water and sewer discharge significantly depend on the location of the plant. For example, the disposal cost for a plant next to shore is much lower than the cost for a plant several hundred meters away, as in the second case, longer pipelines or/ and pumping units are required.

Although most desalination plants are located near sea shores, a significant number of plants are located in the inland to desalinate brackish water ([Gude, 2018](#page-19-0)). For these inland plants, deep-well injection and evaporation ponds could be suitable options. Deep-well injection is a relatively cost-effective method for both brine disposal and hazardous waste disposal [\(Knape, 2005](#page-20-0); [Shammas and Wang, 2009](#page-21-0)). However, this method is not very favorable in highly seismic areas such as Greece due to the risk of groundwater pollution ([Burton et al., 2003](#page-18-0)). Thus, detailed site-specific studies must be performed to minimize the risk of well integrity failure, resulting in high implementation complexity. Evaporation pond is the most expensive disposal method as its treatment capacity is proportional to its footprint area. Moreover, it is only effective in areas with dry climate and high evaporation rates such as UAE, Oman, etc. ([Rodríguez et al., 2012;](#page-21-0) [Ladewig and Asquith,](#page-20-0) [2011\)](#page-20-0). Last but not least, land application can achieve beneficial disposal of brine through irrigation on salt-tolerant plants and grasses. However, this method is practiced exclusively for low brine volumes as its treatment capacity is proportional to its footprint area as in the evaporation ponds.

4. Brine treatment and zero liquid discharge (ZLD) approach

Increasing public awareness of the adverse impacts of desalination brine on the environment has contributed to the adaptation of stricter regulations for brine disposal that may restrict several conventional disposal methods (surface water discharge, sewer discharge, deep-well

Table 3

An overview of current desalination brine disposal methods.

injection, evaporation ponds and land application) in the coming years [\(Roberts et al., 2012](#page-21-0); [Abualtayef et al., 2016\)](#page-17-0). These urgent demands motivate engineers to develop a desalination system that can potentially improve water recovery to the highest level by reducing the brine (to the lowest level) with the least environmental damage. Hence, these demands can be fulfilled by employing a treatment system known as Zero Liquid Discharge (ZLD). As its name indicates, ZLD can be described as a combination of desalination technologies aimed at producing high-quality freshwater with the complete elimination of liquid waste from the plant [\(Alnouri et al., 2017](#page-17-0); [Barrington and Ho, 2014;](#page-18-0) [Bazargan, 2018\)](#page-18-0).

The freshwater produced from ZLD is highly pure (achieving 95–99% water recovery) and can be utilized for various purposes such as drinking water, irrigation, process cooling water, etc. At the same time, the compressed solid waste can either be disposed of in an ecofriendly way to the local environment or transported for further processing to be used as a useful material [\(Xiong and Wei, 2017;](#page-22-0) [Lux](#page-20-0) [Research, 2017](#page-20-0)). There are generally different variations in the design, arrangement and operation of ZLD systems and therefore each system is unique. Therefore, having a uniform ZLD system for all desalination plants is not feasible.

However, a typical ZLD system consists of three stages. These stages are (i) preconcentration, (ii) evaporation and (iii) crystallization. In the first stage, water recovery and minimization of the brine's volume are achieved through membrane-based technologies. This stage is crucial for the system as it significantly reduces the size of the next two stages that are very expensive. In the next two stages, water recovery, minimization of the brine's volume and production of a solid product are achieved mainly through thermal-based technologies.

Thus, the technologies used in brine treatment/ZLD systems can be classified into two categories: membrane-based and thermal-based technologies. Membrane-based technologies are described in Section 5, while thermal-based technologies are described in [Section 6.](#page-11-0) The design of a ZLD system depends on numerous factors such as the composition of the feed brine, the purity demand of freshwater and the final concentration of the concentrated brine needed for either safe disposal or other beneficial applications. As a result, some or even most of the treatment technologies (Sections 5 and 6) may be included in a ZLD system [\(Tufa et al., 2015](#page-21-0); [Cui et al., 2017](#page-18-0)).

5. Membrane-based technologies for brine treatment

5.1. Reverse osmosis and high-pressure reverse osmosis

The most commonly used membrane-based technology for desalting saline water is the pressure-driven reverse osmosis (RO). In the RO, hydraulic pressure is applied to the compartment of higher salt concentration, forcing water molecules to move through a semipermeable membrane in the compartment of lower salt concentration. The applied pressure gradient has to overcome the difference in osmotic pressure between the feed brine (Π_f) and the permeate liquid (Π_p). The result is that the solute (concentrated brine) is retained on the pressurized side of the membrane while the pure solvent (freshwater) is allowed to cross on the other side [\(Paul, 1972](#page-20-0); [Nagy, 2019\)](#page-20-0). A typical schematic diagram of RO is presented in Fig. 3(a).

Despite its commercial success, the salinity constraints of conventional RO make the technology unpromising for high-TDS brine treatment. As shown in Fig. 3(b), the osmotic pressure of a saline solution, such as sodium chloride (NaCl), is directly proportional to its concentration.

The osmotic pressure (Π) of the saline solution was calculated by van't Hoff's equation:

$$
\Pi = \nu_i \cdot R \cdot T \cdot C_i \tag{6}
$$

where Π is the osmotic pressure in bar, R is the gas constant $[R = 8.3145]$ $\cdot 10^{-5}$ m³ \cdot bar/(K \cdot mol)], T is the absolute temperature (K), v_i is the number of different dissociated ions and C_i is the concentration of com-ponent i (mol/m³) [\(Atkins et al., 2018\)](#page-18-0). Specifically, Fig. 3(b) reveals that the osmotic pressure of NaCl ranges from 59 bar to 211 bar for salinities of 70,000 mg/L to 250,000 mg/L, respectively. The current conventional membranes and modules can be used for pressures of up to 82 bar and TDS feed concentrations of up to approximately 70,000 mg/L, making them suitable for BWRO and SWRO. However, for high-TDS feed brine of up to 70,000 mg/L, water recovery in conventional RO is only up to 50%. [Aines et al. \(2011\)](#page-17-0) pointed out that conventional RO technologies can be implemented to a feed brine of up to 85,000 mg/L TDS with only 10% water recovery. Except for the practical pressure limits of RO membranes and modules, their performance under high pressure could lead to higher energy demand for separation, along with a high risk of scaling deposition and fouling due to the high level of hardness in brine. Overall, these limitations result in the feed salinity of conventional RO technologies being limited to about 55,000–70,000 mg/L TDS ([Alspach, 2014](#page-18-0)).

However, specialized membranes and modules can handle pressures above 82 bar, enabling the application of high-pressure RO (HPRO), defined as RO operating above 82 bar, for the treatment of brine with >70,000 mg/L TDS ([Davenport et al., 2018\)](#page-18-0). Today, there are only a few commercially available membranes that can handle pressures above 82 bar. Most remarkable is the Disc Tube (DT) module system developed by Pall Corporation for the treatment of landfill leachate ([Renou et al., 2008\)](#page-21-0). However, despite the variety of commercially available DT module configurations (82–150 bar), the average freshwater production per module is extremely low $(3 \text{ m}^3/\text{day})$ ([Pall](#page-20-0) [Corporation, 2019\)](#page-20-0). Moreover, Dow Chemical Company has recently started manufacturing advanced HPRO membranes that can handle pressures of up to 120 bar [\(The Dow Chemical Co., 2017](#page-21-0)). However, the water recovery observed so far has also been extremely low (<8%) [\(The Dow Chemical Co., 2016](#page-21-0)). Saltworks Technologies Inc. has recently developed HPRO membranes (maximum operating pressure ~124 bar) that can concentrate the RO brine to a concentration of up to 130,000 mg/L TDS and thus reduce the initial RO brine volume by half. However, scaling compounds may prevent achieving maximum water recovery and thereby pretreatment is required ([Saltworks](#page-21-0)

Fig. 3. (a) A typical schematic diagram of RO (b) Osmotic pressure calculations for NaCl at 25 °C. For simplification reasons, it is assumed that feed brine solution contains only pure NaCl (c) A typical schematic diagram of FO (d) A typical schematic diagram of OARO.

[Technologies Inc., 2019\)](#page-21-0). The specific energy consumption (SEC), in kWh per $m³$ of freshwater produced, of RO technology is 2–6 kWh/m³, whereas of HPRO technology it is 3–9 kWh/m³ [\(Schantz et al., 2018](#page-21-0); [Miller et al., 2015](#page-20-0)). The cost of RO is approximately US\$0.75/m³, while for HPRO it is approximately US\$0.79/m³ [\(Valladares Linares et al., 2016](#page-21-0); [Schantz et al., 2018\)](#page-21-0).

5.2. Forward osmosis

Forward Osmosis (FO) is a membrane-based technology that, unlike RO/HPRO, uses osmotic pressure gradients rather than hydraulic pressure [\(Ahmed et al., 2019](#page-17-0)). In the FO, a solution of remarkably high concentration (referred to as the 'draw solution') is used to produce an osmotic pressure gradient across a semipermeable membrane, resulting in the transport of water molecules from the less concentrated feed brine solution to the highly concentrated draw solution. Hence, freshwater and draw solution are separated, with the second being recycled to the FO module [\(Amjad et al., 2018](#page-18-0); [Abdullah et al., 2019](#page-17-0); [Tang and Ng,](#page-21-0) [2008](#page-21-0)). A typical schematic diagram of FO is illustrated in Fig. $3(c)$.

Compared to RO/HPRO, FO without draw solution recovery (also called 'regeneration') is more energy efficient since no external pressure is required. Although early studies indicated that FO membranes were low-fouling, recent studies working at commercially reasonable flows (e.g., 15–20 $L/m^2 \cdot h$) revealed that fouling is also an issue in the FO [\(Bell et al., 2017\)](#page-18-0). Draw solution has a principal role in establishing osmotic pressure gradients and therefore the FO technology is affected by the concentration of draw solution [\(Johnson et al., 2018](#page-19-0)). An ideal draw solution should be inexpensive, commercially available, provide high water flux, have low fouling potential, low reverse solute diffusion, low or no toxicity to microorganisms and ease of recovery/regeneration [\(Zhao et al., 2016\)](#page-22-0). Several draw solutions, including organic solutes [\(Cui and Chung, 2018;](#page-18-0) [Kim et al., 2016;](#page-19-0) [Yu et al., 2017\)](#page-22-0), inorganic salts [\(Nguyen et al., 2015;](#page-20-0) [Roy et al., 2016](#page-21-0); [Ahmed et al., 2018](#page-17-0)), nanoparticle-based [\(Na et al., 2014;](#page-20-0) [Guo et al., 2014](#page-19-0); [Zhou et al.,](#page-22-0) [2015a](#page-22-0)), volatile solutes ([Stone et al., 2013](#page-21-0)) and their corresponding recovery methods (thermal separation, membrane separation, precipitation and combined processes) have been investigated and described in research studies [\(Giagnorio et al., 2019](#page-19-0)). Based on the current findings, each draw solution has built-in advantages/disadvantages and therefore no particular draw solution can be considered 'ideal'. Except for the unavailability of efficient and universal draw solutions, the disadvantages of the FO technology are the absence of enhanced and stable specifically-designed membranes, the energy demand for the draw solution recovery step, reverse salt flux, as well as internal concentration polarization (ICP) and external concentration polarization (ECP) in FO membranes [\(Gao et al., 2014;](#page-19-0) [Johnson et al., 2018\)](#page-19-0).

Regarding the above issues, recent research studies have focused on the modification of existing membranes and the fabrication of novel membranes. Specifically, membrane modification is commonly performed through the surface coating on the active membrane layer (mostly thin-film composite membrane) to improve antifouling and increase surface hydrophilicity, resulting in reduced ICP and higher water flux. Surface modification materials, such as polydopamine and nanoparticle-decorated graphene oxide nanosheets (AgNP-GO) have recently been used and promising results have been shown ([Guo](#page-19-0) [et al., 2018](#page-19-0); [Soroush et al., 2016\)](#page-21-0). In addition, novel FO membranes such as membranes with sulfonated carbon nanotubes incorporated into the active layer or membranes fabricated via interfacial polymerization with graphene quantum dots (GQDs) incorporated are promising for the future ([Li et al., 2018](#page-20-0); [Xu et al., 2018\)](#page-22-0).

[McGinnis et al. \(2013\)](#page-20-0) selected $NH₃/CO₂$ as the draw solution with a thin-film composite FO membrane for the treatment of feed brine solution (73,000 \pm 4200 mg/L TDS). It was observed that the water recovery was 64 ± 2.2 % and the TDS concentration of the obtained concentrated brine was 180,000 \pm 19,000 mg/L. Despite that this draw solution produces good fluxes, the reverse solute diffusion of ammonia is an issue contaminating the feed stream [\(Li et al., 2015](#page-20-0); [Seker et al., 2017;](#page-21-0) [Shaffer et al., 2015\)](#page-21-0). In another study, [Eusebio et al. \(2016\)](#page-19-0) used four NaCl draw solutions (50, 75, 100 and 200 g/L, respectively) to optimize the operating conditions of a FO system treating RO brine (41 g/L TDS). It was noted that the 100 g/L draw solution was the most appropriate for the FO system as an optimized permeate flux and reverse solute flux of 3.46 L/m² \cdot h and 0.24 mol/m² \cdot h respectively were achieved. More recently, [Liden et al. \(2019\)](#page-20-0) investigated the feasibility of using FO with thin-film composite hollow fiber membranes to treat brine solutions with TDS levels varying from 16,000 mg/L to 210,000 mg/L. They observed that FO can be used effectively in the treatment of high-TDS brine.

Currently, only a few FO units that are suitable for high-TDS brine are commercially available. FO membranes designed for 65,000 mg/L TDS feed brine are available from [Fluid Technology Solutions Inc. \(2019\).](#page-19-0) Furthermore, Oasys Water Inc. has developed a pilot-scale thermalbased hybrid FO system for high-TDS brine (N70,000 mg/L TDS). The test results indicated that this FO system shows 60% water recovery and good freshwater quality ([Eyvaz et al., 2018\)](#page-19-0). Compared to RO/ HPRO, the SEC of FO without draw solution recovery is much lower $(0.1 - 0.85 \text{ kWh/m}^3)$, however, including the draw regeneration step, the SEC can be higher (up to 13 $kWh/m³$) ([McGinnis et al., 2013;](#page-20-0) [Kolliopoulos et al., 2018\)](#page-20-0). The cost of this treatment technology is approximately US\$0.63/ $m³$ of freshwater produced [\(Valladares Linares](#page-21-0) [et al., 2016](#page-21-0)).

5.3. Osmotically assisted reverse osmosis

Recent developments in the RO field resulted in a new technology called 'osmotically assisted reverse osmosis' (OARO). OARO is a pressure-driven membrane-based technology that integrates the principles of RO and FO ([Bartholomew et al., 2017](#page-18-0)). Similar approaches to OARO are the CounterFlow Reverse Osmosis (CFRO) by MIT Boston (Lienhard group) and the Cascading Osmotically Mediated Reverse Osmosis (COMRO) by Columbia University (Yip group). Both use the same core OARO technology, but arrange their modules or stages into different configurations ([Bouma and Lienhard, 2018](#page-18-0); [Chen and Yip, 2018](#page-18-0)). Similar to the RO, OARO applies hydraulic pressure to transport water molecules across a semipermeable membrane, but in this case, a lower osmotic pressure sweep solution on the membrane's permeate side is added to decrease the difference in osmotic pressure. This modification thus increases the water flux and a number of consecutive stages are used to increase the inlet TDS concentration limit from which freshwater can be recovered. A typical OARO system includes a series of OARO stages and the final stage of RO, as shown in [Fig. 3](#page-7-0)(d) [\(Bartholomew](#page-18-0) [et al., 2018](#page-18-0)). Furthermore, no highly pressure-resistant materials are required for pipes and modules and therefore cost savings in equipment can be anticipated ([Peters and Hankins, 2019](#page-20-0)). A disadvantage that exists in both FO and OARO is that OARO is not a process of direct desalination as it is a process of dilution through stages organized in series. [Bartholomew et al. \(2017\)](#page-18-0) reported that the OARO process can treat a brine solution of 100,000–140,000 mg/L TDS, resulting in a water recovery of 35–50%. In addition, the SEC of this technology ranged from 6 $kWh/m³$ to 19 kWh/m³. More recently, five different OARO arrangements to desalinate brine were investigated by [Peters and Hankins](#page-20-0) [\(2019\)](#page-20-0). Specifically, they noted that the maximum water recovery was 44% and the average SEC was 6.37 kWh/m³ for a feed brine solution of 70,000 mg/L TDS. Commercially, a multi-stage OARO system developed by Hyrec successfully concentrated SWRO brine at a final TDS con-centration of 250,000 mg/L with an average SEC of 5.8 kWh/m³ ([WDR](#page-22-0), [2018\)](#page-22-0). Due to the immaturity of OARO, both the SEC $(6-19 \text{ kWh/m}^3)$ and the treatment cost (US\$2.4/ $m³$) are higher than in the previous osmosis-related technologies; however, these values are expected to become much lower as this young technology advances in the coming years ([Bartholomew et al., 2018;](#page-18-0) WDR[, 2018\)](#page-22-0).

5.4. Membrane distillation

Membrane Distillation (MD) is a thermal-driven membrane-based technology. It is based on a vapor pressure gradient that can be produced by the temperature differential across the hydrophobic microporous membrane. The hydrophobic nature of the membrane prevents liquid molecules from moving through the pores while allowing vapor molecules to pass through. Thus, separation is achieved by enabling the recovery of a high-purity freshwater and a high rejection rate over 99% ([Jönsson et al., 1985](#page-19-0); [Ashoor et al., 2016\)](#page-18-0). The MD units can be categorized into four main configurations: (i) direct contact MD (DCMD), (ii) air gap MD (AGMD), (iii) sweeping gas MD (SGMD) and (iv) vacuum MD (VMD). Among these configurations, DCMD is most common for brine treatment applications ([Eykens et al., 2016;](#page-19-0) [Ali et al., 2015a\)](#page-17-0). In the DCMD, the feed brine solution is heated before reaching the membrane. On the one side of the membrane, the heated brine flows and the vapor can pass through the open pores of the membrane. Subsequently, the vapor is recovered as a cold distillate (freshwater) via condensation on the other side of the membrane, whereas the concentrated brine is retained by the hydrophobic membrane [\(Park et al.,](#page-20-0) [2019;](#page-20-0) [Karam et al., 2017;](#page-19-0) [Wang and Chung, 2015\)](#page-22-0). A typical schematic diagram of DCMD is illustrated in Fig. 4(a).

MD can treat extremely high-TDS brine (up to 350,000 mg/L TDS) as there are no theoretical restrictions on the salinity of the feed brine [\(Tun](#page-21-0) [and Groth, 2011](#page-21-0)). An advantage of MD over conventional distillation technologies is its lower operating temperature (40–80 °C) allowing the use of low-grade or waste heat streams ([Abdallah et al., 2015](#page-17-0); [Abdelkader et al., 2018](#page-17-0)). Similar to the FO, low permeate flux and unavailability of enhanced membrane fabrications are significant issues. Other issues with MD include pore wetting, flux reductions due to concentration polarization and poor thermal efficiency [\(Fortunato et al.,](#page-19-0) [2018;](#page-19-0) [Ali et al., 2015a\)](#page-17-0).

So far, MD technology relies on hydrophobic polymeric membranes, with polypropylene (PP) [\(Gryta, 2013](#page-19-0)), polyethylene (PE) ([Zuo et al.,](#page-22-0) [2016\)](#page-22-0), polytetrafluoroethylene (PTFE) ([Liu et al., 2018\)](#page-20-0) and poly(vinylidene fluoride) (PVDF) [\(Abdel-Karim et al., 2019\)](#page-17-0) being the most commonly investigated polymeric membranes. Recently, chemically modified ceramic membranes have great potential in MD configurations as they have high mechanical strength, thermal resistance and improved lifetime [\(Hubadillah et al., 2018;](#page-19-0) [Yang et al.,](#page-22-0) [2017\)](#page-22-0). In this effort, [Kujawa et al. \(2017\)](#page-20-0) grafted various hydrophobic coupling agents to aluminium oxide (Al_2O_3) and titanium dioxide $(TiO₂)$ ceramic membranes for desalination by AGMD. The results indicated that membranes had a NaCl retention coefficient higher than 98%, as well as a good permeate flux. In addition, omniphobic membranes have recently been examined and applied in MD to overcome the barrier of wetting, with satisfactory results to date ([Chen et al., 2018](#page-18-0); [Deng et al., 2018\)](#page-18-0). Another study, led by [Xiao et al. \(2019\)](#page-22-0), developed for the first time a patterned superhydrophobic PVDF membrane with porous micropillars through the micro-molding phase separation technique. In this approach, the superhydrophobic membrane had outstanding anti-scaling properties in the treatment of a saturated NaCl solution (250,000 mg/L) in DCMD.

[Yan et al. \(2017\)](#page-22-0) used a DCMD unit with PVDF membranes to treat artificial RO brine. The recovery obtained from the DCMD was higher than 70%, while the permeate conductivity was lower than 11 μS/cm. However, significant scaling occurs as CF goes beyond 3.3, resulting in severe pore wetting and reduced thermal efficiency. In an effort to improve the DCMD performance, [Sanmartino et al. \(2017\)](#page-21-0) used different chemical pretreatments (NaOH, Na₂CO₃ and BaCl₂) and different PTFE membrane pore sizes (329 and 553 nm) to treat RO brine (55 \pm 2.5 g/L). The results indicated that the most effective options (up to 377 g/L TDS concentrated brine) were to use the membrane with the larger pores size and chemical pretreatment with $BaCl₂$. However, BaCl₂ pretreatment is expensive and also not recommended due to the toxic residual barium. [Swaminathan and Lienhard \(2018\)](#page-21-0) investigated the treatment of a 70 g/L NaCl feed brine using an MD process with different recirculation strategies (batch, semi-batch, continuous and multi-stage). They remarked that the batch operation was the most effective, achieving a water recovery of 72.1%. In a study conducted by [Bindels et al. \(2018\)](#page-18-0) a semi-batch AGMD system from Aquastill was used to treat brine (44 g/L TDS). The brine concentration was increased to 107 g/L TDS, resulting in a water recovery of approximately 58.8%. Due to the utilization of thermal energy in the MD, both the SEC (39-67 kWh/m³) and the treatment cost (US\$1.17/m³ of freshwater produced) in MD are higher than in the most osmosis-related

Fig. 4. (a) A typical schematic diagram of DCMD (b) A typical schematic diagram of ED (c) A typical schematic diagram of EDR (d) A typical schematic diagram of EDM.

technologies [\(Lokare et al., 2018](#page-20-0); [Jantaporn et al., 2017;](#page-19-0) [Kesieme et al.,](#page-19-0) [2013](#page-19-0)).

5.5. Membrane crystallization

Membrane crystallization (MCr) is an extension of the MD that offers the option not only to obtain freshwater, but also to obtain valuable solid crystal salts at the same time [\(Quist-Jensen et al., 2015](#page-21-0)). In the MCr, the feed solution containing a non-volatile solution that is likely to be crystallized is in contact with a hydrophobic microporous membrane, while on the other side the membrane is in contact with the distillate [\(Drioli et al., 2012\)](#page-18-0). Thus, the vapor pressure gradient between the two parts leads to the evaporation of the volatile compounds (including water), transport across the membrane and condensation on the distillate side. This occurs until supersaturation is reached and nucleation of crystals is induced. Because of this behavior, the MCr system presents well-controlled nucleation and growth kinetics, as well as higher crystallization rates (Di Profi[o et al., 2017](#page-18-0); [Curcio and Di Pro](#page-18-0)fio, [2019](#page-18-0)).

Even though MCr inherits all of the advantages in MD, very few studies in the present literature have investigated the MCr. [Ali et al. \(2015b\)](#page-17-0) conducted experiments (both lab-scale and semi-pilot scale) for freshwater and salt recovery using a high-saline feed solution (248,000 mg/L TDS) with PP and PVDF hollow fiber membranes. The observed water recovery was 37% and 16.4 kg of NaCl crystals (>99.9% purity) were recovered from 1 $m³$ of feed solution. [Quist-Jensen et al.](#page-21-0) [\(2017\)](#page-21-0) pointed out that both MD and MCr can treat industrial wastewater with high Na_2SO_4 content, as well as that both technologies are more appropriate for direct treatment of unfiltered wastewater than wastewater pretreated by nanofiltration (NF). Both the SEC (39–73 kWh/m³) and the treatment cost (US\$1.24/m³ of freshwater produced) in MCr are slightly higher than in MD ([Ali et al., 2015b;](#page-17-0) [Curcio and Di Pro](#page-18-0)fio, 2019; [Ruiz Salmón and Luis, 2018;](#page-21-0) [Lokare et al.,](#page-20-0) [2018](#page-20-0)).

5.6. Electrodialysis and electrodialysis reversal

Electrodialysis (ED) and Electrodialysis Reversal (EDR) are voltagedriven membrane-based technologies that have been commercially successful in BW desalination. As illustrated in [Fig. 4\(](#page-9-0)b), ED is based on the selective transport of ions in solutions and uses an applied electrical voltage gradient to drive cations and anions in opposite directions through semipermeable membranes. A conventional ED stack contains a series of alternating cation exchange membranes (CEM) and anion exchange membranes (AEM) between a cathode and an anode. Cations are moved toward the negatively charged cathode, while anions are moved toward the positively charged anode. Thus, freshwater and concentrated brine solutions are separated ([Sonin and Probstein, 1968;](#page-21-0) [Tado et al., 2016](#page-21-0)). The EDR has the same electrochemical principles as the ED, except that a reversal of DC voltage is performed in the EDR (3–4 times per hour) to reverse ion transport and minimize scaling/ fouling [\(Asraf-Snir et al., 2018](#page-18-0); [Qureshi and Zubair, 2016](#page-21-0)). A typical schematic diagram of EDR is presented in [Fig. 4](#page-9-0)(c).

[Jiang et al. \(2014\)](#page-19-0) used a semi-batch three-stage ED system with different commercial membranes to recover freshwater and salt from artificial RO brine (107 g/L TDS). Results indicated that the feed brine could be concentrated up to 271.3 g/L TDS with a water recovery of 67.78%. The purity of the freshwater produced, however, was extremely low (2.7 g/L TDS), equivalent to brackish water. On the contrary, results from the treatment of NaCl brine (195 g/L) in a 10-stage ED system showed that high-purity freshwater can be produced (0.24 g/L TDS) [\(McGovern et al., 2014a\)](#page-20-0). Furthermore, they suggested that a hybrid ED-RO system could also treat high-TDS brine [\(McGovern et al.,](#page-20-0) [2014b](#page-20-0)). In another study, [Reig et al. \(2014\)](#page-21-0) used an ED pilot plant to treat SWRO brine (70,000 mg/L TDS) under full-scale conditions. The brine was successfully concentrated to 245,000 mg/L TDS, while it was reported that less concentrated brine was obtained at higher inlet temperatures, but higher production flows and lower energy consumption were achieved. Many researchers reported successfully operating three-stage ED systems for brine treatment, as [Yan et al. \(2018\)](#page-22-0) concentrated brine from 3.5 g/L to 20.6 g/L TDS and [Zhang et al. \(2017\)](#page-22-0) concentrated SWRO brine (45,000 mg/L TDS) with 82% water recovery. However, both researchers noticed that the third stage was more energy intensive than the previous two stages.

Unlike silica, organic matter along with high SO_4^{2-} can foul the membranes and may therefore require pretreatment [\(Asraf-Snir et al., 2016;](#page-18-0) [Mikhaylin and Bazinet, 2016](#page-20-0)). In this effort, [He et al. \(2013\)](#page-19-0) assessed pretreatment techniques for EDR during the treatment of RO brine and obtained an overall water recovery of roughly 96%. In a recent study, [Zhao et al. \(2019\)](#page-22-0) investigated the feasibility of a lab-scale EDR system for water recovery from RO brine and volume minimization of the resulting concentrated brine. An 85% water recovery was attained and thus the volume of the RO brine was reduced by about 6.5 times. Commercially, an EDR system called the non-thermal brine concentrator 'NTBC' or 'Aquasel', developed by GE, treated BWRO brine and achieved an overall water recovery of 99% [\(General Electric Company,](#page-19-0) [2013\)](#page-19-0). In addition, Saltworks Technologies Inc. has designed a variety of EDR systems capable of concentrating the RO brine at a concentration of up to 180,000 mg/L TDS. However, the TDS concentration of the feed brine has to be lower than 80,000 mg/L ([Saltworks Technologies Inc.,](#page-21-0) [2018](#page-21-0)). The SEC of this technology is 7-15 kWh/ $m³$, while the cost is ap-proximately US\$0.88/m³ of freshwater produced ([Yan et al., 2018;](#page-22-0) [Gonzalez et al., 2017;](#page-19-0) [Lopez et al., 2017\)](#page-20-0).

5.7. Electrodialysis metathesis

Due to the presence of sparingly soluble salts on the concentrate side of the ED/EDR membranes, water recovery is decreasing as multivalent ions such as SO_4^{2-} , HCO₃ and PO₄² are intended to scale with Mg²⁺ or $Ca²⁺$ when concentration rates increase. To minimize the scaling problems and improve the performance, an ED modification called 'electrodialysis metathesis' (EDM) was developed [\(Václavíková et al., 2017;](#page-21-0) [Alhéritière et al., 1998\)](#page-17-0). Except for water recovery, EDM can find application in the synthesis of inorganic salts ([Sharma et al., 2016](#page-21-0); [Jaroszek](#page-19-0) [et al., 2016](#page-19-0)) and ionic liquids ([Haerens et al., 2012](#page-19-0)).

In contrast to ED/EDR, there are four solution compartments (two for the concentrate, one for the diluate and one for the NaCl) and four EDM membranes (one standard CEM, one standard AEM, one monovalent selective CEM and one monovalent selective AEM). As soon as an electrical field is applied and the feed brine solution is transferred through the cell, the cations migrate through the cation exchange membrane and the anion migrate through the anion exchange. When NaCl is added to an adjacent cell, concentrated calcium chloride $(CaCl₂)$, magnesium chloride ($MgCl₂$), NaCl and sodium sulfate ($Na₂SO₄$) are formed [\(Camacho et al., 2017;](#page-18-0) [Han, 2018](#page-19-0)). A typical schematic diagram of EDM is illustrated in [Fig. 4](#page-9-0)(d).

A research team conducted experiments with a full-size ED stack treating BWRO brine from a desalination plant in Beverly Hills, California (USA). The results indicated that EDM successfully treated the BWRO brine with an energy consumption of roughly 0.6 kWh/m³ while recovering 95% of the BWRO brine as freshwater. However, the TDS concentration of the feed brine was very low (3200 mg/L) ([Bond](#page-18-0) [et al., 2015](#page-18-0)). In a recent study, a pilot-scale EDM system was investigated in Almeria (Spain) under the 'Zelda EU Life' project from 2015 to 2017. The results of this pilot study showed that EDM can concentrate BWRO brine from approximately 34,000 mg/L to 163,000 mg/L TDS. At the same time, the initial brine volume was reduced by five times while the SEC of the system was 5.1 kWh/m^3 ([Nunen and Panicot, 2018](#page-20-0)). More recently, [Chen et al. \(2019\)](#page-18-0) investigated the treatment of SWRO brine using EDM. It was observed that this technology is technically feasible to treat brine without scaling problems and the 170 g/L TDS is the final optimal concentration in the multi-batch EDM process. The cost of

this treatment technology is approximately US0.60/m³$ of freshwater produced [\(Bond et al., 2015](#page-18-0)).

6. Thermal-based technologies for brine treatment

6.1. Brine concentrator and crystallizer

Brine concentrators and brine crystallizers are the most commonly used brine treatment technologies in a ZLD system. Brine Concentrator (BC) is mainly designed as a vertical tube or falling film evaporator, but horizontal spray-film and plate-type evaporators can also be used. In the BC, the feed brine is supplied to a heat exchanger that elevates brine's temperature at the boiling point and then proceeds to a deaerator that removes non-condensable gases. Brine is then inserted into the evaporator sump and mixed with the recirculating slurry. Thus, the brine slurry is pumped to the top of the concentrator and flows into a bundle of heat transfer tubes. The flowing brine creates a thin film on the inner tube surface where water evaporation occurs. A portion of brine evaporates and moves through mist eliminators before inserting the vapor compressor, at which extra heat is added. Subsequently, vapor from the compressor passes to the outside of the evaporator tubes, where its heat is transferred to the colder brine that falls inside the tubes [\(Spellman, 2015\)](#page-21-0). As the compressed vapor releases heat, it condenses as freshwater and is pumped through the feed heat exchanger, where its heat is transferred to the incoming brine stream. A typical schematic diagram of BC is illustrated in Fig. 5(a). The SEC of this technology is 15.86-26 kWh/ $m³$ [\(Mickley, 2008;](#page-20-0) [SUEZ, 2017\)](#page-21-0).

The primary characteristic of the BC is the circulation of a slurry of $CaSO₄$ crystals that function as seeds. $CaSO₄$ and other scale-forming compounds, such as SrSO₄ and BaSO₄, preferably precipitate on circulating seed crystals rather than on heat transfer areas, preventing scaling. This system can effectively treat the majority of brine streams. For feed brine streams that are insufficient in CaSO₄, an amount of CaSO₄ is added as required to maintain the seeded slurry process, while for streams saturated in CaSO₄, BC operates without any external addition. The water recovery of a typical commercial BC system ranges from 90 to 99% and can be used for brine up to 250,000 mg/L TDS. Furthermore, this technology produces high-quality freshwater as its TDS concentration varies from 5 mg/L to 20 mg/L [\(Veolia Water Technologies, 2018\)](#page-22-0). Nevertheless, capital costs of BC are high due to the use of high-priced materials such as super duplex stainless steel and titanium, which are required to avoid corrosion by boiling brine ([Bostjancic and Ludlum,](#page-18-0) [2013;](#page-18-0) [Shaffer et al., 2013\)](#page-21-0).

Brine CRystallizers (BCr) are designed primarily as vertical cylindrical vessels with heat input from an available steam source or vapor compressor. The most common type of crystallizer for brine treatment is the forced circulation crystallizer. In this technology, the brine is initially fed into the crystallizer sump. The incoming brine then mixes with the circulating brine and is then pumped into a shell-and-tube heat exchanger where it is boiled by vapor from the vapor compressor. Since the tubes in the heat exchanger are submerged, the brine is under pressure and does not evaporate. The recirculating brine inserts at an angle into the crystallizer vapor body and swirls in a vortex. A small portion of the brine evaporates, forming crystals. A large amount of the brine is recirculated to the heater while a small stream of the recirculating loop is transferred to a centrifuge or filter to remove the remaining water from the crystals. The vapor is compressed in a vapor compressor and heats the recirculating brine as it condenses on the heat exchanger [\(Spellman, 2015](#page-21-0)). Finally, freshwater is collected and dry solid is produced. A typical schematic diagram of BCr is illustrated in Fig. 5(b). BCr can be applied directly to brine, but its capital cost and energy demand are much higher than for an equal capacity BC. The main advantage of BCr, however, is that it can be used for brine up to 300,000 mg/L TDS. The SEC of this technology is 52–70 kWh/m³ [\(Mickley, 2008;](#page-20-0) [Fluid Technology Solutions Inc., 2016\)](#page-19-0). The cost of BC is approximately US\$1.11/ $m³$ of freshwater produced, while for BCr it is approximately US\$1.22/ $m³$ ([Stanford et al., 2010\)](#page-21-0).

6.2. Multi-stage flash distillation and multi-effect distillation

Multi-Stage Flash distillation (MSF) and Multi-Effect Distillation (MED) are the leading thermal-based desalination technologies. Although these commercial technologies are originally developed for BW/SW desalination, they could be appropriate for brine treatment after material upgrades ([Mabrouk and Fath, 2015](#page-20-0)). In the MSF, the feed brine is preheated utilizing condensing vapors from the flash units and conclusively reaches a maximum temperature (up to 110–120 °C) with an external heat source, the brine heater. The hot feed brine is transferred through successively lower vapor pressure (and temperature) flash units in which a portion of the feed solution is evaporated and condensed in the feed preheat exchangers. Thus, the condensed water vapor is the freshwater whereas the concentrated brine is the liquid that exits from the final flash unit in the series

Fig. 5. Typical schematic diagrams of (a) BC (b) BCr (c) MSF (d) MED.

[\(Clelland and Stewart, 1966;](#page-18-0) [Khoshrou et al., 2017\)](#page-19-0). The MED technology is similar to the MSF, except that (i) vapor condensation occurs in heat exchange with the liquid in the subsequent distillation effect and (ii) the maximum temperature is up to $70-75$ °C ([Elsayed et al., 2018;](#page-18-0) [Al-Shammiri and Safar, 1999](#page-18-0)). Typical schematic diagrams of MSF and MED are illustrated in [Fig. 5\(](#page-11-0)c) and (d), respectively.

Although these technologies have been widely used in BW/SW desalination, their application in ZLD systems has not been reported in the literature. Currently, MSF and MED systems are made of common stainless steel grades (e.g., UNS S31600 and UNS S31603) that are suitable for BW/SW desalination, but not for high-TDS brine treatment due to corrosion problems from the high Cl[−] environment ([ISSF, 2010;](#page-19-0) [Deyab,](#page-18-0) [2019\)](#page-18-0). Construction materials such as super duplex stainless steel grades (e.g., UNS S32750 and UNS S32760), titanium, or high nickel alloys must therefore be used to achieve maximum corrosion resistance [\(Nada, 2010](#page-20-0); [Boillot and Peultier, 2014\)](#page-18-0). Recently, hyper-duplex stainless steel grades (e.g., UNS S32707 and UNS S33207) have been developed with even higher corrosion pitting resistance and strength among existing duplex stainless steel grades ([Chail and Kangas, 2016;](#page-18-0) [Ho et al., 2018\)](#page-19-0). The drawback of these materials is their cost, as they are expensive, in contrast to the conventional materials used so far. Meanwhile, these technologies require a high energy input. The SEC of MSF is 12.5–24 kWh/m³ and for MED it is 7.7–21 kWh/m³, respectively [\(Al-Karaghouli and Kazmerski, 2013](#page-17-0); [Ihm et al., 2016;](#page-19-0) [Filippini et al.,](#page-19-0) [2018\)](#page-19-0). Nonetheless, the main advantages of MSF/MED are the highquality freshwater produced $\left($ <10 mg/L TDS) and the minimum required pretreatment ([Chua and Rahimi, 2017\)](#page-18-0). The cost of MSF is approximately US\$1.40/m³, while for MED it is approximately US\$1.10/ $m³$ ([Kesieme et al., 2013](#page-19-0)).

6.3. Spray dryer

Spray Dryers (SD) are an alternative technology to crystallizers for the concentration of brine, by converting the brine into a dry powder of mixed solid salts ([Tillberg, 2014\)](#page-21-0). To date, spray drying has been widely used in the food (e.g., instant coffee, coffee whitener, baby foods), chemical and pharmaceutical industries [\(Petersen et al., 2017;](#page-20-0) [Al-Khattawi et al., 2017\)](#page-17-0). A typical SD system includes a feed brine tank, a vertical spray drying chamber and a dried brine separator (bag filter) to collect the dried solids, as presented in Fig. 6(a). In this technology, the concentrated slurry is diffused into the chamber by a centrifugal atomizer and at the same time, hot air is pulled into the chamber. The bag filter separates the dry powder from the hot air stream. Thus, the powder is collected, while air exits to the environment ([AIChE,](#page-17-0) [2010](#page-17-0)).

The competitive advantage of this technology over crystallizers is the ability to control certain standards of solid salts such as particlesize distribution, particle shape and bulk density [\(Spellman, 2015;](#page-21-0) [Mackey and Seacord, 2008\)](#page-20-0). There are currently several SDs available with water evaporation capability ranging from 0.5 kg/h to 70 kg/h [\(GEA Process Engineering, 2019](#page-19-0); [Kerone, 2018\)](#page-19-0). The SEC of this technol-ogy is 52–64 kWh/m³ ([Mackey and Seacord, 2008;](#page-20-0) [Nasr et al., 2013](#page-20-0)). The cost of this treatment technology is approximately US\$0.09/kg of solid produced ([Stanford et al., 2010\)](#page-21-0).

6.4. Eutectic freeze crystallization

Eutectic Freeze Crystallization (EFC) is an extension of the freeze crystallization technology that utilizes the different densities between the ice and the salt produced [\(Williams et al., 2015;](#page-22-0) [Van der Ham](#page-21-0) [et al., 1998\)](#page-21-0). The principle of the EFC is that each saline solution has a eutectic point (EP). As presented in Fig. 6(b), the EP is a particular point in the phase diagram of a salt-water mixture in which there is an equilibrium between ice, salt and a specific concentration of the solution. This specific concentration is called the 'eutectic concentration' (EC) and the equilibrium temperature is called the 'eutectic temperature' (ET). Specifically, EFC is operated at the EP, at which both ice and salt crystallize. The EP is different for different aqueous electrolyte solutions, e.g., for NaCl (−21.2 °C and 23.3 wt%); for KCl (−11.1 °C and 19.6 wt%); for MnSO₄ (-4.2 °C and 20.6 wt%); for CuSO₄ (-1.6 °C and 11.9 wt%); for MgCl₂ (-33.6 °C and 21.6 wt%); for CuCl₂ (-40 °C and 36 wt%) ([Enis](#page-19-0) [and Lieberman, 2019\)](#page-19-0). Thus, pure water and salt can be obtained concurrently from aqueous solutions by EFC at a very high water recovery [\(Hasan et al., 2017\)](#page-19-0). A typical schematic diagram of EFC is illustrated in Fig. $6(c)$.

Fig. 6. (a) A typical schematic diagram of SD (b) Phase diagram of a binary solid-liquid system at constant pressure (c) A typical schematic diagram of EFC (d) A typical schematic diagram of WAIV.

Table 4

An overview of desalination brine treatment technologies.

Table 4 (continued)

Technology	Ability to treat high-TDS brine	Maximum water recovery (%)	Advantages	Challenges	Technological maturity & SEC	Cost Impacts	References
Thermal-based BC and BCr	- Inlet TDS up to 250,000 mg/L (for BC) - Inlet TDS up to 300,000 mg/L (for BCr) - Solid product is filtered and dried - Salt contains impurities	Up to 99%	- Established technology specifically developed for the treatment of high-TDS brine - High-quality freshwater is produced (<20 mg/L TDS)	- High capital costs due to the expensive materials (stainless steel or titanium) required to avoid corrosion - Salt contains impurities, so improvement can be considered through brine pretreatment or specialized design - Energy intensive technology	Commercially available technology For BC: 15.86-26 kWh/m ³ For BCr: $52 - 70$ kWh/m ³	For BC: US \$1.11/m ³ of freshwater produced For BCr: US \$1.22/m ³ οf freshwater produced	(Mickley, 2008; Fluid Technology Solutions Inc., 2016; Stanford et al., 2010; Spellman, 2015; Shaffer et al., 2013)
MSF and MED	- Current systems are not designed for the treatment of brine - Partial treatment with corrosion-resistant materials is feasible for brine with 70,000 mg/L to 180,000 mg/L TDS	Up to 85-90%	- Technology is commercially available and can be further upgraded to treat high-TDS brine - High-quality freshwater is produced - Possibility of utilization low-grade thermal energy, including geothermal or waste heat, allowing to reduce operating costs and carbon footprint	- High capital costs, due to the expensive materials (stainless steel or titanium) required to avoid corrosion - Intensive pretreatment processes (softening, pH adjustment, ultrafiltration, ion exchange, etc.) to avoid scaling and fouling problems - Energy intensive technology	Commercially available technology For MSF: $12.5 - 24$ kWh/m^3 For MED: $7.7 - 21$ kWh/m^3	For MSF: US \$1.40/m ³ of freshwater produced For MED: US \$1.10/m ³ of freshwater produced	(Al-Karaghouli and Kazmerski, 2013; Ihm et al., 2016; Filippini et al., 2018; Kesieme et al., 2013; Deyab, 2019)
SD	- Inlet TDS up to 250,000 mg/L - Solid product is collected and dried - Salt contains impurities	No recovery	- Simple technology - Ability to achieve specific standards, such as particle-size distribution, particle shape and bulk density	- Highly unlikely to be economically viable on a large scale. - Recovery of freshwater from outlet gas would be difficult and expensive - Salt contains impurities so that improvement can be considered through pretreatment of the brine or specialized design	Commercially available technology $52 - 64$ kWh/m ³	US\$0.09/kg of solid produced	(Mackey and Seacord, 2008; Nasr et al., 2013; Stanford et al., 2010; Petersen et al., 2017; GEA Process Engineering, 2019)
EFC	- Inlet TDS up to 250,000 mg/L - Solid products are collected - Salt are high-pure (purity $>90\%)$	Up to 98% Theoretically can be up to 100%	-No addition of chemicals is required -Corrosion of materials is reduced due to the low operating temperature	- High capital costs - This technology hasn't been applied extensively in multicomponent brine solutions - Formation of an ice scale layer in the crystallizer surfaces	Emerging technology $43.8 - 68.5$ kWh/m ³	US \$1.42/m ³ of freshwater produced	(Randall et al., 2014; Pronk et al., 2008; Salvador Cob et al., 2014; Chivavava et al., 2014)
WAIV	- Inlet TDS up to 100,000 mg/L - Solid product is collected - Salt contains impurities	No recovery	- Simple technology - Compact and modular design - Higher evaporation rate than evaporation pond	Higher capital and operating costs than evaporation ponds	Emerging technology $0.3 - 1$ kWh/m ³	US \$1.37/m ³ οf freshwater evaporated	(Basile et al., 2018; Murray et al., 2015; Gilron et al., 2003; Macedonio et al., 2011)

Various researches about EFC have focused on the recovery of one salt from a simple binary or ternary system. Until today, EFC has been successfully applied to treat various binary aqueous solutions, such as $CuSO₄$ ([Van der Ham et al., 2004\)](#page-22-0), Mg $SO₄$ ([Genceli et al., 2005](#page-19-0)), Na2SO4 ([Lewis et al., 2010](#page-20-0); [Peters et al., 2016](#page-20-0); [Becheleni et al., 2017;](#page-18-0) [Leyland et al., 2019](#page-20-0)) and a KNO₃-HNO₃ ternary system ([Vaessen et al.,](#page-21-0) [2003](#page-21-0)).

Nevertheless, the ability to use EFC to separate multiple salts from multicomponent brine has not been fully investigated. A research conducted by [Randall et al. \(2011\)](#page-21-0) on RO brine using EFC resulted in a 97% water recovery as well as recovery of pure $Na₂SO₄$ (96.4% purity) and pure $CaSO_4$ (98% purity). Thus, the sequential removal of salts from a multicomponent mixture is apparently feasible as each salt crystallizes at its unique eutectic temperature. [Salvador Cob et al. \(2014\)](#page-21-0) studied the application of EFC to RO brine rich in HCO $_3^-$ and Na $^+.$ The application of EFC crystallizer to this solution resulted in the formation of ice and 5.8 wt% NaHCO₃ at -3.9 °C. Furthermore, it was observed the overall water recovery by the application of EFC to the RO brine was increased from 98.0% to 99.7%. In another study, [Chivavava et al. \(2014\)](#page-18-0) investigated the effects of residence time and supercooling on ice

formation in an EFC crystallizer with a $Na₂SO₄$ aqueous solution. It was observed that longer periods of residence (45 min instead of 20 min) increased the average crystal size while increasing supercooling resulted in a larger average ice equivalent diameter. In 2016, the implementation of a large-scale EFC in South Africa was reported. The facility was built at the Eskom Research and Innovation Centre in Rosherville and acts as a training platform and demonstration plant for treatment experiments [\(Eskom, 2016\)](#page-19-0). The SEC of this technology is 43.8–68.5 kWh/ $m³$ ([Pronk et al., 2008\)](#page-21-0). The cost of this treatment technology is approximately US\$1.42/ $m³$ of freshwater produced [\(Randall et al., 2014](#page-21-0)).

6.5. Wind-aided intensified eVaporation

Wind-Aided Intensified eVaporation (WAIV) is a thermal-based technology used for brine volume minimization. In this technology, vertical wetted packing towers use wind power to evaporate denselypacked wetted surfaces. Specifically, pressurized air is diffused via the distribution pipes and is vertically moved to the surface of the brine. Commonly, the evaporation surface consists of woven nettings, nonwoven geotextiles or volcanic tuff organized in trays ([Gilron et al.,](#page-19-0) [2003\)](#page-19-0). A typical schematic diagram of WAIV is presented in [Fig. 6\(](#page-12-0)d).

By using evaporation surfaces in large lateral arrays, maximum wind power is used because the air is not completely saturated with the vapor [\(Basile et al., 2018\)](#page-18-0). So far, prospects of WAIV as a salt recovery method have hardly been investigated. [Oren et al. \(2010\)](#page-20-0) investigated the treatment of RO-EDR brine. The results showed that the WAIV unit produced final brine with TDS higher than 300,000 mg/L and presented potential as a method for recovering mineral by-products such as magnesium salts. In another study, led by [Macedonio et al. \(2011\),](#page-20-0) a RO-MCr unit was combined with WAIV and overall water recovery of up to 88.9% was achieved. More recently, a full-scale demonstration in Roma (Queensland, Australia) showed that the evaporation performance of the WAIV unit was at least 10 times higher than that of the equivalent-size conventional evaporation pond ([Murray et al., 2015](#page-20-0)). Among all technologies, WAIV has the lowest SEC (up to 1 kWh/ $m³$) as exploits wind energy for the evaporation and requires only electric energy for the pumps [\(Basile et al., 2018](#page-18-0); [Murray et al., 2015](#page-20-0)). The cost of this treatment technology is approximately US\$1.37/ $m³$ of freshwater evaporated ([Gilron et al., 2018\)](#page-19-0)

7. Evaluation and comparison of desalination brine treatment technologies

An overview of desalination brine treatment technologies is presented in [Table 4](#page-13-0). The purpose of this side-by-side comparison is to evaluate the technologies based on their ability to effectively treat the desalination brine. Furthermore, a brine treatment technology framework is introduced in Fig. 7.

7.1. Energy consumption

The intensive energy consumption of ZLD systems is a significant problem that limits their further implementation as well as the advancement of membrane-based and thermal-based technologies [\(Barrington and Ho, 2014;](#page-18-0) [Wenten et al., 2017\)](#page-22-0). [Fig. 8](#page-16-0) illustrates a comparison of the SEC for (a) membrane-based and (b) thermal-based technologies at their inlet TDS concentration limit. Membrane-based technologies have lower SEC values compared to thermal-based as they do not require a phase change (from liquid to vapor). Thus, membrane-based technologies avoid energy losses associated with evaporation and condensation [\(Whitaker, 2013\)](#page-22-0). As shown in [Fig. 8a](#page-16-0), the SEC of membrane-based technologies ranges from 0.6 kWh/ $m³$ to 19 kWh/m³, except for MD and MCr. These technologies are the only thermal-driven membrane-based technologies and therefore have a much higher energy demand (39-73 kWh/m³). Regarding the

thermal-based technologies, two different subgroups can be identified in [Fig. 8b](#page-16-0): (i) technologies used in the evaporation stage (SEC: 7.7–26 kWh/ $m³$) and (ii) more energy intensive technologies used in the crystallization stage (SEC: $43.8-70$ kWh/m³). This significant increase in the energy demand is unavoidable as crystallizers treat feed brine solutions with much higher salinity and viscosity ([Leyland et al.,](#page-20-0) [2019;](#page-20-0) [Spellman, 2015\)](#page-21-0).

7.2. Overall performance

The water recovery and the cost of freshwater produced by the treatment technologies are summarized in [Fig. 9](#page-16-0). Although RO is the most widely used desalination technology, RO can hardly be used in brine treatment due to salinity constraints $($ <70,000 mg/L TDS) and low recovery $(<50%)$. Accordingly, RO is commonly used first to desalinate BW/SW and is then followed by more effective technologies in the ZLD systems [\(Mickley, 2008;](#page-20-0) [McGovern et al., 2014b;](#page-20-0) [Nayar et al.,](#page-20-0) [2019\)](#page-20-0). HPRO can treat 1.7 times more concentrated brine but has similarly limited performance to RO; however, new advanced membranesmodules appear promising to enhance HPRO ([Davenport et al., 2018](#page-18-0); [Shin et al., 2019\)](#page-21-0). OARO, together with its variants (CFRO and COMRO), is the most recent technology (the first study was published just only three years ago) that achieves better recovery $($ <72%) at higher feed salinities compared to RO/HPRO [\(Bartholomew et al., 2018\)](#page-18-0). However, it is currently the most expensive technology due to the incorporation of multiple FO/RO stages. Costs associated with OARO could be indirectly decreased as FO has made significant progress in recent years [\(Ang and Mohammad, 2019](#page-18-0)). Compared to the previous technologies, FO is more cost-effective and available for even higher salinities (up to 200,000 mg/L TDS). However, the absence of a universal draw solution and membrane issues are the main concerns that limit its adoption. Except for FO, MD/MCr are very promising since they significantly extend the feed TDS concentration to 350,000 mg/L; however, membrane issues limit also this technology. The electrical-driven technologies (ED/EDR/EDM) are less efficient than FO/MD/MCr but are suitable to treat brine with high silica content as silica is neutrally charged ([Tong et al., 2019](#page-21-0)). Among the three technologies, EDM is more promising since it removes troublesome salts from the brine of the main desalter and thus increases the recovery without the use of costly multiple ED/EDR stages [\(Cappelle et al., 2017](#page-18-0)).

BC and BCr, the commercial ZLD technologies, although they have excellent performance (<99% recovery), their capital & operating expenses are so high that other alternatives are being considered. For example, MSF/MED could be good alternatives due to their lower energy consumption. Nonetheless, the scaling risk in the heat exchangers is still high, even if pretreatment (e.g., chemical precipitation, ion-

Fig. 7. Brine treatment technology framework.

Fig. 8. (a) SEC comparison of membrane-based technologies at their inlet TDS concentration limit (b) SEC comparison of thermal-based technologies at their inlet TDS concentration limit.

exchange) is performed [\(Zhao et al., 2018](#page-22-0); [Vanoppen et al., 2016](#page-22-0)). SD differs from the other crystallization technologies as it is the only technology that can produce solid products with preferred quality standards. However, to use this benefit, the feed brine solution must contain specific ions e.g., Na⁺ and Cl[−] to produce pure NaCl salt crystals that could be sold (US\$30–50/t) and thus decrease the overall desalination cost ([Al Bazedi et al., 2013](#page-17-0); [Basile and Nunes, 2011\)](#page-18-0). In contrast to SD, EFC has not the prior feed composition limitation as it produces high-purity solid salts (>90% purity). Nevertheless, the capital costs for this technology are also high, and so far, the EFC research studies on multi-component solutions are very limited. WAIV is the simplest technology for the crystallization stage as it is an advanced alternative to conventional evaporation ponds, requiring both a lower footprint area and recurrent salt removal. As in the SD, there is no water recovery as brine evaporates in the open atmosphere.

7.3. Environmental impacts, challenges and future prospects

Although ZLD has the primary objective of maximizing freshwater recovery and minimizing waste, its implementation can lead to unintentional environmental impacts. The mixed solid salts produced cannot be reused, and if stored in evaporation ponds, produce odors and may harm wildlife or even pose a danger of leakage ([Water](#page-22-0) [Environment Research, 2012](#page-22-0)). Thus, to prevent potential contamination from the solid waste, impervious liners and consistent monitoring systems are required [\(Sridhar, 2018](#page-21-0)). Nowadays, a rapidly increasing approach is to produce multiple high-purity solid salts instead of a compact mixed solid salt for two purposes: (i) to eliminate the need and costs of solid waste disposal and (ii) to sell the high-purity salts and adopt a circular economy strategy. In this approach, salts such as NaCl, CaCO₃, Na₂SO₄ and CaCl₂ are of interest [\(Al Bazedi et al., 2013\)](#page-17-0). Consequently, various ZLD systems can be developed to recover both freshwater and high-purity solids salts in accordance with the characteristics of the feed brine solution [\(Sorour et al., 2014](#page-21-0); [Liu et al., 2016](#page-20-0); [Ji et al.,](#page-19-0) [2018](#page-19-0)).

As discussed previously, ZLD technologies consume large amounts of energy, contributing to significant emission of greenhouse gases (GHGs). To overcome this barrier, authors suggest incorporating lowgrade waste heat or renewable energy sources (RES), such as solar thermal energy, wind power or geothermal energy ([Zhou et al., 2015b;](#page-22-0) [Ghaffour et al., 2014\)](#page-19-0). Through this approach, GHGs associated with ZLD systems are expected to be reduced. According to the authors, future research should focus on enhancing various aspects of the technologies. For example, novel materials with advanced properties lowpriced and cost-effective materials, advanced system configurations could boost the sustainability of ZLD systems for brine treatment. Novel membranes (e.g., omniphobic, superhydrophobic, etc.) have recently shown great potential in this direction, as previously discussed [\(Chen et al., 2018;](#page-18-0) [Deng et al., 2018](#page-18-0); [Xiao et al., 2019](#page-22-0)). Furthermore, process simulations, techno-economic analyses and life-cycle assessments

Fig. 9. Water recovery and cost of freshwater produced from membrane-based and thermal-based technologies.

Fig. 10. (a) Challenges for brine treatment technologies in the ZLD systems (b) Present and future prospects for ZLD systems.

of GHGs are needed to evaluate the viability of treatment technologies in the different ZLD systems. Overall, the major challenges of desalination brine treatment technologies in ZLD systems are summarized in Fig. 10(a), while present and future prospects for ZLD systems are summarized in Fig. 10(b).

8. Conclusions

Brine management is becoming an important aspect of the water processing industry. Brine discharge into open water bodies, along with other disposal methods, is environmentally unsustainable and not always available. Meanwhile, environmental concerns and increased regulations are factors that have led to increasing demand for brine concentration. ZLD systems can be a viable alternative to disposal methods as their dual aim is to recover freshwater and solid salts, thus avoiding wastewater disposal in the environment. Besides water recycling, resource recovery may be an additional economic motivation for the development of ZLD technologies. Different membrane-based and thermal-based technologies can be used as so far there is no single treatment technology to achieve ZLD and therefore a technology combination is required.

Commercial desalination technologies RO, MSF and MED are not appropriate for brine treatment. Due to osmotic constraints, RO can handle feed solutions of only up to 70,000 mg/L TDS, whereas thermal-based MSF/MED are highly energy intensive and must be constructed from expensive anti-corrosion materials. The purpose-designed technologies, BC and BCr, are effective; however, their very high cost is the factor that has led to the need for alternatives. Several emerging technologies, including OARO, FO, MD/MCr, EFC, EDM, and WAIV show promise in high-TDS brine treatment. For example, some RO issues have been resolved by new variations on the standard RO technology, such as HPRO and OARO, but some other issues remain, such as recovery limited by membrane properties and scaling/fouling. Additionally, incorporating low-grade waste heat or RES into thermal-based ZLD technologies can contribute to lower energy costs and GHGs emissions. However, further studies are needed on a larger scale to assess the effectiveness and sustainability of these technologies. Thus, techno-economic studies and life-cycle assessments of GHGs of the various treatment technologies and their different combinations must therefore be carried out in the future.

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