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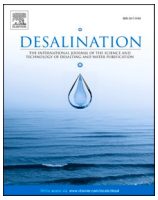

A comprehensive review of pre- and post-treatment approaches to achieve sustainable desalination for different water streams

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HIGHLIGHTS

- Overview of pretreatment technologies and scrutinize its potential role in the desalination industries.
- Potential environmental impact of the waste brines with reference to the zero liquid discharge and their management
- Pre and post treatment mapping to support desalination industries.
- Explore options in the potential reduction of the environmental damage via zero liquid discharges

Abbreviations: ABF, ammonium bifluoride; AC, absorption chiller; AGMD, air gap membrane distillation; BMED, bipolar membrane electrodialysis; BOD, biological oxygen demand; BWRO, brackish water reverse osmosis; CASTMF, conventional activated sludge with tertiary membrane filtration; COD, chemical oxygen demand; COMRO, cascading osmotically mediated reverse osmosis; CST, concentrated solar tower; D2EHPA, di-(2-ethlhexyl)phosphoric acid; DAF, dissolved air floatation; DCL, direct coal liquefaction; DCMD, direct contact membrane distillation; DLE, direct lithium extraction; ED, electrodialysis; EDR, electrodialysis reversal; EFC, eutectic freeze crystallisation; ETC, evacuated tube collectors; FBBR, fluidized bed bio-adsorber reactor; FD, freeze desalination; FM, freezing-melting; FO, forward osmosis; FPW, flowback produced water; GAC, granular activated carbon; GHG, greenhouse gas; GMF, granular media filtration; GOR, gained output ratio; HDH, humidification-dehumidification; HPRO, high-pressure reverse osmosis; ICL, indirect coal liquefaction; LCE, lithium carbonate equivalent; LCOW, levelised cost of water; LFR, linear Fresnel reflectors; MBC, membrane brine concentrator; MBR, membrane bio-reactor; MD, membrane distillation; MDC, membrane distillation crystallisation; MED, multi-effect distillation; MF, micro-filtration; MLD, minimal liquid discharge; MLSS, mixed liquor suspended solids; MLVSS, mixed liquor volatile suspended solids; MSF, multi-stage flash; MVC, mechanical vapour compression; MVR, mechanical vapour recompression; NF, nano-filtration; NG, natural gas; NTU, nephelometric turbidity unit; OARO, osmotically assisted reverse osmosis; OD, osmosis distillation; ORC, organic Rankine cycle; PAC, powdered activated carbon; PAN, polyacrylonitrile; PE, polyethylene; PECH, polyepichlorohydrin; PES, polyether sulphone; PFAS, per- and polyfluoroalkyl substances; POME, palm oil mill effluent; PP, polypropylene; PS, polysulphone; PTC, parabolic trough collectors; PTFE, polytetrafluoroethylene; PV, photovoltaic; PVP, polyvinylpyrrolidone; PV/T, photovoltaic/thermal panels; PVDF, polyvinylidene fluoride; RO, reverse osmosis; SAGD, steam assisted gravity drainage; SCW, supercritical water; SCWD, supercritical water desalination; SDI, silt density index; SDS, sodium dodecyl sulphate; SEC, specific energy consumption; SED, selectrodialysis; SGMD, sweeping gas membrane distillation; SGPW, shale gas produced water; SIC, specific investment cost; SMHS, submerged membrane hybrid system; SMR, small modular reactor; sPPO, sulphonated poly(2,6-dimethyl-1,4-phenylene oxide); SWRO, seawater reverse osmosis; TBT, top brine temperature; TDS, total dissolved solids; TEP, transparent exopolymer particles; TOC, total organic carbon; TSP, tri-sodium phosphate; TSS, total suspended solids; TVC, thermal vapour compression; UF, ultra-filtration; VCD, vapour compression distillation; VMD, vacuum membrane distillation; WAIV, wind-aided intensified evaporation; WGMD, water gap membrane distillation; WWTP, wastewater treatment plant; ZLD, zero liquid discharge.

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ABSTRACT

Desalination is an energy intensive process requiring adequate pre- and post- treatment. The novelty of this paper is that it jointly reviews the technologies for pre-treatment, desalination and post-treatment and bridges the gap between them while comparing the treatment methods needed depending on the type of feed water including seawater, brackish water, municipal and industrial wastewater. Those different streams show wide variability, sometimes containing organics, oil or scaling precursors which require adequate treatment. Nowadays, membrane pre-treatment methods have become promising alternatives to conventional pre-treatment techniques thanks to their flexibility. Hybrid desalination technologies have shown great potential in reducing energy consumption. Moreover, desalination plants produce large quantities of brines which require post-treatment to reduce environmental impacts. Current research on post-treatment is looking into recovering salts, metals and potable water from brines to achieve zero liquid discharge (ZLD). Thermal-based ZLD technologies are capable of extracting those resources while membrane-based ZLD methods are mostly limited to pre-concentration and water recovery due to fouling issues. Several studies have shown that ZLD systems can lower the cost of water and increase profitability if crystals and water are recovered and sold for additional revenue.

1. Introduction

Over 2 billion people live in regions affected by water stress with nearly 3.6 billion people experiencing water scarcity for at least one month per year. By 2050, this number is expected to increase to 4.8–5.7 billion people as a result of population growth and climate change [1]. Improving water management is crucial to minimise water scarcity and achieve sustainability. Seawater desalination is a widely recognised solution to water scarcity because seawater is effectively an unlimited resource. By 2019, there were at least 15,906 desalination plants in operation worldwide, of which 48 % were in the Middle East and North Africa. The global production from desalination plants is about 95 million m^3/day of freshwater and 142 million m^3/day of brines [2]. The different pre-treatment technologies are categorised as conventional and novel methods. Conventional methods usually involve filtration techniques and chemical dosing while novel methods include membranes. The most widespread desalination technologies are reverse osmosis (RO) and multi-stage flash (MSF) but other technologies such as multi-effect distillation (MED), membrane distillation (MD) and forward osmosis (FO) are gaining attention [2,3]. The management of brines is a major issue in desalination plants as traditional practices include brine discharge back to the sea which causes major environmental impacts on aquatic ecosystems [4]. ZLD processes aim at utilising brines to recover additional water as well as valuable salts which can be sold to various industries and including the construction sector. This approach is deemed to be sustainable by avoiding brine discharge and recovering valuable resources for additional revenue [5,6]. However, most of the ZLD technologies face several challenges and require further development for industrial applications. To our knowledge, no other paper has reviewed the link between the pre-treatment, desalination and post-treatment methods, nor their applications to different water streams, which is therefore the aim of this comprehensive review, which bridges the gap between those processes by considering the feed water quality to provide an overview of the current trends. Researchers are looking into sustainable and carbon neutral desalination using renewable energies like solar, geothermal or wind, and through the integration of ZLD which aims at the recovery of minerals to achieve a circular economy where brines are treated as a resource instead of waste.

2. Challenges of waste water streams

Desalination is commonly applied to seawater or brackish water because those are abundant and are often the only source of water in regions such as Middle Eastern and North African countries. But other water sources that are considered as waste can be used to recover water such as textile effluents, flue gas desulphurisation brine, produced water from oil and gas industries, dairy wastewater, municipal wastewater, and brines from desalination industries. Table 1 shows the average composition of the different water streams considered here. Recovering water from waste streams is sustainable because it produces valuable water that can be reused by the industries that produced them, or even agriculture and communities, which reduces their water consumption, while avoiding discharge into natural water bodies. The composition of those streams will define the selection of the appropriate pre-treatment method to avoid scaling and fouling issues. The presence of Mg, Ca, chlorine, oil, grease, dyes may prevent the use of certain pre-treatment methods, especially membrane technologies, and may require conventional pre-treatment.

3. Importance of pre-treatment technologies before desalination

An efficient pre-treatment system is the backbone of any desalination technology. Pre-treatment of the feed water is required to reduce turbidity and the concentration of microorganisms, colloids, dissolved organics and inorganics, TDS, silt density index (SDI), and any pollutant to acceptable levels for the subsequent process. The commercially available pre-treatment methods can be broadly categorised as conventional and membrane-based methods. Conventional processes include physical methods such as sedimentation and filtration; biological methods such as aeration and bio-reactors; chemical methods such as coagulation, flocculation and chlorination; and disinfection methods [17].

Pre-treatment depends on the composition of the water and the type of desalination system. Desalination processes are sensitive to various contaminants, notably, scaling precursors. In complex cases, pre-treatment construction may reach as much as 10–20 % of the total desalination plant capital cost. Typically, the pre-treatment must achieve SDI < 3–5, turbidity <0.2–0.5 NTU, zeta potential >−30 V, total organic carbon (TOC) < 2–3 ppm, soluble organic matter <1 ppm, oil and grease <0.1–0.5 ppm and bacterial count <106 CFU/mL. To avoid membrane fouling, it must achieve Fe^{2+} < 2 ppm, Fe^{3+} < 0.05 ppm, Mn^{2+} < 0.1 ppm and oxidised manganese forms <0.02 ppm. High turbidity above 50 NTU may lead to fouling and usually requires filtration and dissolved air floatation (DAF). TOC above 2–3 ppm can promote biofouling. Silica content >20 ppm can accelerate fouling, chlorine content >0.01 ppm can damage RO membranes and oil content >0.02 ppm can accelerate organic fouling. Finally, feed temperature < 12 °C increases energy use while above 35 °C facilitates mineral scaling and biofouling and operating above 45 °C can permanently damage RO membranes [18].

There are different types of fouling including scaling, particulate fouling, biofouling, and organic fouling. Scaling refers to the precipitation of inorganic salts. Scalants will normally precipitate when the ionic product exceeds its solubility product. The desalination process leads to the graduate concentration of ions in solution through water withdrawal resulting in increased ionic product and higher risk of precipitation.

Anti-scalants are commonly dosed to the feed water to keep the concentration below the scale limit. Water recovery is usually limited to a maximum brine concentration of 60,000–70,000 ppm TDS after which scaling occurs. This usually corresponds to 40 % water recovery [19,20].

Feed waters can be contaminated with suspended and colloidal particles such as clay. They can cause particulate fouling by deposition and agglomeration onto surfaces like membrane pores causing clogging. Their presence is monitored by the SDI (measure of the risk of colloidal and particle fouling), water turbidity, and particle counts. Usually, over 90 % of seawater particle foulants are larger than 1 μm. To prevent colloidal fouling, membrane manufacturers usually recommend a SDI < 4. Surface water after conventional pre-treatment has a SDI between 2 and 4 while that of aquifer water is usually below 1. Seawater and brackish water can have a SDI of up to 200 depending on the location [19,20].

Biofouling refers to the accumulation of microorganisms like bacteria or algae onto surfaces. The biofouling potential depends on many factors including concentration and speciation of the microorganisms, biodegradable compounds, composition of nutrients and temperatures. Over time, a thick biofouling cake forms leading to considerable permeate flow resistance, flux reduction, increased operating pressure, membrane telescoping and membrane damage. Biofouling is prevented by disinfection [19,20].

Feed water streams like surface waters, municipal and industrial wastewater normally contain dissolved organics like humic substances, oil or grease which can cause organic fouling which can be monitored by the TOC. Organic contaminants adsorb on surfaces and lead to a decline in permeability and flux. The presence of colloidal matter in addition to organics can lead to the formation of a thick foulant layer. The TOC of surface waters varies between 0.5 and 20 mg/L. Pre-treatment is necessary when exceeding 3 mg/L TOC or if the concentration of oil and grease is above 0.1 mg/L. Organic fouling is usually prevented by clarification or activated carbon [19,20].

A mapping of the different processes used in the desalination

Table 1
Average composition of the different water streams considered in this study [7–16].

Parameter	Seawater	Brackish water	Brine from seawater desalination	Brine from brackish water desalination	Textile effluents	Flue gas desulphurisation brine	Produced water from oil and gas industries	Dairy wastewater	Municipal wastewater
TDS (ppm)	15,000–45,000	1000–15,000	50,000–82,000	7500–22,000	1500–50,000	5000–50,000	5000–400,000	8000–120,000	600–4000
T (°C)	10–30	10–30	25–60	25–60	35–45				
pH	6.5–8.5	6.5–7.7	6.4–7.0	7.5–7.7	6–10	7	5.18–8.9	7.3–7.6	
COD (mg/L)					150–12,000	705–745		800–3200	740
BOD (mg/L)					80–6000			152–773	350
TSS (mg/L)					15–8000				450
Oil and grease (mg/L)					10–30				
Cl^- (mg/L)	16,476–27,098	670–2674	30,500–35,000	2933–5413	200–6000	5270–8820	36–238,534		188–600
NO_3^- (mg/L)	2.2–3.3	4.8–416.3	3–3.4	15.9–47.2	<5				7.85–13.5
PO_4^{3-} (mg/L)	<0.1				<10			66.5–190	
SO_4^{2-} (mg/L)	1325–3700	265–1329	3931–4602	756–2444	600–1000	493–111,020	<15,000	20.8–222.4	75.7–504
HCO_3^- (mg/L)	100–140	133–678	117–125	347–753				915–3776	
Na^+ (mg/L)	9290–15,850	498–1310	15,100–17,700	1170–3190	45–7000	191–2170	400–126,775	46–177	136–1213
Ca^{2+} (mg/L)	320–636	48–263	617–760	173–1180	5.65–2379	969–3389	4–52,920	68–288	53.5–212
K^+ (mg/L)	210–661	11–300	767–950	34.1–84.5	30–50			11.7–93.6	0.15–7.20
Mg^{2+} (mg/L)	742–2300	79–245	2150-2660	311–644	4.39–210	411–910			
Sr^{2+} (mg/L)	4.56–13	3.73–5.05	7.2–11.5	10.7–21.1					
SiO_2 (mg/L)	1–15.04	32.3–70	1.1–19.9	82.8–164.1	<10				
F^- (mg/L)	0.6–1.8	<11.1	0.9–2.3	0.1–1.6	<10	54–58			
Zn^{2+} (mg/L)	<0.5	<0.05	<0.5	0.05–0.07	<10		6.3–17.4		
Ni^{2+} (mg/L)					<10		2.7–9.5		
Mn^{2+} (mg/L)	<0.06	<0.5	<0.07	<0.05	<10		1.4–8.1		
Fe^{2+} (mg/L)	<0.27	<28.9	<0.37	0.05–0.08	<10		0.1–0.5	<10	
Cu^{2+} (mg/L)	<0.5	<0.05	<0.5	<0.05	<10		0.3–2.7		
Cr (mg/L)	<0.5	<0.26	<0.5	<0.12					
B (mg/L)		0.21			<10		5–95		
As (mg/L)		<0.005			<10		0.17–0.9		
Li^+ (mg/L)	0.17		0.29				4.6–572		

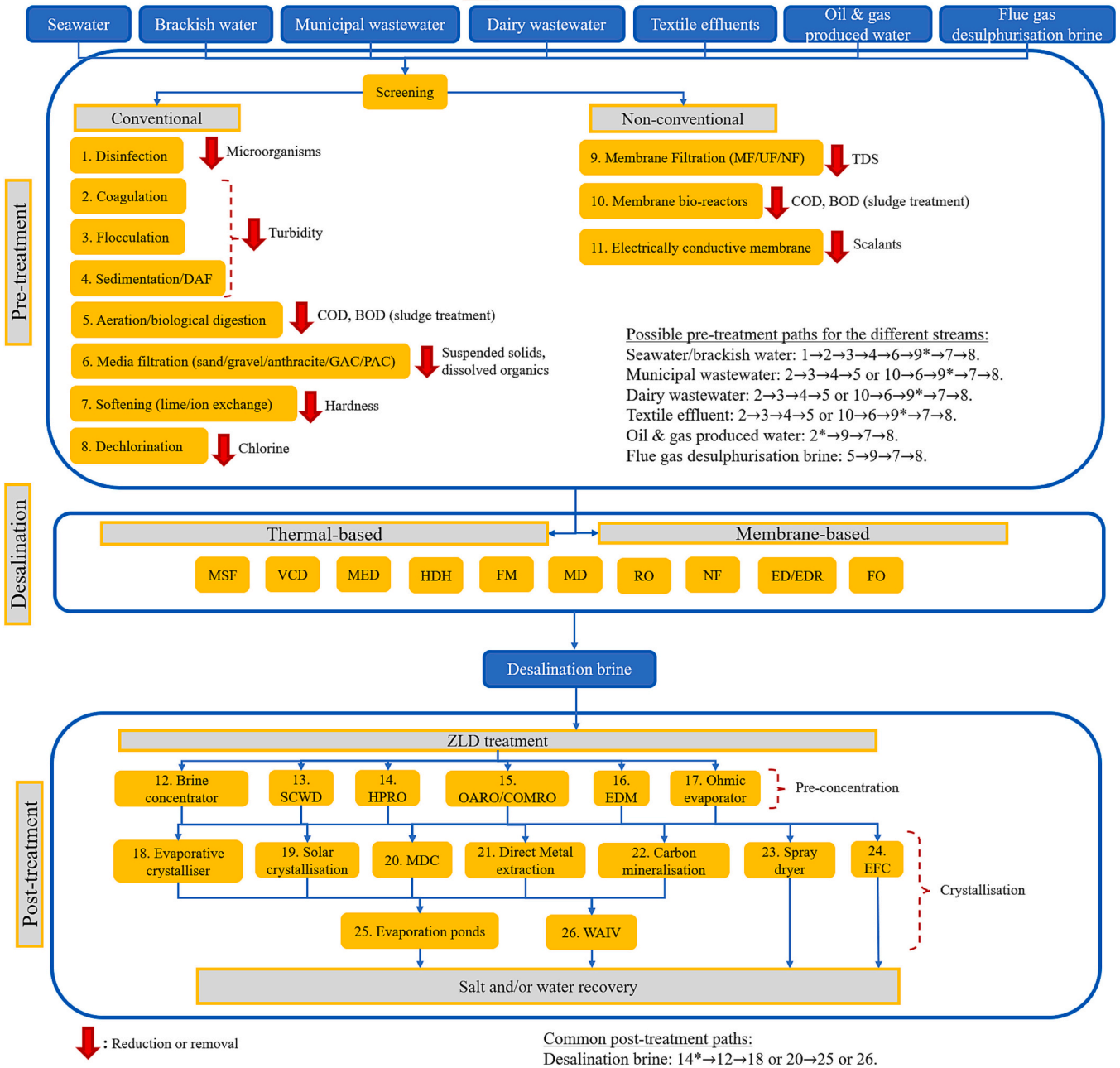

Fig. 1. Mapping overview of the different pre- and post-treatment paths for desalination for different streams. *Optional.

industry is presented in Fig. 1 to illustrate the different pre- and post-treatment options applied to the different water sources. There are different possible paths for each stream, especially with hybrid technologies, but the most common ones are reported to give an overview. Streams containing sludge, organic matter and high BOD and COD, like dairy wastewater, are usually pre-treated similarly to municipal wastewater using biological sludge treatment methods [21].

Conventional pre-treatment methods include disinfection, clarification and media filtration. Typically, clarification is used to reduce turbidity below 0.5–1 NTU with a target of 0.2 NTU for drinking water [1]. Filtration methods are used to reduce TDS concentration. Novel pre-treatment methods include membrane techniques using micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), electrically conductive membranes and membrane bio-reactors (MBR). Membrane systems are very sensitive to fouling/scaling and thus require adequate pre-treatment steps. This increases the life expectancy of membranes which are expensive to replace [22,23].

3.1. Removal of microorganisms

Disinfection is used to kill microorganisms (bacteria, viruses, algae) responsible for water-borne diseases and biofouling. Disinfection techniques are categorised as chemical, electrical, ultrasonic and UV light. Chemical agents are the most common and include ozone and chlorine species such as sodium hypochlorite, hypochlorite ions, chloramines, hypochlorous acid, and chlorine dioxide. However, ultrasound and UV light are gaining importance due to their superior effectiveness in killing bacteria and lack of the need for a dechlorination step [24].

Chlorination is one of the most widely used chemical disinfectants approaches. It produces hypochlorous and hydrochloric acids.

Hypochlorous acid partly dissociates and oxidizes the microorganisms, but it is more effective at low pH. Chlorine dioxide has also been widely researched due to its insignificant corrosive effects and high efficiency. Besides serving as a disinfectant, addition of chlorine helps coagulation and alleviates odour in water. Usually, intermittent chlorination is more effective than continuous chlorination as it promotes coagulation of colloid polymers while continuous chlorination adds to fouling [25].

Ozonation is a well-known technology for wastewater treatment because of the effective ability of O_3 to oxidize many organic contaminants. Its advantages include: (i) no increase in produced sludge; (ii) it takes only one step to remove colour and organic matter; (iii) it can be installed easily on site; (iv) it is less harmful than other oxidative processes; (v) the end products of ozone are generally nontoxic [26]. However, ozonation for water and wastewater treatment requires a significant amount of energy. Ozonation of seawater can improve calcium complexation leading to the conversion of dissolved organic matter into colloids [27].

In recent years, ultrasound has been gaining ground due to its effectiveness as a pre-treatment method to mitigate biofouling in RO membranes [28]. It is an effective alternative to chlorination and UV light for de-agglomerating bacterial clusters through acoustic cavitations which kill bacteria. The process may be combined with pressure (manosonication), temperature (thermosonication) or both (manothermosonication) to enhance its effectiveness and decrease the required energy consumption [25].

3.2. Chemical upcycling for turbidity improvements

Clarification refers to the use of coagulation, flocculation and sedimentation (Fig. 2) to remove colloids and suspended particles responsible for high turbidity. A coagulant is added to neutralise the negatively charged particles which can then be agglomerated into high-density flocs with the addition of a flocculant such as polyacrylamide [29]. Commonly used coagulants are ferric chloride, ferric sulphate and aluminium sulphate [30,31]. These coagulants are used because of their rapid neutralisation and low cost. In water, iron and aluminium ions start to form precipitates containing metal hydroxide which adsorb and tangle suspended particles, leading to an easier removal of particles [32–35]. Coagulation has been shown to be a successful method for improving the water quality not only in conventional pre-treatment technologies, but also in low pressure membrane pre-treatment technologies. Seawater obtained from open intake usually has a turbidity of above 30 NTU and therefore requires clarification [36]. Depending on the solubility of the coagulants, sulphuric acid may be added to maintain pH at 5.5–6 to optimize floc formation [37]. Coagulation occurs in a rapid-mixing tank to maximise collisions between the coagulant and the colloids while flocculation occurs in a slow-mixing tank to allow agglomeration of the flocs. Furthermore, coagulation can be used efficiently for arsenic removal with iron-based coagulants which were found to be better compared with the aluminium-based coagulants [38].

Electrocoagulation is another form of coagulation where water is passed over metallic electrodes to cause metallic coagulants to become charged and bond with the colloids and particulates (Fig. 3) [30,39,40]. Electrocoagulation has high potential for mitigating organic and biofouling by removing dissolved organic matter and microorganisms. The effect of electrocoagulation with aluminium electrodes to remove organic matter from seawater has been tested which showed that high current density and low pH effectively removed 70.8 % of dissolved organic matter by 70.8 % and 100 % of microorganisms [41]. Electrocoagulation has also been able to remove >99 % of TSS [42]. Coagulation is also effective in removing heavy metals such as manganese [43]. Electrocoagulation was also tested to pre-treat hydraulic fracturing produced water containing 23,254 ppm TDS [44]. In 2 min, the system was able to reduce TDS, TSS and TOC by 70 % which significantly reduced fouling in the subsequent FO unit. This system was also tested on hydraulic fracturing produced water containing 11,340 ppm TDS as a pre-treatment before a FO-MD unit to remove 78 % of TOC and 96 % of TSS [45].

Sedimentation aims at reducing turbidity below 2 NTU. It is typically used before granular media and membrane filters for feed waters with a daily average turbidity above 30 NTU or above 50 NTU for over 1 h. However, above 100 NTU, conventional sedimentation basins are often inadequate [19]. In this case, sedimentation basins are coupled with lamella plates which consist of slanted plates over which the flocs settle and sediment . Sedimentation effectiveness depends on the suspended particles' settling velocity, the volume/area of the tank, and the flow rate [35].

However, algal cells, oil, and grease have lower density than water and float at the surface which prevents their sedimentation. DAF is used in this case as an alternative to sedimentation and consists of injecting fine air bubbles into the tank to carry light particles and organic substances to the surface where they are skimmed off (Fig. 4) [30,46]. It can also be used to remove phosphorus [47]. It is effective at treating water containing algae blooms with turbidity at 30–50 NTU and high coloration [47–49]. DAF has demonstrated its ability to remove about 90–99 % of algal cells, compared to only 60–90 % by sedimentation [50]. DAF integrated with pre-sedimentation is an attractive method to control the specific raw water characteristics, especially during an unexpected increase in turbidity. DAF has rapidly gained importance as a RO pre-treatment with many full-scale operations reported [46]. A case study of a seawater RO (SWRO) plant in the Persian Gulf using DAF coupled with granular media filtration (GMF) showed good removal of turbidity [51].

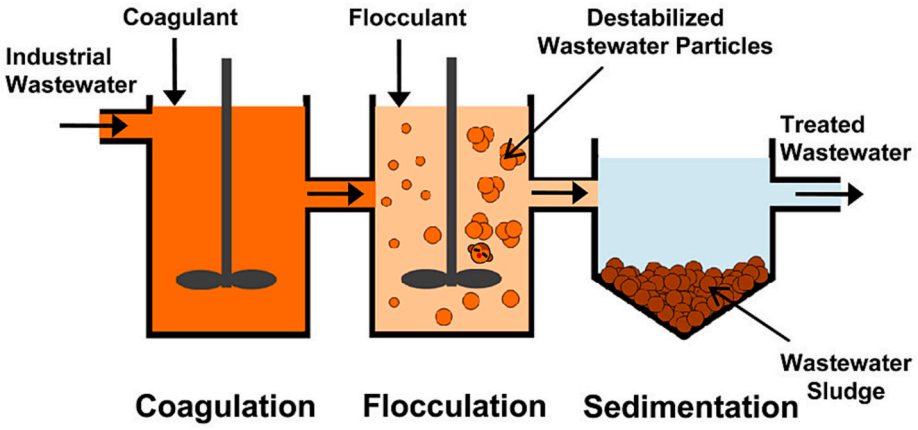

Fig. 2. Schematic diagram of the clarification process with sedimentation. Reprinted from [52] with permission from Elsevier. Copyright 2016 American Chemical Society.

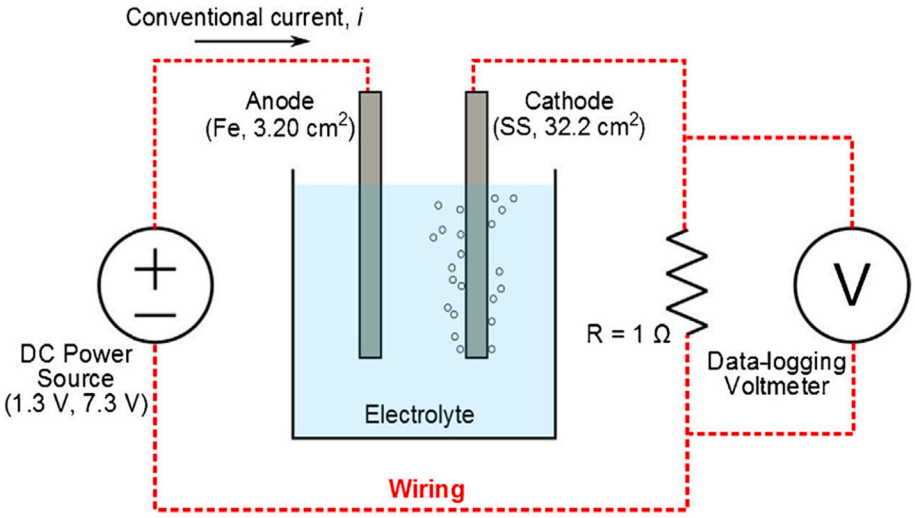

Fig. 3. Schematic diagram of the electrocoagulation process. Reprinted from [39] with permission from Elsevier.

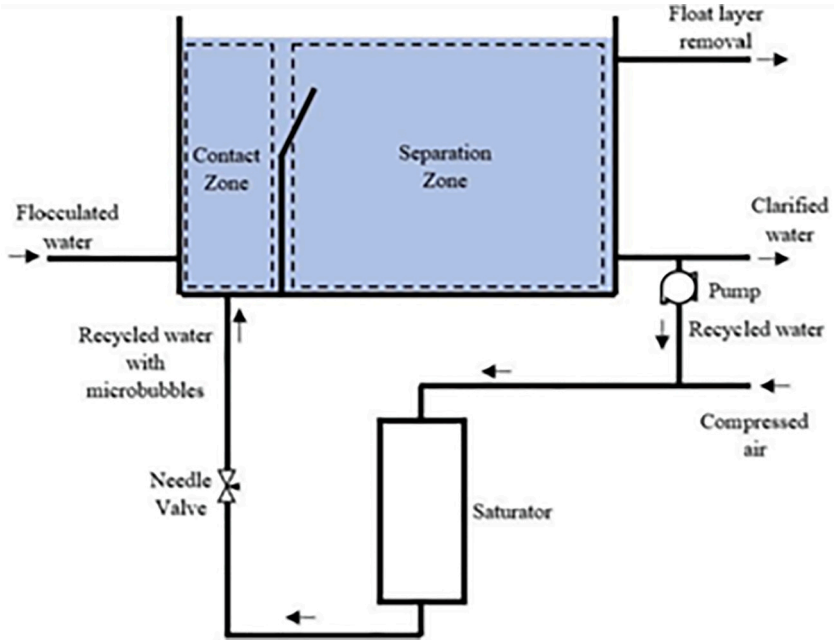

Fig. 4. Schematic diagram of the DAF process. Reprinted from [53] with permission from Elsevier.

3.3. Filtration of suspended solids and dissolved organics

Clarification often fails to remove 100 % of suspended solids. Media filtration can be effective at removing remaining impurities through a bed of porous granular material. Media filtration is the process of removing suspended particles in water when it passes through a media of sand or gravel [54]. Suspended particles adsorb onto the surface of the individual media grains and become trapped within the pores. Granular media filters are the most commonly used in existing full-scale SWRO plants [55]. The media type, uniformity, size and depth are of the key parameters. Media filter are categorised as single- or multi-media depending on the number of layers. Granular media materials include sand, gravel, diatomaceous earth, sponge, cotton, activated carbon and anthracite which have different pore sizes [30]. Granular media filters are effective in removing particles in the order of 1–0.1 μm. Dual media filters typically include a layer of 0.4–0.8 m of anthracite over a layer of 1–2 m of sand. Deep dual media filters are often used to achieve enhanced removal of soluble organics from seawater by biofiltration and the depth of anthracite level is then increased to 1.5–1.8 m. When the feed water is relatively cold (15 °C) and contains high level of organics, a layer of granular activated carbon (GAC) is used instead of anthracite so that a portion of the organics are mainly removed by adsorption [56]. When the feed water contains a large amount of fine silt or experiences micro algal blooms (0.5–20 μm), a tri-media filter consisting of 0.45–0.6 m of anthracite, 0.2–0.3 m of sand, and 0.1–0.15 m of garnet or limonite can be used (Fig. 5) [19]. Two different media filters applied to seawater pre-treatment in the Gulf of Oman and the Persian Gulf were tested [51]. For the Gulf of Oman, single stage dual filtration rendered a SDI < 3.3 for raw water with SDI < 15 while for the Persian Gulf, double filtration was used with two coagulation injections to treat seawater with a SDI of 21.7 which resulted in a SDI < 3. GMF has become the most popular conventional pre-treatment process used for large-scale SWRO plants due to its economic advantages [57]. A comparison of three different pre-treatment technologies in terms of production capacity for the world's 49 largest SWRO plants installed between the years 2001 and 2013 showed that GMF dominates over DAF and UF [46].

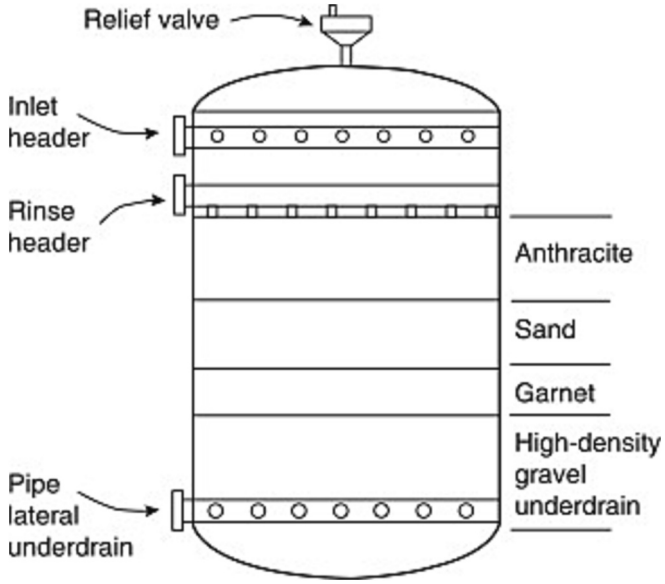

Fig. 5. Schematic of a multi-media filter. Reprinted from [58] with permission from Elsevier.

There are two types of media filters: gravity filters and pressure filters [56]. Gravity filters are used for both large and medium size filtration plants [59]. Rapid sand filters are among the most frequent types of gravity filters. Water flows vertically through the sand bed with activated carbon layer or anthracite coal in the upper layer. The upper layer eliminates natural components, affecting taste and odour [34,60]. Pressure filters work on the same principle as rapid gravity filters but the media is contained inside a vessel where water is forced under pressure through the filter media. The benefits of gravity filters are as follows: (i) sieve much smaller particles than other sand filters; (ii) sieve effectively all particles larger than their specified pore sizes; (iii) water flows through them quite rapidly; (iv) they can endure a difference of pressure across them of around 2–5 bars; (v) easily cleaned by backwash [34,48,60].

Activated carbon filtration is an effective physico-chemical treatment process based on the principle of adsorption to remove dissolved organics and heavy metals from aqueous solutions [21]. Activated carbon filters can be made from different materials such as coal, coconut shells or wood and are often used in the form of cartridge filters after multi-media filtration. The advantage of using adsorption is the low cost and the availability of different types of adsorbents which can come from natural sources or as industrial by-product materials. Activated carbon is used in drinking water and wastewater pre-treatment plants since it can effectively remove particles and organics [23]. There are two popular forms of activated carbon: powdered (PAC) and GAC. PAC is used to remove organic or inorganic impurities in high levels due to its high surface area and high micro-porosity. PAC is the most common absorbent and can be coupled with UF to enhance the overall treatment process efficiency. This combination can improve fouling control and removal of dissolved organics [61]. Additionally, biological activated carbon is another alternative and refers to the combination of ozonation before an activated carbon filter which has been shown to increase biological activity in the filter allowing to increase the removal of dissolved organics [23].

3.4. Sludge treatment for BOD and COD reduction

Sewage from a clarifier, municipal wastewater or industrial wastewater from oil & gas, paper mill or textile industries can contain organic matter or sludge that are commonly treated through a biological process of aeration or activated sludge [62,63]. It consists of passing air though the feed water to promote aerobic biodegradation of the organic pollutants by bacteria that are present in the sludge (Fig. 6). Aeration is provided by pumping air bubbles into an aeration basin. Bacteria will agglomerate onto the suspended organic solids to form activated sludge to break down the organic matter into harmless compounds. After sufficient biodegradation time, the mixture of wastewater and activated sludge, called mixed liquor, then flows into an adjacent secondary clarifier where flocculant is added to extract water on one side while bacteria and sludge particles agglomerate together and sediment to form return activated sludge on the other side. This return activated sludge is partially recycled back into the aeration basin to increase the number of microorganisms to accelerate biodegradation. The excess activated sludge is discharged and often used as fertiliser. The food-to-microorganism ratio is an important parameter used to balance the BOD with the required number of microorganisms which depends on the concentration of suspended solids defined as either mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS). Typical wastewater usually have MLSS ranging from 1500 to 5000 mg/L [62,63]. The use of an activated granular sludge process was tested to treat real textile dyeing effluents to reduce COD, TSS and remove oil and grease [62]. Results show that increasing the MLSS from 1733 to 2333 mg/L increases the removal of COD from 91.2 % to 94.5 %, the removal of TSS from 83.5 % to 98 % and the removal of oil and grease from 62.5 % to 74.4 %. The application of an aeration system for domestic wastewater was shown to be able to reduce COD by 34–43 % [63].

A membrane bio-reactor (MBR) refers to the integration of a membrane system like MF/UF/NF to a biological treatment step which is used to treat wastewater containing organic matter. Configurations include side-stream or submerged (Fig. 7). It is usually used after the aeration step for municipal wastewater as an alternative to media filtration. Experimental results showed that the usage of MBR for pre-treatment resulted in less RO membrane fouling when compared with conventional activated sludge with tertiary membrane filtration pre-treatment (CASTMF) [65]. MBR can limit calcium phosphate scaling in RO by lowering phosphate concentration (0.1 ppm) [66]. MBR using UF membranes was able to remove 60 % of biopolymers while it was not able to remove low molecular organics or humic acids effectively [22]. Permeate water produced by MBRs using MF or UF membranes inside the bioreactor has proven to be of good quality. A MBR coupled with PAC can achieve better performance with $FeCl_3$ coagulation as shown in Table 2 [67]. Biopolymers were the major foulants detected on the RO membrane surface which were completely removed with the addition of $FeCl_3$. In spite of this, 16.7 and 14.8 μg/cm^2 of biofouling cake were observed on the RO membrane surface after pre-treatment with PAC and PAC + $FeCl_3$, respectively, compared to 23.5 μg/cm^2 with MBR alone.

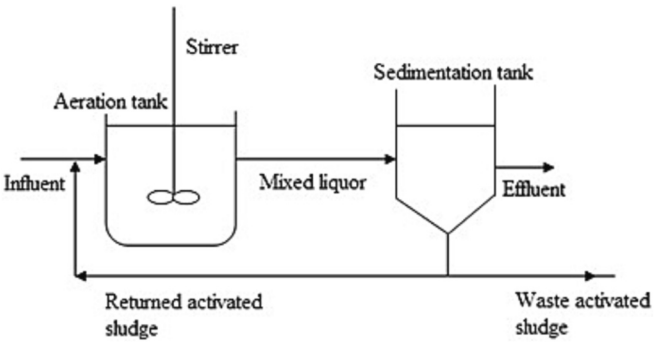

Fig. 6. Activated sludge process diagram. Reprinted from [64] with permission from Elsevier.

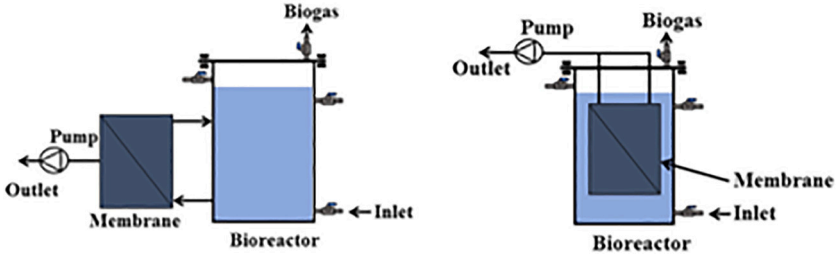

Fig. 7. Schematic of a MBR system, left: side-stream, right: submerged. Reprinted from [68] with permission from Elsevier.

Table 2
Comparison of the integration of MBR with PAC with and without $FeCl_3$ coagulation for water pre-treatment [67].

Pollutant removal	MBR + PAC without $FeCl_3$	MBR + PAC + 0.5 ppm $FeCl_3$
Dissolved organics	76.6 %	83.9 %
Biopolymers	92.3 %	100 %
Humic	70 %	89 %
Building blocks	89.5 %	92.5 %
Neutrals	88.9 %	87.8 %

3.5. Softening and scale control

Mg and Ca ions are the main scaling precursors encountered in water treatment because of the low solubility of calcium carbonate and magnesium hydroxide. Injection of lime or NaOH and ion-exchange resins are the most common solutions to reduce hardness and avoid alkaline scaling caused by $CaCO_3$ and $Mg(OH)_2$. The addition of hydroxide ions induces the reactive precipitation of $Ca(OH)_2$ and $Mg(OH)_2$ which can be removed from the liquid. Anti-scalant is usually done after GMF at a dosage between 5 and 10 ppm, depending on the content and effectiveness [20]. Ion exchange is a process used to remove scaling precursors by exchanging them with other ions with the same polarity. The process uses ion-exchange resins with particular molecular structures containing acidic or basic ions. This process can be used to remove magnesium, calcium, silica or barium [21]. Ion-exchange resins or zeolite-packed columns are commonly employed to replace undesired ions with other ions usually protons or hydroxide ions. Common resins replace Ca^{2+} and Mg^{2+} ions with Na^+ or K^+ ions as a softening method. In addition, ion exchange resins are used to remove heavy metals such as mercury, lead, and arsenic [69,70]. Alkaline scales can also be conveniently removed from water by electrolysis. [20]. Fluidised bed reactors can be used as a softening alternative using calcium carbonate pellets to remove Ca^{2+} ions. The use of pellets allows a greater surface area for the growth of $CaCO_3$ crystals which prevents quick supersaturation compared to lime softening. Likewise, calcium silicate pellets can also be used to remove silica. Similarly, seeded slurry precipitation is used to precipitate calcium sulphate and silicon dioxide [21].

Another alternative approach includes the use of zinc which react with Ca ions through redox reactions. $CaCO_3$ scale suppression by Zn ions can prevent flux decline using 2 ppm Zn. But this technique is limited to relatively low pH. At high pH, Zn ions can be depleted from the solution by precipitating in the form of smithsonite ($ZnCO_3$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) [20]. Other anti-scalants include phosphates, phosphonates, polycarboxylates, and organophosphates [30,71]. However, polyphosphate-based anti-scalants enhance the membrane biofouling by acting as a phosphorous source of nutrients [72]. Organophosphates act as anti-scalants for insoluble aluminium and iron ammonium bifluoride (ABF) can also be used as an anti-scalant for silica in improving the RO membrane performance [73].

Secondary treated sewage water can be reused for agricultural irrigation after UF/MF [20]. However, this requires the use of adequate anti-scalants for calcium phosphate. Calcium phosphate can be removed by a fixed bed of magnesia particles which precipitates $Ca_3(PO_4)_2$ at pH > 10.5 [74]. But the regeneration of the bed can only be achieved by acid treatments.

Fouling still poses a serious threat to MF, UF, and NF membrane performance, despite the rapid development of novel membrane materials such as advanced polymeric and ceramic membranes. Electrically conductive membranes have received attention due to their capacity to prevent or remove fouling. The mechanism relies on electrostatic interactions and electrochemical redox reactions at the membrane's surface. Using nanobubbles as cleaning agents is highly effective. Biofouling can decrease by 26–34 % when bubbles are electrochemically produced on pyrolytic graphite surfaces by removing adsorbed proteins [75]. Carbon nanotube membranes can be used because they are highly electrically conducting, allow fast water flux and have improved mechanical properties [76]. The electrical conductivity of the membranes varies between 24 and 58 S/cm and can reject >80 % of trace organics. Pore size can, however, only be controlled to some extent with these self-supporting membranes [77]. An integrated polymeric MF membrane with a stainless steel mesh is reported as an example of a composite conductive membrane [78].

Temperature plays an important role in scale control. In thermal desalination plants, the top brine temperature (TBT) is usually limited to 120 °C because the risk of scaling on the heat transfer surfaces increases with temperature due to the solubility curves of $CaCO_3$, $CaSO_4$ and $CaSO_4{\cdot}2H_2O$ [5,6]. Commonly encountered scaling species include, $Mg(OH)_2$, $CaSO_4$, $CaSO_4{\cdot}2H_2O$, $SrSO_4$, $BaSO_4$, CaF_2 and SiO_2. Scaling reduces process performance and increases energy needs to maintain production. Scaling is defined as soft scale and hard scale based on the hardness of water. Soft-scale refers to the precipitation of $CaCO_3$ above 60 °C and $Mg(OH)_2$ above 85 °C. Hard-scale refers to the precipitation of $CaSO_4$ and its hydrates above 100 °C. The addition of polyphosphates prevents the formation of $CaCO_3$ up to 85 °C and the addition of acids like HCl or H_2SO_4 prevents it up to about 100 °C. However, hard-scale formations are difficult to prevent beyond 110 °C. It was established that using both seeding and ultrasound pre-treatment on heat exchanger tubes reduced $CaSO_4{\cdot}2H_2O$ fouling by 64 % [79].

3.6. Dechlorination

The residual chlorine present in the feed water can cause damage to the RO membranes by oxidation and hence the process of dechlorination is necessary before the feed enters a RO system. The common agent used for this process is sodium bisulphite $NaHSO_3$. The damage to the membrane by the amount of chlorine in water depends on various factors like membrane material, pH and temperature. The deterioration of membrane is faster in alkaline pH than in neutral or acidic conditions and at higher temperatures. Alternatively, activated carbon is also used to reduce the residual chlorine levels [24].

3.7. PFAS treatment

The term per- and polyfluoroalkyl substances (PFAS) refers to a wide range of manmade aliphatic compounds with at least one carbon-

fluorine (C-F) bond which are highly resistant to other degradation processes [80]. A number of PFAS are harmful to human health as they bioaccumulate in humans and animals, primarily through ingestion. There has been evidence of PFASs in the ocean, across continents, as well as in remote parts of the world, with several ecosystems in the USA, China, and Europe being affected by them. As a result of their excellent water-, grease-, and stain-resistant properties and high resistance to thermal degradation, PFAS are widely used in industrial, commercial, military, and firefighting fields. Effluents and sludge from wastewater treatment plants (WWTPs) can be a source of PFAS and therefore pose a risk to the environment [81]. PFAS production, use, and disposal are closely connected to the water cycle through their interactions with aquifers, surface water, sediment, drinking water and wastewater treatment, land application, landfills, waste thermal treatment, and food production. By using activated carbon or RO, PFAS can be collected and concentrated rather than destroyed. The treatment residuals such as spent carbon and RO concentrate must be disposed of in landfills or other engineered systems, which are becoming increasingly critical PFAS repositories. Although physical separation methods exist for removing PFAS from a liquid phase, both types of treatment facilities rarely use processes to remove and destroy PFAS, and thermal processes (combustion) can be used to destroy residual streams. The recalcitrance of PFAS makes them irreversible, allowing them to return to the treatment facilities in an endless cycle if released into the environment or disposed of in landfills. In addition to pyrolysis and gasification, other wet thermal and nonthermal processes for solid- and liquid-phase treatment are being investigated in laboratory settings [82].

3.8. Current trends of pre-treatment approaches

3.8.1. Seawater and brackish water pre-treatment

Conventional pre-treatment has been applied in numerous seawater pre-treatment plants for many decades due to its simple operation methods. Fig. 8 shows an example of a possible pre-treatment process before SWRO. Disinfection is used to prevent biofouling followed by clarification to reduce turbidity and media filtration to remove remaining suspended solids. A MF, UF or NF membrane may be placed after the media filtration step to increase the removal of TDS which reduces the energy requirement for the RO membrane. Softening and dechlorination are used to avoid membrane scaling and damage [51,83]. MF and UF have gained popularity as pre-treatment methods in the last decade. This is due to their capabilities to produce a desired quality of feed water. After the seawater passes through the membrane filtration, most pollutants such as turbidity, bacterial content and TDS will be greatly reduced. It is therefore possible to use the RO membrane for up to half a year before it must be replaced. As MF and UF can continuously produce good quality water at low pressure levels, they are attractive pre-treatment techniques. MF and UF thus provide better reliability and economics since they do not require any labour, work fully automatically, use minimal chemicals and have compact designs [84]. In addition to RO, some researchers may prefer NF. By removing a high level of turbidity and bacterial content from seawater before RO processes, NF pre-treatment prevents membrane fouling, prevents scaling by reducing scale-forming ions and reduces the pressure required to operate RO plants by removing TDS from the feed water. Combination of ozonation with MF/UF can also be attractive to reduce fouling. Moreover, it has been suggested that ozonation improves the biodegradability of brines [23,85].

3.8.2. Wastewater pre-treatment

Municipal wastewater are commonly treated by clarification followed by aeration and activated sludge process to remove sludge, and then media filtration. Similarly, new approaches consist of placing membrane filters (MF, UF, NF) after media filtration to recover clean water before softening and dechlorination. These membranes can remove bacteria like E. Coli, viruses, and spores of sulphite-reducing clostridia [86]. A MF/UF treatment process was used to reuse wastewater generated from the glass industry [87]. By using a membrane with a pore size of 0.45 μm, almost all the particles, such as fine clay and glass particles, can be removed. Furthermore, ozonation is an effective oxidising process, where organic compounds are reacted directly or via radicals. The ozonation can be used as a pre-treatment stage to NF for biologically treated textile wastewater [88]. Typically, about 67 % of the COD reduction is accomplished by biological pre-treatment, while the expulsion of refractory organic compounds is acquired totally by the membrane system. The quantity of the microbial cells and their growth determine the kinetics and yields of the process [86]. Applied to textile effluents, coagulation with aluminium sulphate was tested and showed removal of 98 % of dyes and reduction of TOC by 50 % and COD by 40 % [89]. In textile wastewater, ferric chloride and cationic polymer can remove turbidity and colour by 64 % and 92 % respectively, preventing fouling [90] while using ferrous sulphate in combination with lime and cationic polymers reduces colour by 80–90 % and COD by 50–55 % [91]. Also, 97 % of colour and 73 % COD can be removed by using polyaluminium chloride and electrochemical treatment. Chemical precipitation successfully removes >90 % of colour and turbidity from print dyeing wastewater [92]. Such systems combined with NF appears to be economical for the recovery of water from textile effluents. However, conventional pre-treatment is not suitable in refinery industries as there are severe biofouling problems due to a failure of pre-treatment in reducing cell numbers and organic carbon at higher feed temperatures [93]. Textile, papermill and petrochemical industries are water-intensive and can greatly benefit from reusing treated effluents since it reduces water consumption and hazardous pollutants released into surface waters. Municipal wastewater plants can also benefit from it by producing drinking water to generate new revenue.

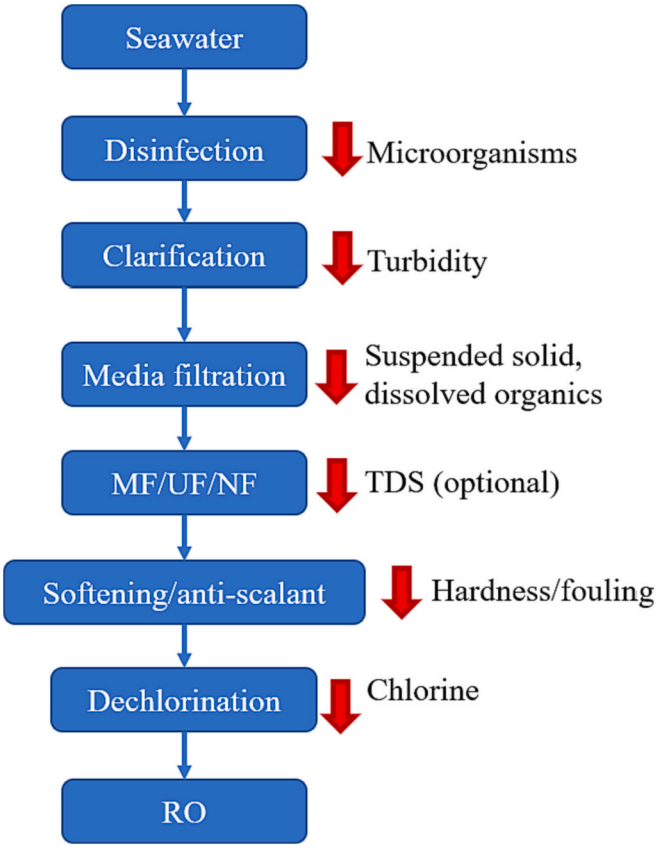

Fig. 8. Example of a possible pre-treatment process for SWRO.

3.9. Emerging membrane pre-treatment methods

Membrane pre-treatment technologies consist of MF, UF and NF. MF and UF are normally used as alternatives to rapid sand filtration where the removal of microbial contaminants and other particles can be effectively achieved. Membrane pre-treatment processes have gained immense importance over the past decade. Colloids and suspended particles tend to pass through conventional filters but are removed in MF (0.1–10 μm), UF (0.01–0.1 μm) and NF (1–10 nm) based on their sizes (Fig. 9) [94–98]. UF remains the most popular choice in pilot tests and large-scale desalination plants due to its greater operational flexibility and optimum balance between permeate production and contaminant removal [71]. These membrane improve water quality but require higher energy demand and capital costs. Permeate with membrane pre-treatment attain SDI < 2 and turbidity <0.05 NTU [99] which increases RO flux, water recovery, RO membrane lifetime, and reduces chemical consumption, and membrane cleaning frequency [100]. Membranes can be classified as isotropic or anisotropic. The composition and physical structure of isotropic membranes are uniform. A wide variety of MF membranes are made up of microporous isotropic membranes. In contrast, anisotropic membranes have layers with different structures and compositions and are not uniform over the membrane area [101]. Membranes are classified by their material composition as organic or inorganic. Most pressure-driven membranes are made from synthetic organic polymers. Among them are polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene, and cellulose acetate [101,102]. Materials such as ceramics, metals, zeolites and silica are used in inorganic membranes. Chemically and thermally stable, they are used widely in industrial applications such as UF, MF and hydrogen separation. There are equilibrium, non-equilibrium, pressure-driven and non-pressure-driven membrane processes (Fig. 10) [103]. Table 3 gives an overview of the different membrane processes. Table 4 summarises results from different studies that have applied membrane pre-treatment for wastewater streams. The use of MF/UF/NF before RO has been studied to treat different wastewater streams to recover water. MF-RO can remove pesticides and pharmaceuticals but fails to reduce TDS before RO. UF and NF however can reduce TDS content before RO. UF-RO is seen as the optimum configuration due to its intermediate filtration capacity and cost between MF and NF. Indeed, UF-RO can remove dissolved metals, organics, inorganics, oil, grease, TOC, COD, BOD, TDS, turbidity, urea and dyes. UF-RO removed up to 99.8 % of contaminants from metal finishing industry wastewater and it was estimated to save >53,340 €/year at a scale of 30,000 m^3/year thanks to water recovery at a LCOW of 1.78 €/m^3 [104]. On the other hand, NF-RO can achieve higher water recovery up to 95 %, and slightly higher TDS removal as well as complete colour removal but is more sensible to fouling due to its smaller pore size.

MF and UF are commonly used as pre-treatment for SWRO plants [122]. Bacteria, colloids, suspended solids, fibres, granules and starch can be effectively removed by MF operating between 0.1 and 10 bar [94–98]. Using MF pre-treatment increases water flux and decreases SDI below 3 [123]. There are two types of MF units based on the driving filtration force: pressure filters and vacuum filters. Vacuum-driven filters operate at 0.1–0.8 bars, while pressure filters operate between 1.0 and 10 bars [56,95,97,98]. To reduce the likelihood of biofouling, early studies recommended combining MF with other techniques, such as chlorination and strainers. The hybridisation of submerged MF with coagulation and adsorption yields higher flux and 72 % removal of dissolved organics [124]. Applied to municipal wastewater, MF before RO can reduce flux decline by up to 50 %, increase salt rejection by up to

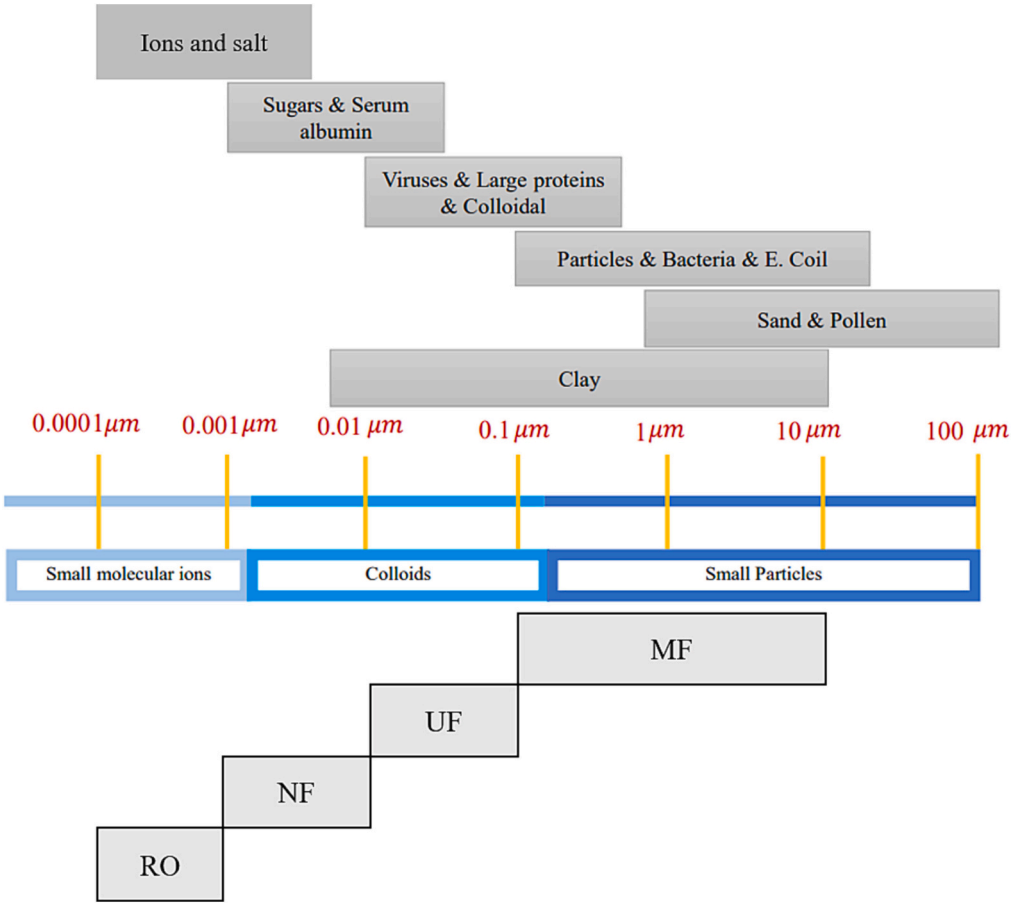

Fig. 9. Retention capacity of the different membrane technologies. Adapted from [18,30,105].

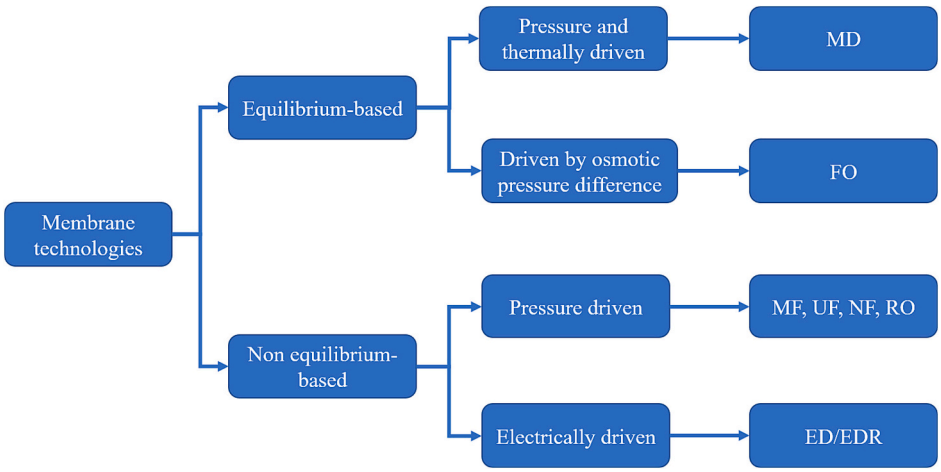

Fig. 10. Categorisation of membrane processes.

Table 3
Overview of the different membrane processes [6,30,101,106–108].

Membrane process	MF	UF	NF	RO	MD	ED/EDR	FO
Step	Pre-treatment	Pre-treatment	Pre-treatment or desalination	Desalination or brine pre-concentration	Desalination or brine pre-concentration	Desalination or brine pre-concentration	Desalination or brine pre-concentration
Pore size	0.1–10 μm	0.01–0.1 μm	1–10 nm	0.1–1 nm	0.1–0.5 μm	1–10 nm	0.1–1 nm
Operating pressure	0.1–10 bar	1–10 bar	5–50 bar	10–83 bar	0.1–1 bar	4.8–6.2 bar	Osmotic pressure difference: 20–330 bar
Common membrane materials	PVDF, PES, PAN, PE	PS, PES, PVP, zeolite, composite	Thin-film composite polyamide, PES, carbon nanotubes, graphene oxide	Thin-film composite polyamide, metal oxide nanoparticles, carbon nanotubes, nanoporous graphene, zwitterion	Ceramic, graphene oxide composite, chemically-modified, PP, PTFE, PVDF, carbon nanotubes	Polystyrene, PE, PS, PES, graphene oxide, sPPO, PECH, PVDF, PAN, poly (phenylsulphone)	Cellulose acetate, thin-film composite, graphene oxide, chemically-modified, carbon nanotubes, PS, PES

4.5 % and reduce biofouling [125]. The MF market is dominated by polymeric membranes because of their ease of processing and low cost including polyvinylidene fluoride (PVDF), polyether sulphone (PES), polyacrylonitrile (PAN) and PE. As compared to other conventional pre-treatment techniques, polypropylene membranes with 0.2 μm pore diameter can increase RO flux by 40 %. Optimized operating conditions coupled with $FeCl_3$ coagulation can produce high-quality permeate with SDI < 2 [126].

UF typically operates between 1 and 10 bar [95,97,98] and is effective in removing viruses, colloids, large proteins, polysaccharides and tannins [95,97,98,127,128]. Experimental research has made UF pre-treatment for SWRO the most promising technology in recent years. Since UF membranes have a larger pore size than NF membranes, they allow higher water flux [129]. A significant reduction in biofouling has been observed for SWRO membranes when UF filters are preceded by GMF [130]. Using micropore membranes with polymeric or ceramic compositions avoids the need of coagulants in the removal of dissolved matter [86,104,131]. UF pre-treatment was used at the Wangtan Datang SWRO plant in China to produce water with SDI < 2.50 and remove turbidity by 98–99.5 % [132]. Pilot trials in Singapore compared UF and MF pre-treatment methods and found UF pre-treatment gave SDI in the range of 1.0–2.0, while MF pre-treatment gave SDI in the range of 2.0–3.0 [133]. Nonetheless, hybrid systems integrating UF with other conventional pre-treatment techniques are more efficient in producing permeates with lower SDI than stand-alone systems [134]. It was recently reported that GAC can be used before UF to remove 70 % of dissolved organics and 90 % of colloids [135]. For Gibraltar surface seawater, a combined coagulation-UF system was used before RO to reduce SDI from 13 to 25 to 0.8 [136]. The removal of large hydrophobic compounds and reduction of humic acids by coagulation can delay membrane fouling, which delays membrane cleaning frequency [137]. Table 5 lists some large-scale SWRO plants utilizing UF as a pre-treatment to RO. Additionally, UF may rupture algal cells during an algal bloom, causing biofouling of RO membranes if driving pressures are high enough [138].

NF is a relatively recent membrane filtration process commonly used for waters with low TDS concentrations [142]. NF operates between 5 and 50 bar and is efficient at removing colloids, particulates, microorganisms, polymers, ions, sugars, organic acids, polyphenols, aroma molecules, colour and pesticides and can reduce hardness [94–98]. NF membrane types include isotropic micro-porous, nonporous, dense, electrically charged, asymmetric, ceramic, and liquid membranes [143]. Water softening applications commonly use NF since it removes divalent ions [106,144]. NF membranes retain 60–70 % of monovalent ions, reduce the TDS and reduce osmotic pressure. Reducing osmotic pressure and increasing recovery allows to reduce the operating pressure, the energy consumption, cleaning frequencies and membrane replacements of RO [145] and result in operational cost reduction [55]. Additionally, the operating pressure and investment of NF membranes are relatively low compared to RO membranes which makes it an attractive pre-treatment method. Moreover, NF can remove mineral salts, low molecular weight organics and pesticides from low-quality streams which MF and UF cannot, which reduces scaling risks. As a result, NF has emerged as a promising membrane pre-treatment technology to overcome the shortcomings of MF and UF technologies [146]. Because of its retention capacity, NF membranes can be used in a wide variety of applications such as desalination pre-treatment, water reuse, industrial wastewater treatment, and drinking water sectors to remove scaling ions and low-molecular-weight organics and partially NaCl [96]. Using NF as a pre-treatment step prior to SWRO for water softening can reduce the

Table 4
Case studies on the applications of membrane pre-treatment methods for waste streams.

Process	Water stream	Results	Reference
MF	Synthetic emulsified oily wastewater	95 % removal of organic contaminants.	[109]
UF	Poultry slaughterhouse wastewater	COD and BOD removal >94 %, fats (99 %), suspended substances (98 %).	[110]
UF	Vegetable oil factory	Removal: COD (91 %), TSS (100 %), TOC (87 %), PO^{3-} (85 %), Cl^{-} (40 %).	[111]
NF	Textile effluent	Removal: COD (57 %), colour (100 %), salinity (30 %).	[112]
MF-RO	Urban wastewater	Removal of 20 different pesticides and 28 different pharmaceuticals to the discharge limit.	[113]
UF-RO	Metal finishing industry wastewater	91.3–99.8 % removal of suspended solids, nickel, ammonium, sulphate, COD, BOD.	[104]
UF-HPRO	Oily wastewater	Removal: Oil and grease (100 %), TOC (98 %), COD (98 %), TDS (95 %), turbidity (100 %).	[114]
UF-RO	Wastewater from reactive dye printing	Contaminants including urea, sodium alginate, reactive dye and oxidizing agents were removed.	[115]
UF-RO	SGPW	Removal: TDS (98.9 %), COD (98.6 %), Cl^{-} (99.1 %). The permeate could meet current standards for surface water discharge.	[116]
NF-RO	Dumpsite leachate	95 % water recovery.	[117]
NF-RO	Distillery wastewater	Removal of 100 % colour, 99.8 % TDS, 99.9 % COD, 99.99 % K.	[118]
UF-NF-RO	Phenolic wastewater from paper mill	Removal: COD (95.5 %), phenol (94.9 %).	[119]
Coagulation + UF-NF	SGPW	Removal: TDS (70 %), turbidity (99.9 %), COD (94.2 %), Ca^{2+} (72.8 %), Mg^{2+} (86.3 %), Ba^{2+} (82.8 %), Sr^{2+} (80.1 %), SO_4^{2-} (91.7 %). UF membrane fouling was decreased by 64–84 % under optimal coagulant dosage.	[120]
MF + FO	Hydraulic fracturing produced water	Removal: TOC (52 %) and turbidity (98.5 %).	[121]

Table 5
Large-scale SWRO plants utilizing UF pre-treatment [56,139–141]. Note: "pressure vessels/train" indicate the number of vessels per train. A train is a group of RO pressure vessels connected in series. Trains connected in parallel form a stage.

Plant/country	Plant capacity (m^3/day)	UF-RO system	Energy	Water recovery
Tuas, Singapore	318,500	2 RO stages: 17 trains with 216 pressure vessels/train (stage 1) + 9 trains with 132 pressure vessels/train at low pressure (stage 2).	411 MW combined cycle power plant	
Adelaide, Australia	300,000	Submersible UF membranes. 2 RO stages: 20 trains (stage 1) + 10 trains (stage 2) with 180 pressure vessels/train.		48 %
Ashdod, Israel	275,000	2 RO stages: 5250 pressure vessels at 82 bar (stage 1) + 31 bar (stage 2).		
Honaine Tlemcen, Algeria	200,000	10 RO racks with 15,540 membranes total.		45 %
Addur, Bahrain	140,000	PES hollow fibre UF membranes with 0.02 μm pore diameter.		
Ajman, UAE	115,000	14 UF racks. 1 RO stage: 4 trains with 700 pressure vessels/train at 68 bar.		40 %
Tangshan, China	110,000	1536 UF modules.		
Chennai, India	100,000	248 RO pressure vessels and 8600 membranes.		
Fukuoka, Japan	50,000	2 RO stages with 1000 membranes total.		60 %
Yu-Huan, China	36,000	Submersible UF membranes. 6 RO trains.	1.7 kWh_e/m^3	
Palm Jumeirah, UAE	32,000	3 PES/PVP UF racks with 0.02 μm pore diameter. 2 RO stages.		
Kindasa, Saudi Arabia	25,500	8 UF racks.		50 %

total hardness by 86.5 %, together with slight rejections of Cl^{-}, Na^{+} and K^{+} ions [147]. Here, it was found that NF, operating at 22 bars, could reduce the turbidity and the content of microorganisms, as well as reduce the content of Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^{-} ions. Due to the low TDS of 200 ppm obtained by the SWRO plant, the plant could achieve water recovery rates of up to 70 % without requiring secondary RO treatment. Additionally, operating at 25 bar and a pH of 6 resulted in a 42 % increase in production rate. In comparison with other pre-treatment techniques, NF produced the highest flux and removed both inorganic scalants and colloids.

NF pre-treatment before thermal vapour compression (TVC) at 100 °C was able to avoid scaling with a low LCOW of 0.89 $/$m^3$ [148]. NF pre-treatment before MSF was also able to reduce sulphate scaling by 95 % operating at a TBT up to 175 °C [149]. In an integrated MF-NF-RO-MD system for seawater treatment [145], water recovery was increased by as much as 92.8 % due to improved hardness removal and reduced osmotic pressure. Furthermore, MF prior to NF has been found to be critical in reducing membrane fouling at later stages. Moreover, the use of UF–NF membrane pre-treatment was able to reduce TOC by 96.3 %. Unfortunately, the presence of hydrocarbons and extracellular materials can cause membrane fouling which prevents its application to oilfield produced water without additional conventional pre-treatment [99]. Disinfection prior to NF is also important to prevent microbial growth and membrane biofouling. Other challenges include improving solute separation, new and improved modelling and simulation tools, and insufficient pollution rejection [150]. A hybrid system consisting of conventional pre-treatment with NF is a viable option in most cases. Table 6 compares the membrane pre-treatment methods.

In some cases, NF membranes can be used as direct desalination method for low-salinity brackish water. But the lifetime of NF membranes is affected by the TDS concentration which increases the operating costs compared to RO. As a result, when applied to direct desalination, NF systems can consume more energy than RO by 60–150 % but can be combined with other technologies to lower water costs [96].

3.9.1. Membrane degradation challenges

Degradation of membranes and structural parts can increase maintenance and replacement costs and can lead to system failure. The severity of material degradation can further accelerate with increased temperature. So, reducing the operating temperature can reduce degradation of pre-treatment components, improve flexibility in

Table 6
Advantages and limitations of membrane pre-treatment technologies [18].

Method	Advantages	Limitations
MF	- Cost-effective operations. - Chemical dosage reduction. - Downtime reduction of RO systems. - Cost-savings on cartridge filters. - Cost-savings on RO membrane replacement.	- Sensitive to oxidizing agents. - Incapable of rejecting viruses. - Hard particles larger than 0.1 mm can damage membranes. - Biological and suspended matter present economic concerns in highly concentrated concentrates.
UF	- Reduction in sludge production. - pH increase is prevented before RO. - Adaptable to unfavourable variations in feed water quality. - Reduced continuous chlorine additions or intermittent dosing. - A wide range of contaminants can be rejected, including organic suspended particles, silt, pathogens and viruses.	- Individual phenolic fractions cannot be isolated by UF alone. - Periods of high algal blooms can cause biofouling on RO membranes. - The distribution of pore sizes may cause irreversible fouling which is difficult to control.
NF	- High rejection for multivalent ions and small organics. - No additional chemical pre-treatment needed. - Significantly reduced RO membrane replacement. - Reduced need for RO disinfection and cleaning. - By removing hardness, RO membrane scaling is reduced. - Possibility for higher RO design flux and recovery. - Reducing seawater feed TDS by 30–60 % decreases the required pressure for SWRO plants. - Low operating pressure and maintenance cost. - Stable and continuous flow rate.	- Limited simulations and modelling tools available. - Chemical resistance and limited lifetime of membranes. - Subject to salt precipitation causing NF membrane scaling.

desalination design, and lower the material and manufacturing costs by using cheap and readily available materials. Reduced fouling and scaling are crucial to allow competitiveness between the different pre-treatment techniques. Materials with high thermal stability and anti-fouling and scaling properties are therefore essential. Deformation and fracture of the materials can be caused by asymmetric material configuration, extension of a small defect which is accidentally included during fabrication, and thermal, chemical, and mechanical stress generation during operation. These components eventually degrade the performance of pre-treatment over time and eventually lead to system failure. A system reliability analysis for pre-treatment consists a solution to reduce degradation based on physical modelling and experimental results to identify causes of failure such as excessive coagulation, flocculation, sedimentation, filtration, excessive removal of soluble salts, thermal strain, disinfection, variations between steady state and transient operations, sudden mechanical shock to surface and structural parts (environmental factors), and human error due to handling. Future research should focus on the development of pre-treatment structural models representing the relationship between materials and failure probability functions using key operational variables. Also, the development of correlations between stresses and failure probability could be considered, to establish the link between efficiency and failure probability [28,30,103,127,141,151]. By emphasising process monitoring and control utilising non-invasive in situ approaches, it may be possible to decrease the expenses associated with manual sampling, enable early detection, extend the lifespan of membranes, and decrease the frequency of membrane replacement. The advancement of electrical and optical tools gives new possibilities for integrating real-time monitoring [152]. Although researchers continue to place the most emphasis on membrane development, there has been a rise in interest in process optimization techniques over the past five years, particularly those that centre on smart monitoring, hybrid systems, and energy recovery.

3.9.2. Conventional vs. future pre-treatment methods

Conventional pre-treatment methods are either physical or chemical. Physical processes use filters and screeners to remove particulates based on their sizes while chemical processes involve the addition of scale inhibitors, coagulants and disinfectants [24]. Fig. 11 shows a conventional pre-treatment process with the addition of a membrane filter. The main advantages and disadvantages of each pre-treatment technology are presented in Table 7. Conventional pre-treatments are proven and familiar technologies. They improve process efficiencies and increase lifespan but are also associated with a high carbon footprint and high chemical cost. Due to gravity-driven separation and coarse filtration, conventional pre-treatment requires a larger footprint. Moreover, the operation is labour-intensive and requires high levels of chemicals, and it is challenging to control under variable conditions. The selection criterion for the pre-treatment technologies are based on what contaminants must be removed according to Fig. 1. Conventional pre-treatment systems are well-known but the option to add MF, UF, or NF membranes adds complexity to the decision-making process and depends on the subsequent desalination system related to scaling sensitivity. For salinity-sensitive desalination technologies like RO, a UF pre-treatment is usually the optimum approach with intermediate retention capacity and cost. However, NF allows to reach higher water recovery and can be interesting for low-salinity feed water. MF is limited to removing remaining contaminants larger than 0.1 μm after media filtration.

Increasingly membrane filtration technologies are considered for full-scale implementation due to their many advantages. Algae concentration, biopolymer concentration and transparent exopolymer particles (TEP) can be used as indicators to assess the effectiveness of pre-treatment systems [57,130,153,154]. Algae removal in GMF is highly variable (48–90 %) as compared to the more stable MF/UF membranes characterized by higher removal efficiencies above 99 % [130]. High algal removals (>75 %) were also reported for sedimentation and DAF treatments [153]. Biopolymers in the water can be substantially reduced above 50 % by UF while GMF typically removes below 50 % of biopolymers. The comparison of DAF followed by dual-media filtration and UF indicated that both processes provided high removal of particulate and microbial contaminants [59]. Both treatments successfully maintained water turbidity below 0.1 NTU and SDI below 2. UF, however, showed almost 100 % elimination of algae against 60 % with dual-media filtration. Biopolymers were removed at 41 % with UF and 18 % with dual-media filtration. UF systems also have little to no pH reduction before coagulation, and require lower chlorine dosage. Table 8 compares conventional and membrane technologies for pre-treatment. Conventional and membrane pre-treatment technologies should be used together to improve process performance. Consequently, after pre-treatment, water can be fed to a desalination system for further water recovery. The development of desalination technologies will shape the future of pre-treatment methods.

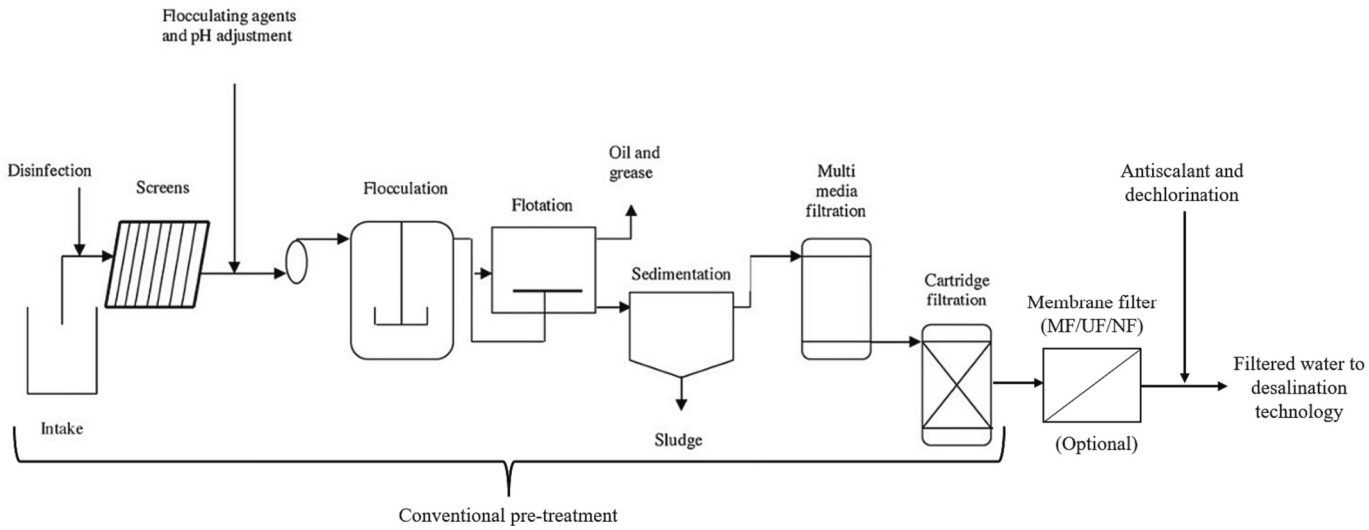

Fig. 11. Conventional pre-treatment system adapted and reprinted from [24] with permission from Elsevier.

4. Global desalination outlook

4.1. Brief overview of conventional desalination

Desalination technologies include thermal and membrane technologies. Thermal desalination technologies are based on the evaporation of the feed water to produce high-quality freshwater, containing typically below 5–25 ppm TDS compared to around 300–500 ppm from membrane technologies [99]. This also means thermal systems require less post-treatment of the freshwater. The other advantages of thermal desalination include the ability to use cheap waste heat and a higher resistance to scaling allowing higher salinity limits and thus requiring less pre-treatment. Additionally, the energy consumption is independent of the salinity or content of the feed water. In comparison, membrane technologies tend to have lower capital costs and lower energy consumptions but are easily damaged from scaling which limits their application to low-salinity feed water [17]. Water recovery from seawater desalination plants is on average 40–45 % while that from brackish water desalination is on average 75 % [155]. Thermal technologies include MSF, MED, Vapour Compression Distillation (VCD), Humidification-Dehumidification (HDH), MD, and Freezing-Melting (FM). RO and NF are the main commercial membrane technologies with electrodialysis/electrodialysis reversal (ED/EDR) and FO still at a research stage. Worldwide total desalination capacity by different technologies is shown in Fig. 12. MSF and MED represent 25 %, while RO, NF, and ED represent 69 %, 3 % and 2 % respectively. Other technologies such as hybrid processes cover around 1 %. The largest desalination plants in the world are listed in Table 9. Most of these plants utilise combined power cycles for co-production of water and electricity using fossil fuels.

RO is a pressure-driven hyper filtration method that removes contaminants with a molecular weight above 150–250 Da [95]. It is also employed to purify different fluids including glycol and ethanol, rejecting other ions and contaminants preventing them from passing through the membrane [17]. The operating pressure depends on the salinity of the feed water which varies from 10 to 28 bar for brackish water and 54–83 bar for seawater [161]. The average electrical specific energy consumption (SEC) of RO is 0.6–4 kWh_e/m^3 for brackish water RO (BWRO) and 2–6 kWh_e/m^3 for SWRO [162]. Water recovery is on average 45 % but reduces when using highly saline water sources with salinities up to 40,000 ppm, yielding recovery efficiency below 30 % for feeds such as the Red Sea, Mediterranean Sea and the Persian Gulf, while BWRO plants can achieve 75–85 % water recovery [163]. Large-scale RO plants use energy recovery devices to recover mechanical energy from brines to increase efficiency up to 95 %. Due to its modular design, RO has a wide range of capacities and can be applied for small to large systems and achieves the lowest levelised cost of water (LCOW) around 0.26–0.70 $\$/m^3$ on average for traditional systems that use fossil fuels [6,164]. RO membranes are particularly sensitive to chlorine and membrane scaling as well as pH, oxidizers, organics, algae and bacteria which damage the membranes. The salinity limit of RO is typically 70,000–75,000 ppm, above which membrane scaling can happen [6,165]. The most significant factors in RO desalination are the substantial electricity requirements for pumping seawater at high pressure and capital costs [166]. Improvements to reduce RO energy consumption by employing a 'batch' technique are also under consideration [167].

MSF is regularly used for seawater desalination due to its simplicity and reliability and can operate with up to 40 stages but modern systems usually consist of 19–28 stages. A typical MSF unit can produce up to 75,000 m^3/day [5]. More stages increase efficiency but also investment costs. In the Middle East and North Africa, MSF and RO desalination plants seize about 40 % each of the desalination market. MSF plants usually operate at TBT of 90–120 °C. Higher temperature tends to increase the efficiency but accelerates scaling. The thermal SEC of MSF varies between 69.4 and 83.3 kWh_{th}/m^3 and the electrical SEC between 3.5 and 5 kWh_e/m^3. But the thermal SEC can be reduced to 44.4–47.2 kWh_{th}/m^3 via cogeneration [5]. The typical gained output ratio (GOR) for MSF is 8 but is limited to 11 due to the lack of latent heat recovery [5,6]. MSF is still a common process but there is now a clear tendency towards MED and RO. The average LCOW of traditional MSF powered by fossil fuels is 0.56–1.75 $\$/m^3$ [6,164].

MED is similar to MSF but utilises direct latent heat recovery from the produced vapour to the next evaporator to reduce energy need. Increasing the number of effects reduces energy consumption. The typical number of effects ranges from 8 to 16 with usually 8 effects being the most cost-effective. A typical MED unit can produce up to 30,000 m^3/day. A small temperature difference between 3 and 5 °C is necessary between each effect to allow heat transfer. The average TBT of MED is 65–70 °C because operating at higher temperature increases fouling risks. The TBT can also be as low as 55 °C to allow the use of cheap waste heat. MED has gained attention because of its better thermal performance than MSF [168,169]. The thermal SEC varies between 41.7 and 61.1 kWh_{th}/m^3 but can be reduced to 27.8 kWh_{th}/m^3 through cogeneration. The electrical SEC varies between 0.5 and 2.5 kWh_e/m^3 [5]. Evaporator configurations include vertical climbing film tube, rising film vertical tube, or horizontal tube falling film and process configurations include forward, backward, or parallel flow [168]. The average

Table 7
Advantages and disadvantages of the conventional pre-treatment methods [18–20,23–26,35,38,43].

Pre-treatment process	Advantages	Limitations
Chlorination	- Odour reduction. - Kills microorganisms and bacteria effectively.	- Polyamide RO membranes are damaged by chlorine. - The use of chlorination is accompanied by the formation of carcinogenic dibutyl phthalate. - Poor effectiveness of chlorine in deactivating protozoa and endospores.
Ozonation	- No increase in produced sludge. - Removes both colour and organics. - Non-toxic.	- Higher energy consumption and cost.
Ultrasound	- Free-chemical technique. - Ability to be used with high suspended solid solutions.	- Costly. - Cooling required.
Ultraviolet light	- Cost-effective. - Simple to implement. - Effectiveness in deactivating process.	- Mutagenic risks. - Low performance on light-screened water. - Breaks down large organic matter into organic acids promoting biofilm formation.
Anti-scalants	- Effective for scale inhibition on RO membranes.	- In case of overdose, biofouling of RO membranes may happen.
Clarification	- Organic, colloidal, and biofouling control. - Provides significant improvements in the removal of colloidal and particulate matter.	- When overdosed, can cause detrimental effects on RO membrane. - Carcinogenic potential of the monomers used for the synthesis of synthetic organic coagulants.
DAF	- Cost-effective. - If optimized, algae cells can be removed up to 99.9 %.	- Non-optimisation may lead to frequent chemical cleaning of RO membranes. - Fouling on cartridge filters requires replacement every 2–8 weeks. - Scraper problem caused by lack of feed water.
Media filtration	- High filtration rates and long filtration runs. - Filters suspended solids. - Pressure filters for small SWRO plants are space efficient and easier to install.	- Sensitive to feed water changes. - Not effective for inhibiting organic and biofouling. - Oil contamination and algal blooms can cause the permeate SDI to vary.
Activated carbon filtration	- Use a variety of different cheap materials. - Large adsorption range. - Reduces residual chlorine level. - Easy backwash cleaning.	- Smaller adsorption range than UF and NF.

Table 8
Comparison of conventional and membrane pre-treatment techniques [18].

Parameter	Conventional pre-treatment	Membrane pre-treatment
Capital cost	Competitive with membrane pre-treatment.	High but potential for development leads to cost reduction.
Carbon footprint	High.	Low (about 30–60 % of the conventional methods).
Energy need	Low.	High due to applied pressure.
Chemical cost	High due to chemical separation.	Low due to membrane separation.
Treated water quality	Varying quality: SDI < 4 for 90 % of the time Turbidity <1.0 NTU.	Reliable quality: SDI < 2.5 for near 100 % of the time Turbidity <0.1 NTU.

LCOW of traditional MED powered by fossil fuels is 0.52–1.10 $/m^3 [6,164].

VCD is often combined with MED systems to increase efficiency. VCD methods include mechanical vapour compression (MVC), which is electrically driven, and TVC, which uses a steam ejector. MVC and TVC are applicable to small and medium scale systems between 100 and 30,000 m^3/day. MVC units operate in single stage with capacities ranging from 100 to 3000 m^3/day, while TVC can operate in several stages to reach higher capacities of 10,000–30,000 m^3/day [170]. The average total equivalent electrical SEC varies between 10 and 55.6 kWh_e/m^3 [5,170]. It is a compact technology that can be designed to be portable but requires high capital and operating costs because steam compressors are expensive and sensible to corrosion. Scaling and corrosion are serious concerns because the evaporators are directly exposed to the feed water [168,171]. The average LCOW of a typical MED-TVC system powered by fossil fuels is 1.12–1.50 $/$m^3$ [164]. Table 10 summarises the advantages and disadvantages of each desalination technology.

4.2. Non-conventional desalination

HDH is suited for small-scale and decentralised applications [172,173]. Here, HDH achieves low efficiency leading to low water production [174]. Although HDH operates with low-grade energy, it is currently not cost-competitive. A HDH set-up consists of a humidifier, dehumidifier and heater. Air is heated and humidified by the hot water received from a heat source, and then dehumidified in a large surface condenser. The hybridisation of HDH systems with other desalination technologies leads to reducing the LCOW [175]. The most commonly used dehumidifiers are flat-plate and finned-tube heat exchangers [191]. Recently, the application of solar HDH to a greenhouse has been tested as a novel self-sufficient system to reduce water and energy consumption [192].

FM uses the principle of removing water by freezing it out from salts as ice crystals. Ice crystals formed under the appropriate conditions can be very pure. The general interest in FM comes from the much lower latent heat of fusion of ice of 333 kJ/kg compared to the latent heat of evaporation of water of 2500 kJ/kg at 100 °C. Energy requirement can be theoretically reduced by 75–90 % [177]. However, FM is currently not commercial because of the cost and complications of refrigeration systems and the need for freshwater to wash the crystals prior to melting [178]. In general, FM units consist of a pre-cooler, a crystalliser to crystallise up to 15 % of the mass, and a filter. The feed water can be pre-cooled in a heat exchanger using the cold product or brine to lower the required energy of the heat pump [179].

MD is an emerging thermal desalination technology where separation is enabled via evaporation through a membrane. Vapour passes through using the pressure difference across a membrane caused by the temperature difference between each side [180–182]. The different MD configurations include sweeping gas (SGMD), direct contact (DCMD), vacuum (VMD), air gap (AGMD) and water gap (WGMD). DCMD is the most studied because it achieves low overall heat transfer resistance,

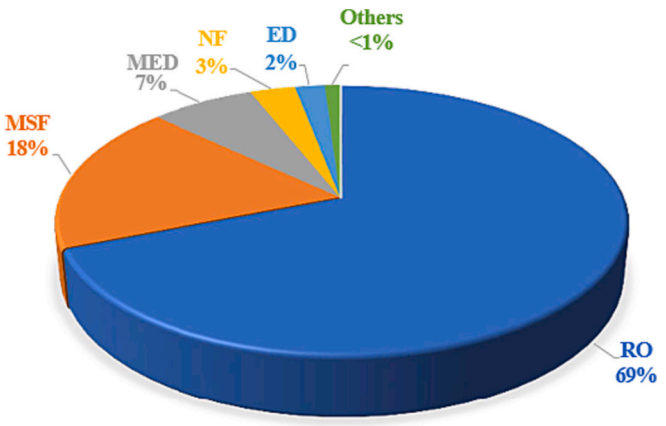

Fig. 12. Worldwide total desalination capacity by technology in 2018. Adapted from the literature [2,3].

however it has a high conductive heat transfer which increases thermal energy loss [183]. In AGMD, an impermeable film is used between the two flows which increases heat recovery, while the use of vacuum in VMD increases mass transfer. MD normally operates between 30 and 80 °C [165]. Here, the main limitations include membrane wetting and scaling which reduce flow and currently limit applications to small and lab scales. MD desalination plants can achieve a LCOW varying between 0.26 and 130 $/m^3 depending on the size and the configurations [193]. It was shown that using waste heat as the energy source for a MD process with a capacity of 30,000 m^3/day can lower the LCOW from 2.2 $/$m^3$ to 0.66 $/$m^3$ [193,194]. Alternatively, osmosis distillation (OD) is a new type of MD technology that uses a concentrated saline solution as a draw solution containing LiBr or $CaCl_2$. However, this technology requires additional energy to regenerate the draw solution [6].

ED/EDR uses cation and anion selective membranes to separate charged ions using direct current. Unlike other desalination methods, ED is only capable of removing ions. Produced water from ED systems needs only limited post-treatment, typically chlorination. In general, ED has a high recovery rate and can remove 75–98 % of TDS. EDR is a similar process, except that the cation and anion periodically reverse due to alternative current. The polarity is reversed 4 times per hour, which creates a cleaning mechanism. Due to the feed water circulation and alternating polarity, EDR has a higher recovery rate up to 94 %. EDR requires little labour and the maintenance costs are generally low, but the energy consumption is proportional to the salinity level which limits its commercial application to low salinity streams. ED/EDR is best used in treating brackish water with TDS up to 4000 ppm and is not economical for higher TDS concentrations. For low salinity levels <2500 ppm, the SEC ranges between 0.7 and 2.5 kWh_e/m^3, and between 2500 and 5000 ppm, the SEC varies between 2.64 and 5.5 kWh_e/m^3 [170]. Yaqub and Lee [165] also reported SEC values between 7 and 15 kWh_e/m^3 and sometimes up to 850 kWh_e/m^3 for highly saline feeds containing around 100,000 ppm. An electrical SEC between 20 and 40 kWh_e/m^3 was also reported alongside a water cost of 5–10 $/$m^3$ [5].

FO is a pressure-driven membrane process that uses a salty draw solution that transfers ions away from the feed water using the osmotic pressure difference across a semipermeable membrane [188]. The increasing attention on FO is mainly due to its potential to achieve high rejection for a wide range of contaminants without the need to apply hydraulic pressure for separation. As such, FO may compare favourably to pressure-driven processes such as RO in that it may have lower demand on electrical energy, and potentially less foulant compaction since no hydraulic pressure is applied [86,186]. The need for development of high-performance FO membranes, the selection of appropriate draw solutions, and the integration of a cost-effective post-treatment for regeneration of the draw solution are challenges for FO. Recent progress on the use of FO membranes to remove metals like boron and other hazardous substances from feed waters potentially allows the production of high-quality water [188]. The electrical SEC of FO varies between 6.8 and 16.7 kWh_e/m^3 and the average cost of water is 0.64 $/$m^3$ [5].

4.3. Techno-economic feasibility case studies

Many countries are looking into powering desalination plants with renewable energy resources such as solar, wind and geothermal or through the use of combined cycles for the co-production of water and electricity [195]. If renewable energy sources are not used for the production of freshwater, desalination has the potential to increase reliance on fossil fuels, increase greenhouse gas (GHG) emissions, and exacerbate climate change. Utilizing renewable energy is expanding thanks to technological advancements, falling equipment costs, and rising awareness of the environmental issues caused by fossil fuels [196]. Water and energy legislators should choose different methods to meet the needs based on the local potentials by paying attention to the desalination processes and power systems since there are numerous conventional desalination methods supported by various types of renewable energy technologies worldwide [197,198]. Arid regions can occasionally employ concentrated solar energy for thermal desalination or electricity produced by PV plants for membrane desalination systems. Intermittency is undoubtedly the biggest issue with employing renewable energy sources, however this issue may be resolved by utilising energy storage systems or combining them with other renewable energies. Geothermal energy however has the advantage of continuous

Table 9
Largest desalination plants in the world above 500,000 m^3/day of freshwater production capacity [156–160].

Country (Year)	Plant	Technology	Water capacity (m^3/day)	Power capacity (MW)	Investment ($)
UAE (2011)	Jebel Ali Power and Desalination Complex	MSF & RO	2,227,000	12,900	
UAE (2008)	Al Taweelah Power and Desalination Complex	MSF & MED	1,355,000	4600	
KSA (2014)	Ras Al Khair	MSF & RO	1,036,000	2650	7200 M
KSA (1983)	Al-Jubail 1 & 2	MSF	1,085,000		
UAE (2022)	Al Taweelah RO	RO & PV	909,000	69	900 M
Qatar (2015)	Ras Abu Fontas Power and Desalination Complex	MSF	909,000	2200	
KSA (2010)	Al-Shuaiba	MSF	880,000	900	2450 M
UAE (2022)	Umm Al Quwain	RO	682,000		797 M
UAE (1979)	Umm Al Nar	MSF & MED	659,000	2200	
Israel (2013)	Sorek	RO	624,000		400 M
KSA (2022)	Jubail 3A IWP	RO	600,000		650 M
UAE (2010)	Fujairah F2	MED & RO	600,000	2000	
Israel (2023)	Sorek 2	RO	570,000		430 M
KSA (2019)	Yanbu	MSF	550,000	2700	1000 M
Kuwait (2001)	Az Zour South	MSF	524,000		
KSA (2000)	Al-Khobar 2 & 3	MSF	503,000		
Kuwait (1985)	Doha West	MSF	502,000	2400	

Table 10
Advantages and limitations of the desalination technologies. Subscripts: th: thermal; e: electric.

Desalination technology	Advantages	Limitations	SEC (kWh/m^3)	LCOW ($/m^3)	References
MSF	- Mature, reliable, simple design - Large-scale production - Easy scaling control due to simple design	- High energy consumption - Low water recovery and no latent heat recovery - High investment - Large footprint - Slow start-up and maintenance needs shut-down	44.4–83.3th	0.56–1.75	[5,6]
MED	- Latent heat recovery yields lower energy consumption than MSF - Lower energy consumption than MSF - Reliable and large-scale production	- High energy consumption - High investment - Large footprint - More complex design than MSF	27.8–61.1th	0.52–1.10	[168,169]
VCD	- Latent heat recovery - Compact and can be mobile - Capacity increases with more effects - Low capital and operating costs - Reliable and simple design - Can be combined with MED - Relatively low energy demand	- Limited to small-medium scale - Expensive steam compressor - High maintenance of compressors	10–55.6e	1.12–1.50	[5,168,170,171]
HDH	- Simple design and installation - Operates at atmospheric pressure - Cheap equipment - Low operating and maintenance costs - Low operating temperature	- Limited to small-scale - Low energy efficiency - Low water recovery			[172–176]
FM	- Lower theoretical energy requirement - No pre-treatment required - Operates at atmospheric pressure - Simple and compact design - Low risk of scaling, fouling and corrosion - Low cost of hydraulic refrigerant compressor - Capacity to recover salts	- Slow process - Cooling requires large temperature difference - R&D stage - Large crystalliser footprint - Difficult mechanical handling of ice - 8–9 stages needed to reach high purity	43.5–85th	1.42	[177–179]
MD	- Low operating temperature and pressure - Modular and compact design - Low membrane strength requirement - High salinity limit	- Not currently commercially viable - Low permeability - Membrane wetting and scaling - High energy consumption - Only lab-scale pilots have been tested	39–67e	0.26–130	[165,180–183]
RO	- Cheapest technology - Low energy consumption - Only needs electricity - Simple operation and fast start-up - Modular design allows small-large scale - Maintenance does not require plant shutdown	- Short membrane lifetime 5–7 years - High cost of membrane replacement - Requires chlorine pre-removal - High sensitivity to fouling and low salinity limit - Mechanical failure at high pressure	0.6–6e	0.26–0.70	[6,17,95,162,184]
ED/EDR	- High membrane life of 7–10 years - Low to moderate operating pressure - Can be used to recover specific ions using selective membranes - Cleaned by backwash	- Energy need is proportional to salts concentration and low salinity limit - Risk of leaks in membrane stacks - Limited to small-scale	0.7–850e	5–10	[11,107,168,185]
FO	- Low electrical energy consumption - High water recovery and high salinity limit - Small footprint - Cleaned by backwash - Low operating pressure because operating at osmotic pressure difference	- Low efficiency - Limited draw solutions - Limited applications - High energy demand when stand-alone	6.8–16.7e	0.64	[86,186–190]

operation but requires drilling of expensive wells at various depths depending on the resource and energy need. Table 11 lists the results from recent studies on the application of renewable energies for desalination. The economic results show wide variations in terms of LCOW. Overall, the use of renewable energies can be competitive with the traditional use of fossil fuels which is essential to transit to sustainable desalination. A techno-economic comparison between WGMD and AGMD powered by either solar thermal collectors, waste heat or fossil fuels was conducted [199]. For freshwater production capacities ranging from 10 to 1000 m^3/day, results show that waste heat is the cheapest option followed by solar collectors, rendering fossil fuels the most expensive choice. This can be explained by the increasing high cost of these fuels. Additionally, it shows that WGMD is more economical than AGMD because of its better performance. A novel concept of MED powered by concentrated solar heliostats around a large glass dome has been suggested by Solar Water Plc in conjunction with Cranfield University as part of the NEOM project in Saudi Arabia [200].

4.4. Emerging desalination technologies

4.4.1. Hybrid desalination approaches

Desalination technologies can be combined to create emerging hybrid systems that integrate the advantages of each other to improve efficiency [221]. These systems can reduce energy consumption, costs and improve water recovery. Hybrid RO-ED is economically viable if the LCOW of the RO unit is 40 % lower than the ED unit used to process the RO concentrate. ED reduces the overall LCOW because higher salinity leads to higher current density and thus lower ED equipment cost. In comparison, RO-ED achieves better performance and economics than stand-alone ED due to higher water recovery [222]. using cheap steam, hybrid RO-MD can be competitive with stand-alone RO if the water recovery and flux of MD are higher than RO [223]. Hybrid RO-gas hydrate can achieve up to 80 % water recovery, 90 % salt rejection and low energy need between 1.4 and 1.9 kWh/m^3 [224].

The combination of FO to RO has been proposed to further minimise

Table 11
Techno-economic results from recent case studies on desalination powered by renewable energies. The energy consumption is expressed either as thermal (th) or electrical (e).

Desalination technology	Renewable energy technology	Capacity (m^3/day)	Energy consumption (kWh/m^3)	LCOW ($/$m^3$)	Reference
MSF	PTC	2230	5e	2.72	[201]
MSF	PTC	1000	3.5e	0.97	[202]
MSF	PTC	4556		2.3	[203]
MED	ORC-PTC-AC	45,461		2.3	[204]
MED	167.8 MW_{th} LFR	13,422	75th	4.31	[164]
MED	460 MW_{th} ORC-PTC-NG	87.1		4.6	[205]
MED	50 MW_e PTC	32,041	55.56th + 1.5e	0.95–1.95	[206]
MED	LFR-biomass-AC	48,476	97.41th	1.30	[207]
MED	ETC-biomass-AC	48,535	105.06th	1.30	[207]
MED	Geothermal	1110-2870	85-156th + 3.71–4.92e	1.89–2.60	[207]
MED	Geothermal	30,000	82.4th + 1.93e	2.48	[207]
MED-TVC	13.6 MW_{th} LFR + fossil fuel back-up boiler	4543	71.79th + 2e	1.43–7.1	[208]
MED-TVC	15.6 MW_{th} LFR	9000	41.6th + 1.5e	1.63–3.09	[209]
MVC	ORC-PV/T	141	6.59e	1.02	[210]
NF-MVC	PV-PTC	500	10.14e	1.54	[211]
HDH	Solar	0.072	159–440.3e	112	[212]
HDH	Solar	0.036–0.168	719.6–828.8th	12	[213]
HDH	heat pump	0.022		14	[176]
Direct absorption HDH	Solar	8.26 L/m^2/day	613th	7–35	[214]
HDH	Solar + thermoelectric cooling	2.64 L/m^2/day		97 $/$m^3$/$m^2$	[215]
SGMD	PV-PTC	0.240		84.7	[194]
DCMD	PTC	10	1017-1536	21–29.7	[216]
SGMD	PTC	10	719–729	17.7–18.6	[216]
VMD	PTC	10	650–660	14.3–14.4	[216]
DCMD	111 MW_e CST-ORC	40.76	1854–1436th	0.396	[217]
WGMD	Solar thermal	10–1000		3.17–5.59	[199]
AGMD	Solar thermal	10–1000		4.07–7.84	[199]
WGMD	Waste heat	10–1000		1.68–3.97	[199]
AGMD	Waste heat	10–1000		2.57–6.22	[199]
WGMD	Fossil fuel	10–1000		3.75–6.06	[199]
AGMD	Fossil fuel	10–1000		4.65–8.30	[199]
RO	545.3 kWp PV farm +3877 kWh battery storage + seasonal water storage	1293	2.4e	2.21–3.06	[218]
RO	PV/T + battery storage	7.4–15.1	1.253–1.84e	0.194–0.440	[219]
RO	1131 kW Wind farm/PV + battery storage	3500	7.68e	0.530–0.574	[220]

the overall energy requirement of FO [190,225]. Hybrid FO-NF can achieve up to 85 % water recovery from wastewater and minor/reversible fouling of the FO unit using Na_2SO_4 and $MgCl_2$ draw solutions [226]. In comparison, hybrid FO-MD can achieve up to 90 % water recovery from oily water sources in a cost-effective way. The cost of membrane replacement could be reduced by combining FO with MED to remove scaling ions. Other hybrid systems such as FO-MSF and FO-ED hold great promise for removal of salinity and organics from water [188]. Hybrid FM-VMD can reach up to 74 % water recovery using half of the distillate from the VMD unit to wash ice crystals from the FM unit and using heat recovery can reduce energy demand by 27 % for cooling and 25 % for heating [227]. Additionally, the use of nanomaterials for FO membranes can improve flux, salt rejection, and anti-fouling capabilities. Due to its adaptability and the high porosity and interconnected porous structure of electro-spun membranes, fabrication techniques like electrospinning have been extensively researched for manufacturing thin film composite FO supports with distinctive designs [228]. A significant obstacle to the industrial application of FO is the absence of low-cost techniques to replenish the draw solution [229].

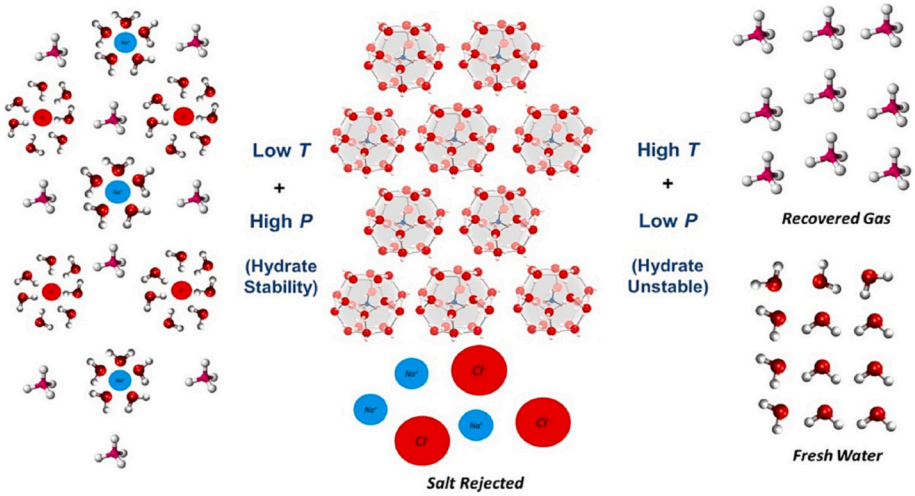

Fig. 13. Working concept of hydrate-based desalination [231].

4.4.2. Hydrate-based desalination

The application of gas hydrates for desalination from brackish water and seawater has been suggested and illustrated in Fig. 13. In a hydrate structure, molecules of a certain size may be clathrated. Under favourable hydrate formation circumstances (low temperature and high pressure), mixing a saline solution with a specific hydrate former causes guest molecules to be integrated into hydrate cages, leaving salt crystals/ions in the bulk aqueous phase behind [230]. The salt ions are thus not included in the hydrate lattice. Fresh water generation may result from the hydrate's subsequent dissociation by heating or depressurisation.

Several studies have looked at the use of simple hydrates that are stable at atmospheric pressure [232]. Careful choice of a hydrate promoter, to boost hydrate production, may drastically lower the process' overall cost. Clathrate hydrate-forming agents called hydrate promoters have been used to make the freeze distillation of saline water easier. Companies like Koppers Co and Sweetwater Co have developed the use of propane hydrates for desalination at pilot plants. A variety of hydrate formers were investigated to study hydrate separation kinetics and continuous flow systems [233]. Efforts to separate hydrate crystals from concentrated brines and to remove dissolved hydrate former gas from recovered water sparked interests into hydrate-based desalination.

The key problems facing hydrate-based applications include increasing the number of hydrates created, enhancing the pace of hydrate development, and to get hydrate slurries that are simple to handle at an industrial scale process. By reducing the temperature and/or raising the pressure, which is accompanied by a considerable energy cost for cooling and compression, hydrate formation can be easily facilitated [230]. The pressure necessary to create hydrates can be significantly decreased by adding thermodynamic promoters. Tiny gas molecules can easily be caught in the remaining small cages since these additives occupy the big cages of sII hydrates at relatively mild temperature and pressure conditions [234]. However, because all of these thermodynamic additives are employed in large amounts, they would not be appropriate for commercial applications without cost-effective recovery. By increasing the gas/liquid contact, mechanical techniques including stirring, bubbling, and spraying can effectively increase hydrate formation rate. Kinetic promoters may be used in low dosage (1 wt %) with thermodynamic promotersto increase hydrate production [230]. Surfactants like sodium dodecyl sulphate (SDS) and sorbitan monolaurate are typical kinetic boosters. The higher gas solubility, the decreased surface tension of the gas-liquid interface, and the capillary-driven water supply are all credited with improved hydrate formation kinetics [235]. Due to their amphiphilic character, several hydrophobic amino acids, like L-leucine and L-isoleucine, are also known to accelerate the kinetics of hydrate formation [236]. Other substances that have more recently been identified as kinetic boosters include hydrophobic particles [237], carbon nanotubes [238], graphene oxide nanosheets [239], and oleic acid potassium soap [240]. However, more research is needed because most studies have looked at water containing only NaCl without considering the effects of the presence of other ions. Additionally, hydrate formers must have good stability to allow recycling.

4.4.3. Economic evaluation of nuclear desalination

A review on the state-of-the-art of nuclear desalination was recently conducted [241]. Nuclear power plants can be coupled with thermal or membrane desalination systems by either recovering waste heat to power thermal desalination or by using the produced electricity to power pumps for membrane technologies. Ten different nuclear desalination plants have been reported around the world in countries like Saudi Arabia, UAE, Chile, Algeria, Uganda, Thailand, Sri Lanka, Peru and Croatia. These co-production plants are mostly combined with MSF, MED and RO. The cost of nuclear desalination ranges between 0.4 and 1.8 $/m^3 making it competitive with traditional desalination powered by fossil fuels. Reactors are classified as small below 300 MW_e, medium between 300 and 700 MW_e and large above 700 MW_e. Small modular reactors (SMR) are the focus of attention because their advantages over large reactors include smaller land area, faster construction, lower investment costs and safer operation. Additionally, SMRs generate lower thermal energy which reduces risks of core meltdown and explosions which facilitates public acceptance [242]. A comprehensive techno-economic analysis on the combination of nuclear energy with hybrid desalination technologies (MED-RO and MSF-RO) has been conducted [243]. Results suggest that hybridisation can lower the cost of water and optimize performance. For capacities ranging between 50,000–200,000 m^3/day, hybrid MED-RO systems are always cheaper than MSF-RO setups because of the better performance of MED with LCOW values ranging from 0.73 to 1.91 $/$m^3$ depending on the degree of hybridisation. Moreover, using rejected hot water from the condenser of the nuclear plant as feed water to the desalination system can be an economic option.

Nuclear desalination is considered carbon-neutral similarly to solar, wind, geothermal or hydropower but requires uranium. In situ leaching is the dominant mining process accounting for 57 % of the global production and consists of dissolving uranium from underground deposits which consumes significant quantities of water and generates large amounts of wastewater and slurries. In 2019, there were 450 nuclear reactors in the world connected to the grid for a total power capacity of 396 GW_e accounting for a uranium demand of 59,200 tU/year. Kazakhstan is by far the largest producer accounting for 40.6 % globally, followed by Australia and Canada [244]. This raises concerns over the energetic dependence from those producing countries, shortages and the sustainability of the resource. To solve these issues, the extraction of uranium from seawater or desalination brines has been introduced (Fig. 14). Integrating uranium extraction from saltwater directly to nuclear desalination plants allows for a cyclic renewal of uranium used as fuel in the nuclear reactor. This cuts the need for external sources of uranium and allows such plants to be energetically independent and sustainable. Any excess uranium production can also be sold to different markets to generate new profit. Several reviews on uranium extraction from seawater have been recently conducted [98,245–248]. Uranium has very low concentration in seawater around 0.0033 ppm present in majority in the form of uranyl UO_2^{2+} [98,246,247,249]. This amounts to about 4.5 billion tons of uranium in the oceans which makes an attractive source of uranium for nuclear energy [246,249,250]. The selective extraction of uranium can be done using adsorbent materials including polymers, hydrogels, chitin-based materials, peptoid-based ligands, nano-ceramics, porous carbon materials, metal-organic frameworks, covalent organic frameworks, porous organic polymers, porous aromatic frameworks, and genetically engineered proteins [245,246]. Amidoxime and amidoxime-based polymers are the most studied adsorbents because of their interesting selectivity, their improving synthesis from poly(acrylonitrile) and their application to large-scale marine tests [245,246]. These polymers can be deployed using floating platforms, flow-through devices or tethered braids using either pumps or natural currents [246]. Passive extraction processes are economically advantageous because they do not consume energy for seawater pumping [245,246]. However, due to seawater's extremely low uranium concentration, passive extraction processes have slow adsorption kinetics, affecting uranium extraction efficiency [245].

Several scale-up projects have been tested in the United Kingdom, Japan and the United States Department of Energy who have shown a great deal of interest in tapping into this source and improve extraction technologies [245,246]. Over the past 35 years, the extraction capacity of uranium sorbents has increased from around 1 g-U/kg of sorbent to over 5 g-U/kg of sorbent while simultaneously reducing the cost of extraction from around 1300–3100 $/kg-$U_3O_8$ down to around 430–580 $/kg-$U_3O_8$ from seawater [246]. On the other hand, the average cost of uranium extraction from brines is between 660 and 1232 $/kg-U [98,247]. However, oceanic uranium is still not competitive with traditional extraction from terrestrial sources at 45–160 $/kg- U_3O_8

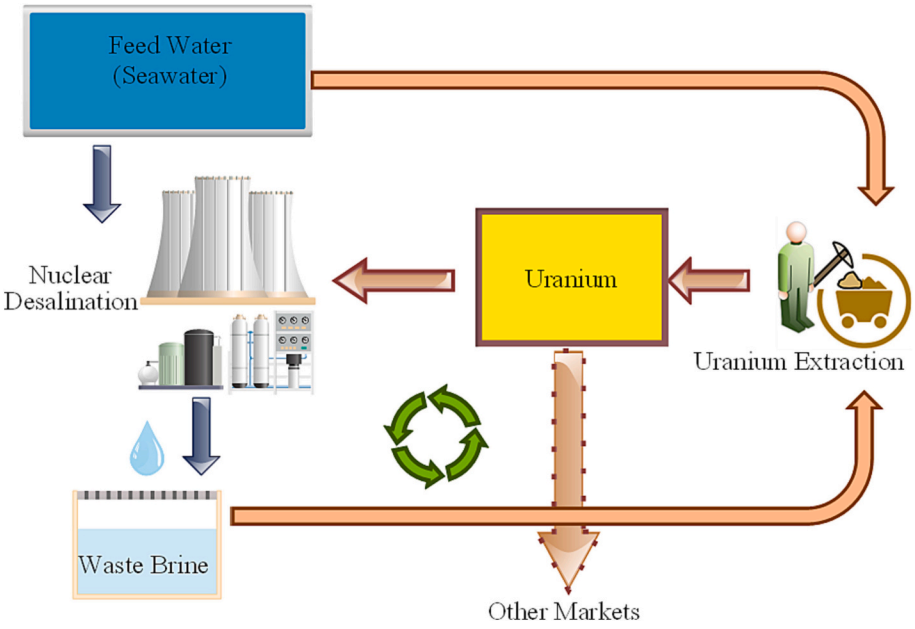

Fig. 14. Nuclear desalination with uranium recovery.

[246,250]. Extraction from brines is more expensive than from seawater because of the higher concentration of iron and vanadium which act as competitors for adsorption [155,248,251]. Thus, improving selectivity as well as adsorption capacity, resistance to biofouling and durability are key to enable commercialisation. Novel biomass-based microporous membranes with polyphenol adsorbent have also been suggested to extract uranium from seawater to achieve up to 84 % extraction in several cycles with an estimated competitive cost of 275 $/kg-U when using tidal power [249]. Adsorption from seawater using a moving belt connected to an offshore floating wind farm was also suggested to produce 1.2 t/year of uranium to supply the equivalent of 5 MW of electricity for a nuclear plant. Results estimated a cost of uranium recovery between 313 and 593 $/kg-U [252,253]. Increasing the recycling of adsorbents is key to lowering the cost of uranium extraction. However, elution processes and biofouling can deteriorate adsorbents, thereby limiting their reusability [245]. Sustainable desalination must also integrate brine post-treatment methods to recover other resources from brines to achieve ZLD.

5. Benefits of ZLD technologies after desalination

5.1. Environmental impacts of ZLD

While desalination plants produce freshwater, they also generate large quantities of brines which are commonly discharged back into the sea, leading to environmental pollution for aquatic ecosystems. Typical brine disposal methods consist of discharging brines into receiving sites for direct disposal without any form of recovery. Those technologies have different disposal costs and include surface water discharge (0.05–0.30 $/m^3), sewer discharge (0.32–0.66 $/m^3), deep-well discharge (0.54–2.65 $/m^3), landfill disposal and land application (0.74–1.95 $/m^3). Sewer disposal is limited to brackish water desalination brine because of the high salinity that can inhibit the biological treatment of WWTPs and prevent disposal of the final effluent due to regulatory issues. Deep-well injection consists of injecting brines into aquifers 500–1500 m deep but risks pollution of adjacent aquifers used for drinking water purposes. Land application includes spray irrigation on salt-tolerant (halophyte) plants but is limited to small volumes of brines and depends on seasonal demand, climate and land availability. This may also pollute aquifers below the land and so is limited to shallow saline aquifers or deep isolated aquifers [4,155]. Disposal of brines into natural water bodies can be safe if diluted properly but often leads to eutrophication, thermal pollution, pH change, high levels of salts and heavy metals, and population drops (fish, oyster, plankton, sea grass) [254]. Therefore, the management of concentrated brines is crucial to achieving environmental protection. The advantages of ZLD include reduction of the volume of waste brines, increased water recovery, improved environmental sustainability and protection and allows resource recovery. Additionally, it facilitates acceptance of the projects by stakeholders and accelerates permitting.

Brines are defined as rejected and highly concentrated water containing >55,000 ppm TDS and sometimes up to 400,000 ppm TDS [4]. The concentration of salts and metals in brines is usually 2 or 2.5-times larger than in seawater [155,255]. Minimal liquid discharge (MLD) and ZLD aim at managing those highly saline brines to recover water and possibly valuable salts, thus reducing or avoiding brine discharge and increasing freshwater production. MLD can achieve up to 95 % water recovery while ZLD corresponds to 100 % water recovery. Brine management is also an issue faced by other sectors such as oil and gas, dairy and textile industries. Currently, the global brine production is 142 million m^3/day with a total freshwater production capacity of 95 million m^3/day, accounting to an average water recovery of around 40 % [5]. This means that brines still contain a large amount of water that could be recovered. The quality of brines depends on the industry, the initial feed water quality and the treatment process. Some brines contain organic pollutants, microorganisms, hazardous heavy metals and residual pretreatment chemicals such as anti-scalants, coagulants, flocculants, acids, bases, oxidizing and reducing agents [4]. ZLD systems consist of a pre-concentration step followed by a crystallisation step. MLD systems often simply use membrane-based technologies while achieving ZLD requires thermal-based technologies often combined with membrane-based technologies. ZLD is better in terms of environmental preservation and sustainability and is sometimes mandatory to comply with standards. Thermal-based technologies can easily achieve ZLD but come at higher costs than membrane-based technologies. As a result, combining membrane-based technologies with thermal-based ones has proven to lower the cost as well as the energy consumption of ZLD systems. Membrane technologies are more sensitive to high salinity levels due to risks of scaling and fouling which can damage the membranes. Thermal-based technologies have higher tolerance to high

salinity levels meaning they can reach high salinity limits. In that case, membrane technologies are used for pre-treatment and pre-concentration steps before thermal treatment. Membrane-based technologies reduce the volume of brines and increase water recovery [5].

Water recovered from ZLD systems can reach high purity as high as 99 % allowing water to be sometimes directly reused on site and minimizing water consumption. Typical ZLD configurations consist of a physical and chemical pre-treatment, an evaporative brine concentrator, a crystalliser and a solid-liquid separator to extract salt crystals [256]. Typical commercial ZLD systems also cost on average $250,000-$2 M for capacities between 5 and 100 m^3/day [255].

5.2. Pre-concentration of brines

Waste brines from desalination plants usually have a concentration of 60,000–70,000 ppm because serious scaling issues can happen above this threshold [6,13]. Before solid crystals can be extracted from waste brines, they must be pre-concentrated to reach a concentration close to the saturation limit. This can be done using different pre-concentration technologies [6,165]. A brine concentrator is a thermal technology that evaporates brines to produce high-quality distillate and highly concentrated brines (Fig. 15). A deaerator is utilised to eliminate non-condensable gases like CO_2 and O_2. In the brine concentrator, brines flow down several heat transfer tubes and a portion of the liquid evaporates. The liquid concentrated brine collects in the sump and mixes with the brine from the deaerator. The sump also recirculates back into the concentrator to increase concentration. The vapour flows through a mesh pad that eliminates any brine droplet from the vapour. Furthermore, the vapour then flows through a MVC that increases pressure to reduce energy consumption from the brine concentrator and the compressed vapour then circulates back into the brine concentrator on the outside of the heat transfer tubes. This vapour condenses on the outside of the tubes, flows down and is collected as a distillate. Consequently, this distillate is pumped through a heat exchanger to pre-heat the feed water. The density of the brine slurry is controlled periodically from small samples [6,165]. Brine concentrators can achieve water recovery up to 95–99 % [5,21,165,257]. Brine concentrators require significant energy between 18.5 and 26.5 kWh_e/m^3 for pre-treated feed water and as high as 39 kWh_e/m^3 for untreated feed water [6,165,183]. Brine concentrators can achieve concentration up to 250,000 mg/L and a concentration of the recovered distillate water below 10 ppm [165]. Brine concentrators are usually followed by a brine crystalliser to increase water recovery and salt extraction. This technology has an average specific investment cost (SIC) of 1800–4400 $/$m^3$/day [6]. The application of a falling film brine concentrator to treat wastewater at 90,000 ppm showed an energy consumption of 4.47 kWh_e/m^3 of feed brine and achieved a GOR of 3.55 [256]. The concentrator achieved 63 % water recovery and had a CAPEX of 1960 $/($m^3$/day) with an estimated annual OPEX of 1.73 $/$m^3$ of feed brine. Fig. 16 shows a diagram of a conventional thermal ZLD system.

Supercritical water desalination (SCWD) is an emerging ZLD technology used to pre-concentrate brines. Supercritical water (SCW) is water above its critical values: $T_c = 374.15$ °C and $P_c = 221.2$ bar. In these conditions, the properties of water change including lower density, viscosity, dielectric constant, and hydrogen bonding. Water loses its polarity and thus its solvation ability for salts which therefore precipitate. The energy needed to turn normal water to SCW is 555 kWh/m^3 of feed water. A SCWD system for ZLD was designed to treat seawater at 300 bar and 460 °C followed by a crystalliser [258]. The pilot was tested on a solution of water with 3.5 wt% NaCl and resulted in the production of 10 kg/h of fresh water with 750 ppm TDS. The thermal energy consumption of the system was 125 kWh_{th}/m^3 of product water. This SCWD system can achieve >93 % water recovery. Nevertheless, the system has to meet different challenges as it needs materials capable of withstanding super critical conditions, it consumes a significant amount of thermal energy, and the removal of salts must be controlled. The application of SCWD for water production from oil and gas reservoirs for feed water at 176,292 ppm for flow rates ranging from 2.3 to 113.6 m^3/h showed that the SCWD had a water production cost ranging between 22 and 109 $/$m^3$ [259]. The combination of a high temperature heat pump and a SWCD system for different feed concentrations to achieve ZLD was studied [260]. When adding the heat pump, for 35,000 ppm and 200,000 ppm feed concentration, the energy consumption of the system was reduced by 36 % and 14 % respectively and the cost of the produced water decreased by 15 % and 10 % respectively. The advantage is that electrical energy can be used to power the heat pump instead of thermal energy. Moreover, compared to a conventional set-up with a brine concentrator and an evaporative brine crystalliser, the heat pump-SWCD system is 20 % more energy efficient and 8 % less expensive when considering 250,000 ppm feed concentration. The capital cost of the system was estimated at 26.9 M$. The energy consumption of the SWCD system was estimated at 138.4 kWh_{th}/m^3 of distillate. The energy demand of the heat pump was 2.4 kWh_e/m^3 of distillate. The minimum LCOW was estimated at 7.6 $/$m^3$ with the heat pump as opposed to 8.9 $/$m^3$ without the heat pump. At 70,000 ppm feed concentration, the net energy consumption of the heat pump-SWCD system was 50.5 kWh_e/m^3

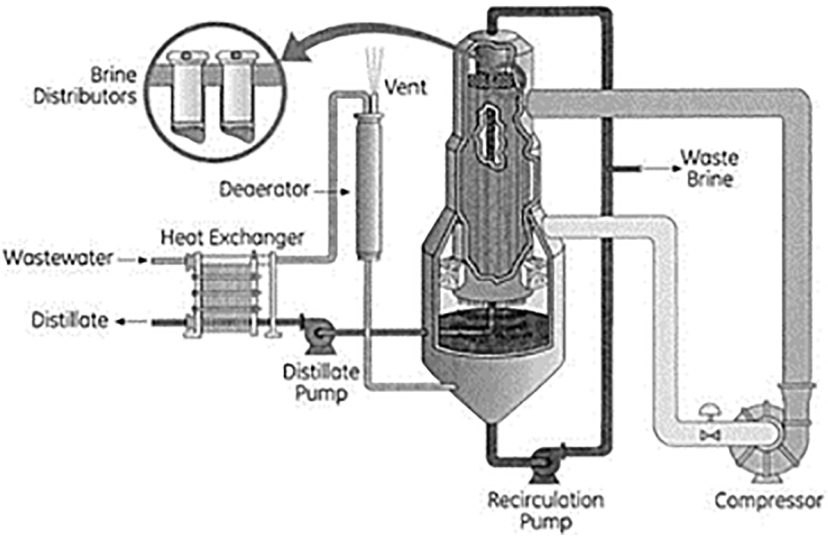

Fig. 15. Schematic of a brine concentrator with MVC. Reprinted from [263] with permission from Elsevier.

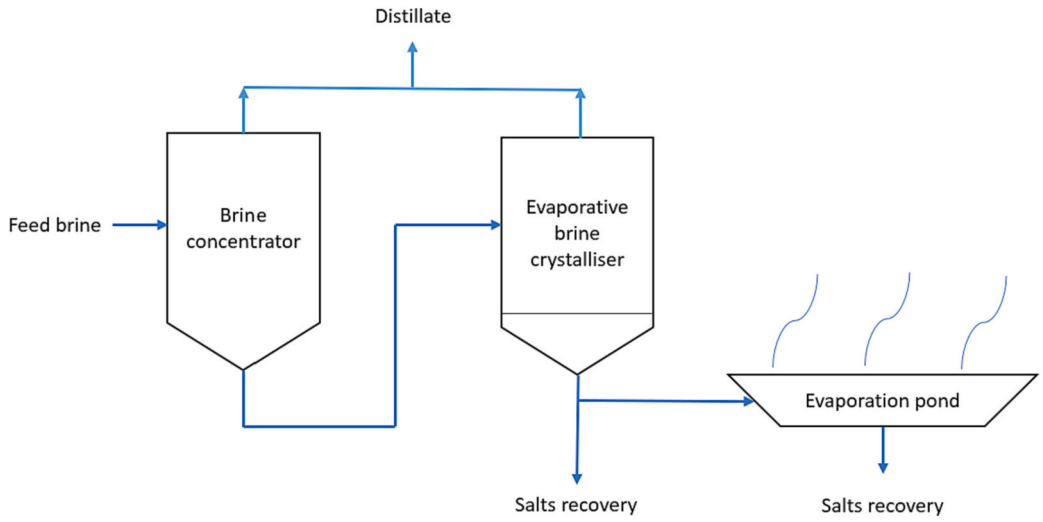

Fig. 16. Conventional thermal ZLD system diagram.

of distillate against 74.2 kWh_e/m^3 for a standalone SWCD system. SCWD was tested to achieve ZLD for brines with 35,000–200,000 ppm using a two-stage expansion-evaporation system [261]. The economic results show that the cost of brines varied from 9.61 $\$/m^3$ at 35,000 ppm to 1.16 $\$/m^3$ at 200,000 ppm because highly saline brines contain more salts that can be recovered and sold. The energy consumption of the system decreases with higher feed concentrations. This is because higher saline content decreases the heat capacity of the feed water which lowers the energy needed for heating. For example, the energy consumption for a feed stream at 140,000 ppm was 205.6 kWh_{th}/m^3 against 150 kWh_{th}/m^3 for a feed contain at 200,000 ppm.

RO systems typically operate at pressures up to 80 bar with a salinity limit at 70,000–75,000 ppm. But higher feed concentrations require higher operating pressure. High-pressure RO (HPRO) consists of using RO membranes operating above 100 bars for concentrations above 70,000 ppm. This operating condition achieves water recovery between 40 and 70 % with a SEC of 3–12 kWh_e/m^3. HPRO membranes capable of operating at 124 bar are now commercially available and can treat brines with up to 130,000 ppm which can be used to pre-concentrate brines [5].

Osmotically assisted RO (OARO) is an alternative to RO applied to highly saline brines. It works like RO but uses a saline sweep solution to lower the osmotic pressure which lowers the required pressure that must be applied to separate water and salts. It reduces energy consumption and cuts the need for materials capable of withstanding high pressures. OARO has been applied to brines with 100,000–140,000 ppm NaCl and water recovery between 35 and 50 %, SEC between 6 and 19 kWh_e/m^3 and a cost of water of 6.6 $\$/m^3$ have been reported [5]. RO systems can be configured in a cascading osmotically mediated RO (COMRO) configuration or in a OARO configuration. Those configurations use several stages of assisted RO in series. The COMRO arrangement has a better energy efficiency for high concentrations. OARO usually achieves 35–70 % water recovery with an energy consumption of 3.16–19 kWh_e/m^3 of produced water. For brines at 50,000–125,000 ppm, OARO costs about 6 $\$/m^3$ of produced water [262].

EDM is a variation of the ED technology and is used to increase the solubility of certain salts which have poor solubility in brines. It uses four ion-exchange membranes and four alternating chambers where the first one contains the feed brine, the second one a substitution solution of NaCl while the other two chambers contain a solution of highly soluble salts. The feed brine exchanges its ions with the substitution solution to produce a solution containing sodium and anions and a separate solution containing chloride and cations. Pilot scales experiments on RO brines reported 90 % water recovery and a SEC of 7–8 kWh_e/m^3. This technology can recover water as well as solid salts and a multi-batch configuration is possible for pre-concentration. EDM is currently limited to 5000 ppm TDS permeate concentration and its combination with other technologies is complex and costly [263]. However, EDM is still at a R&D phase and is highly sensitive to scaling like ED [5]. Additionally, bipolar membrane electrodialysis (BMED) is another form of ED/EDR that functions with bipolar membranes that split H_2O into protons and HO^- [6]. It consists of bipolar membranes and monovalent selective ion exchange membranes in an ED stack. Its advantage is it can regenerate monovalent ions while generating acids and bases. The system can treat brines and produce high purity solutions at about 2 mol/L NaOH and HCl [264]. This technology needs more research to evaluate its commercial feasibility.

Ohmic evaporation utilises alternative current power with a frequency of 60 Hz to create an electrical field strength between 24 and 87 V/cm to evaporate brines on small-scales. It is used to reduce the volume of highly saline brines up to 80,000 ppm and can reach water recovery up to 81–93.5 % [5,21].

5.3. Crystallisation methods

After pre-concentration, brines have a concentration that is high enough to allow crystallisation and salt recovery. There are mainly two types of crystallisers for brine treatment: evaporative crystallisers and eutectic freeze crystallisers (EFC). Evaporative crystallisers use thermal energy to evaporate water from highly concentrated brines – usually from a brine concentrator – to produce high-purity distillate and salt crystals. The concentrated brine is pumped into a heat exchanger to increase its temperature to above its boiling point. The heated brine then enters the brine crystalliser and flashes (Fig. 17). This concentrates the brine to the point where it exceeds saturation leading to the precipitation of salt crystals. The vapour flows through a mesh pad into a MVC. The compressed vapour is then fed into the outside of the heat transfer tubes of the heat exchanger to be recovered as a distillate. Crystallisers can also be arranged in a multi-effect configuration to reduce energy consumption [265]. Brine crystallisers consume a significant amount of energy between 50 and 70 kWh_e/m^3 due to highly saline and viscous nature of the feed brine [6,165,183]. Additionally, evaporative brine crystallisers use expensive materials for their pressure containers to resist corrosion. After precipitation of salt crystals, the water is recovered through a centrifugal pressure filter. Evaporative brine crystallisers can recover high-purity salts like sodium chloride, sodium sulphates, calcium sulphates, calcium carbonate, calcium chloride, magnesium hydroxide and gypsum-magnesium hydroxide [5,13,21]. This

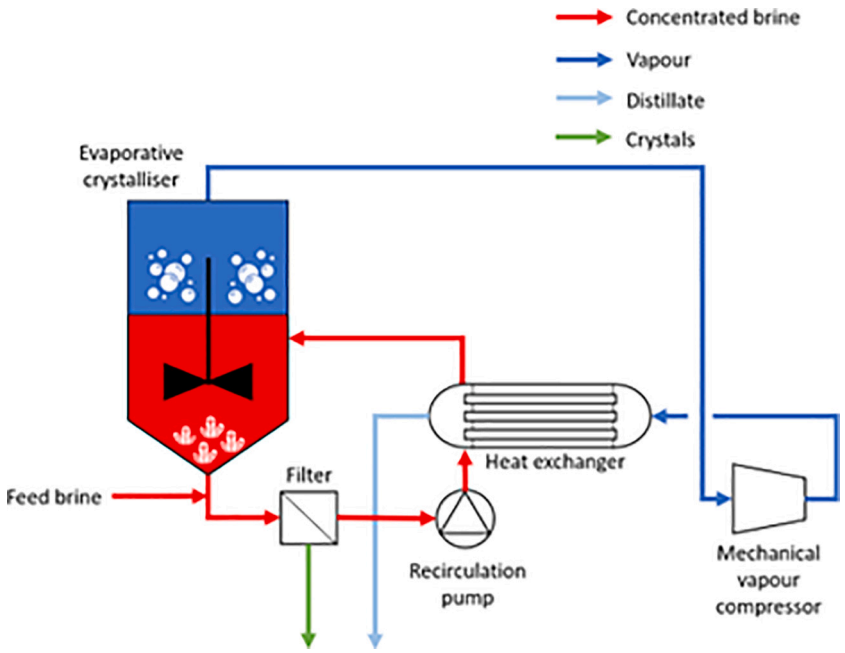

Fig. 17. Schematic of an evaporative crystalliser with MVR.

technology can reach 97–99 % water recovery but comes at high capital and operating costs [5]. A thermo-economic analysis of a WWTP with ZLD powered by solar energy was conducted in Iran [266]. The system consists of a falling film brine concentrator and a forced circulation brine crystalliser. The application of MED and evaporative brine crystalliser to treat brines at 70,000 ppm was also studied [267]. The MED system was set in a forward feed configuration to maximize concentration in the last effect because it has the lowest temperature which minimizes fouling risks. The system capacity and the specific heat consumption varied between 50 and 1000 m^3/day and 167–306 kWh_{th}/m^3, respectively. The energy consumption is reduced with increasing the number of stages. The specific cost of the ZLD system was estimated at 4.17 $/$m^3$. Additionally, the system has the potential to increase profitability by selling crystals. A recent study [183] investigated the cost of crystallisers for different capacities of 10, 100 and 1000 m^3/day and found SIC values of 54,780 $/$m^3$/day, 19,066 $/$m^3$/day and 8542 $/$m^3$/day respectively. As expected, the SIC decreases as the treatment capacity increases due to the economy of scale which offers potential commercial feasibility for large-scale plants.

The application of a solar evaporator with controlled salt precipitation for ZLD desalination has been recently studied [268]. The advantage of solar distillation is that it does not require moving parts, no high/vacuum pressures and functions solely on free solar energy. A 3D cup-shaped solar evaporator pilot was tested with highly concentrated saline brines with 25 wt% NaCl. The results show that the 3D design is capable of higher efficiency than the 2D design because it can absorb reflected light as well as convection heat losses. The results also show that increasing the concentration of the feed brine slightly reduces the evaporation rate. With a feed concentration of 25 wt% under one sun irradiations (1000 W/m^2), the average evaporation rate was measured at 1.36 kg/m^2/h. This corresponds to an efficiency of 88.4 %. This system can be used as a brine crystalliser converting highly concentrated brines from a brine concentrator into crystallised salt to reach ZLD. Later, a similar but improved next generation solar crystalliser for ZLD was designed (Fig. 18) [255]. Results show high removal of water of 1.61 kg/m^2/h when considering one sun radiations on brines with 24 wt % NaCl. Additionally, an array of 12 solar crystallisers presented an evaporation rate of 48 kg/m^2/day which show potential for industrial usage. This design is easily scalable for small and medium scales but might not be effective for large volumes of brines because it would require larger land areas. The design's advantage is that crystals form on the outer side which is cooler which reduces solubility of NaCl to facilitate crystallisation. This improved design shows better performance than that of the system discussed by Shi et al. [268] which is thought to be due to uniformly distributed irradiation. This technology has the potential to achieve low cost thanks to its simple design.

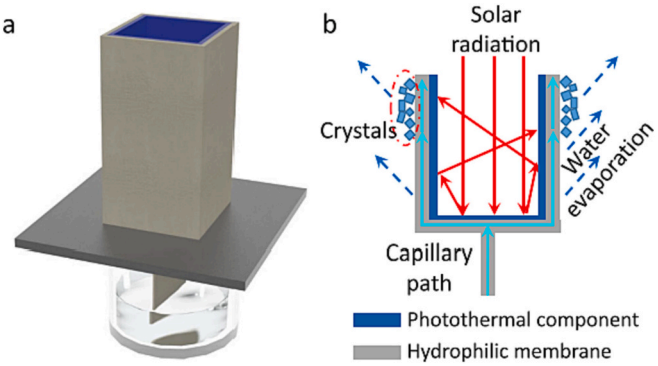

Fig. 18. Schematic of the solar crystalliser [255]. a: 3D schematic of the solar crystalliser; b: cross section view of the solar crystalliser. Reprinted under Creative Commons License (https://creativecommons.org/licenses/by/4.0/).

EFC is similar to FM but can be used to recover salts and water from concentrated brines. It utilizes the density difference between ice and salt and takes advantage of the eutectic temperature for separation. Below the eutectic temperature, water and salt crystallise. Conventional freeze crystallisation systems consume 43.8–85 kWh_{th}/m^3 of feed water with 66.7 % accounting for the refrigerant cycle, 14.2 % for the wash column and 14.2 % for the crystalliser [5,263]. The application of EFC to treat RO brines from industrial mining was studied [269]. 5000 g of brines containing 27,400 ppm TDS with several levels of cations and anions were treated to a temperature of −22 °C. The ice was vacuum filtered and salts were filtered separately. Ice had to be washed off with de-ionised water. The system consisted of 3 stages which gradually crystallise the compounds. The system can recover 97 % of water from the brines as well as 98 % pure calcium sulphate and 96.4 % pure sodium sulphate. The advantage of EFC over evaporative crystallisation is that the latent heat of fusion is 7-times lower than the latent heat of

evaporation. During crystallisation, impurities are removed from ice via gravitational separation due to the density difference. Ice floats on top while salts sediment. The eutectic condition has the potential for 100 % efficiency. Moreover, the low temperature reduces corrosion effects allowing the use of cheaper materials. Water crystallises first for low concentrated solutions. As the temperature decreases, water crystallises while salts remain soluble until the system reaches the eutectic state where salts crystallise too. Using this method, it is possible to crystallise brines containing multiple salts by applying different successive eutectic temperatures for each salt to achieve salt fractionation. The application of EFC was studied to treat copper sulphate solutions and found that EFC consumed up to 70 % less energy than a typical 3-stage evaporative crystalliser [270]. The economics of EFC for solutions containing magnesium sulphate was analysed and found that EFC could reduce the energy costs by up to 60 % compared to conventional evaporative crystallisers [271]. Additionally, Nathoo et al. [272] showed that using EFC to treat two brines consisting of Na_2SO_4 and NaCl could reduce the operating cost by 80 % and 85 % respectively compared to evaporative crystallisers. However, the capital cost of the EFC was 179–208 % larger than the evaporative crystalliser. The application of a brine concentrator with a cascaded fluidised bed freeze crystalliser was also studied [263]. The feed brine was a 77,000 ppm NaCl solution brought from 25 °C to below 0 °C. The system used a cooling cycle consisting of a refrigerant flowing inside a compressor, condenser and expansion valve and a precooler. This ZLD system consumed 74 kWh_{th}/m^3 of feed which is 13 % lower than conventional freezing concentration systems and 56–68 % lower than an evaporative crystalliser.

Evaporation ponds are used to reduce brine volumes and recover salts. They require very low maintenance and are easy to build with an average depth of 0.5–2 m [273]. To avoid leaks of brines into the surrounding groundwater, adequate impermeability is needed. Geosynthetic liners are used to avoid leaks due to seepage. The most common liner materials include reinforced PE and PP because of their easy installation and welding [274]. The land area required varies between 1000 and 4000 $m^2/(m^3/day)$ but this can be reduced when combining solar ponds with other brine management technologies [5]. Evaporation ponds use solar energy which means cheaper energy consumption. They consist of large shallow ponds where water from brines evaporate naturally with solar energy. This technology is suitable for dry regions with large available land areas and abundant solar radiations. However, this can be expensive and it achieves low efficiency and slow evaporation. Evaporation ponds are only cost-effective for small volumes of brines in dry air weathers [263]. The cost of evaporation ponds varies between 3.28 and 10.04 $\$/m^3$ of treated brines [4]. Salinity-gradient solar ponds are another form of solar ponds which can be used to recover salts periodically (Fig. 19). Those solar ponds have three gradient zones: the upper convection zone with low salinity and low temperature, the middle non-convection zone with an intermediate salinity and temperature, and the lower convection zone which has the highest salinity and temperature. This temperature gradient can be used to generate electricity in some cases [251]. A new solar evaporation pond system was also studied [273] by looking at passive and non-contact method to increase evaporation rate by >100 % with a photo-thermal umbrella placed above the pond that transforms solar radiations into mid-infrared light that water absorbs more. The heat is focused on the surface of the water, instead of only the bottom in conventional evaporation ponds, which allows a conversion efficiency of 43 %. This system can be used for different wastewater qualities because of the non-contact feature and has potential for scale-up. The umbrella reaches up to 70 °C and the water surface can heat up to 40 °C. At a lab scale with 250,000 ppm NaCl, this system can achieve an evaporation rate up to 14.3 $kg/m^2/day$.

Passive solar stills consist of an insulated glass cover, a basin, a black plate and water-collection trenches and use the greenhouse effect to evaporate the feed water in the basin. Sunrays are partially transmitted through the glass and then absorbed by the black plate and the water which evaporates and then condenses on the glass cover. The black plate is used to increase radiation absorption and thermal efficiency. Passive solar stills do not require additional energy input except if pumps are needed to drive the feed water into the basin [170]. Freshwater is then harvested inside trenches. Solar stills are used for the small to medium scale desalination. They are cheap, easy to build and require very low maintenance but achieve low freshwater production between 4 and 6 $L/(m^2/day)$. The cost of water from solar stills varies widely between 1.2 and 21 $\$/m^3$ [5,275]. Different solar still geometries include stepped, pyramidal, hemispherical, tubular and double-slope [275]. A double-slope passive solar still was used for brine management with lithium and water recovery [276]. Both experimental and theoretical simulations were carried out to evaluate the potential of this technology as an alternative to conventional evaporitic lithium extraction. Using feed brines highly concentrated with lithium for 12 months, the solar still was able to produce freshwater at an average rate of 2 $L/(m^2/day)$. Active solar stills are similar to passive ones but use additional equipment to increase performance such as solar collectors, internal or external reflectors, wick materials, internal or external condensers, solar tracking systems, phase change materials, hybridisation with HDH, PV/T panels or nanoparticles [275].

Wind-aided intensified evaporation (WAIV) is a technology used to minimise brine discharge and recover salts. It consists of large vertical hydrophilic surfaces onto which brines circulate and evaporate with the wind passing between each surface (Fig. 20). Brines recirculate to increase evaporation rates. The remaining concentrate is collected and post-treated. This technology is an alternative to evaporation ponds that require larger land area. Surfaces are usually made of sheets of fabric such as cotton to increase capillarity or sometimes PP [277]. The evaporation rate is proportional to the difference in partial pressures between the vapour and the liquid phases which depend on the temperature. Studies on a pilot WAIV unit with evaporation surfaces

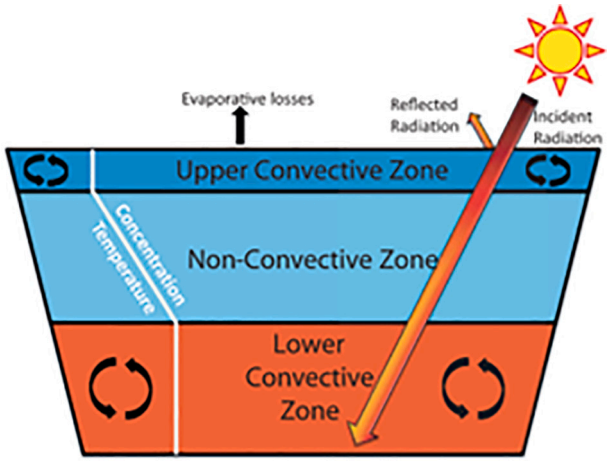

Fig. 19. Schematic of a salinity-gradient solar pond. Reprinted from [349] with permission from Elsevier.

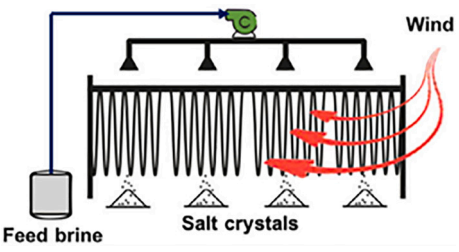

Fig. 20. Schematic of a WAIV system [350]. Reprinted under Creative Commons License.

between 31 and 43 m^2 resulted in evaporation rates of up to 90 % of the total feed volume [278]. Combination of WAIV and membrane distillation crystallisation (MDC) to treat BWRO brines reduces brine discharge between 0.75 and 0.27 % of the raw intake water and can reach higher water recovery between 50 and 90 % [5,279].

A spray dryer consists of a vertical container inside which brines are sprayed alongside a drying gas (hot air) circulating in a centrifugal manner which separates the liquid phase from the solid saline phase via a bag filter, allowing recovery of dry salts. The thermal SEC of spray dryers varies between 52 and 64 kWh_{th}/m^3 with a salinity limit around 250,000 ppm. However, the water that is evaporated is not recovered [5,21].

5.4. Emerging ZLD approaches

5.4.1. Hybrid ZLD approaches

Many studies have been conducted on the combination of different technologies to achieve ZLD. MDC corresponds to the combination of a MD module with a crystalliser and can treat highly concentrated brines using low-grade heat to recover water and salts. MDC is currently the most studied technology for resource recovery from brines. Fig. 21 shows a diagram of a MDC system. It operates in closed-loop where feed water gets gradually concentrated through the membrane after each passage until it reaches supersaturation. Then it passes in the crystalliser to induce precipitation to recover salts. The remaining liquid gets reheated before re-entering the MD module. On the MD side, the permeate must be continuously cooled down to create the temperature difference across the membrane. Thus, MDC needs a combination of heating and cooling which leads to high heat losses and high energy consumption. MDC can be combined with different MD configurations including VMD which can recover 95 % of water and NaCl [280]. Other designs include submerged MD inside the crystalliser which reduces heat losses due to pipe circulation and increases compactness as show in Fig. 22. MDC has the advantage of being more tolerant to fouling and scaling than traditional membrane technologies like RO and NF which allows to reach higher salinity limit at 350,000 ppm [251]. MD modules are seen as a potentially economic alternative to brine concentrators which are expensive [165]. However, MDC applications are still limited to laboratory scale because they achieve low permeate flow, high energy consumption and high investment costs. The thermal SEC of pilot-scale MD systems is on average between 90 and 200 kWh_{th}/m^3. Currently, MDC is the most expensive technology with an average SIC of 6500 $\$/m^3$/day [6]. But large-scale applications have potential to reduce costs due to the modular design advantage over brine concentrators. Additionally, MD modules can use cheap waste heat because they operate at low temperature < 85 °C. Nonetheless, MDC still faces challenges including risks of wetting, fouling and scaling on the membrane as well as volatile pollutants and surfactants that can pass through the membrane which reduces efficiency and thus requires pre-treatment [13,165]. Moreover, compared to concentrators, MD alone consumes more energy on average between 39 and 67 kWh_e/m^3 and has a higher cost of water between 0.6 and 2.0 $\$/m^3$ [4–6]. When combined with a crystalliser, the SEC and water cost of MDC can increase varying from 39 to 73 kWh_e/m^3 and 2.61–2.7 $\$/m^3$ respectively. But the option to sell salts can reduce this cost to 1.24–1.4 $\$/m^3$ and make it competitive [4–6]. The crystallisation can be easily controlled via evaporation through the membrane because it happens uniformly unlike evaporative brine crystallisers [5].

Membrane-based technologies are highly sensitive to high feed concentrations and consume much more energy for high-salinity brines, but evaporative brine concentrators are less sensitive to high concentrations. Thus, placing a RO unit before a brine concentrator reduces the volume of brines fed to the concentrator and crystalliser and lowers the total energy consumption while increasing water recovery. This system is profitable if the brines entering the RO unit have a concentration below 70,000 mg/L. This set-up can save 58–75 % of energy and 48–67 % of the treatment cost in comparison to a brine concentrator-crystalliser-evaporation pond set-up [165]. Different thermal and membrane-based ZLD systems for textile effluents were studied [281]. These effluents were separated between dyebath and wash water and treated using different feed flow rates ranging from 380 to 900 m^3/day using different combinations of RO and NF. The rejects were then processed through a multi-effect evaporator followed by a crystalliser and/or a solar evaporation pond. Results indicated that a biological pre-treatment and UF were necessary prior to the RO unit to reduce COD and SDI to achieve sufficient feed quality. The system can achieve 87 % water recovery and 71 % salt recovery. Similarly, RO systems combined with multi-stage ED/EDR increases the concentration capability of RO and can achieve lower energy consumption than brine concentrators [165].

A techno-economic comparison between four different hybrid ZLD systems was conducted [282] namely (1) evaporation/crystallisation, (2) evaporation/spray drying, (3) MDC and (4) MD/spray drying. The systems were simulated for a feed flow rate of 1500 m^3/day at 80,000 ppm TDS. The results estimated LCOW values for (1) 8.1 $\$/m^3$, (2) 22.1 $\$/m^3$, (3) 8.4 $\$/m^3$, (4) 20.7 $\$/m^3$. So, evaporation/crystallisation and MDC were the cheapest while evaporation/spray drying and MD/spray drying were the most expensive. The application of integrated

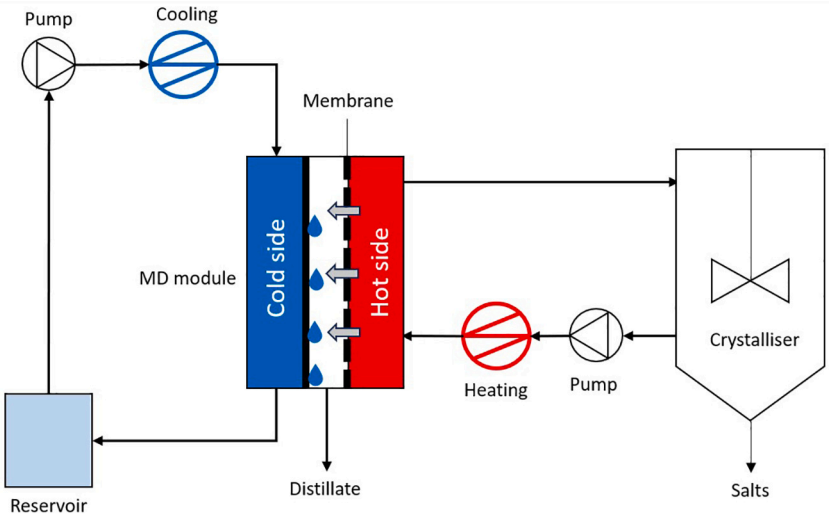

Fig. 21. Schematic diagram of a MDC system.

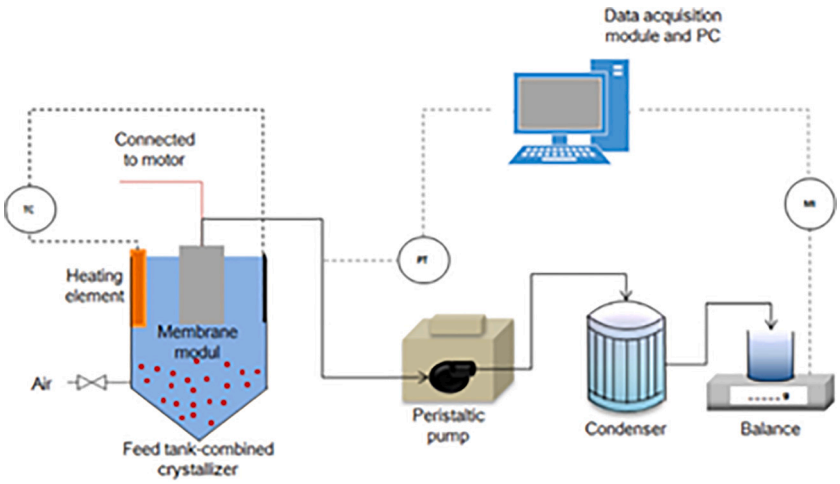

Fig. 22. Schematic diagram of a submerged MDC set-up. Reprinted from [351] with permission from Elsevier.

membrane systems was studied to achieve ZLD for oil & gas produced wastewater [283]. The system combined ED, NF and MD. When considering an initial feed concentration of 2430 ppm TDS, the system was capable of producing brines of extremely high concentrations up to 373,000 ppm TDS and a recovery of 99.8 % without using anti-scalant. Scaling is prevented by separating bivalent positive ions (Mg^{2+}, Ca^{2+}) and negative ions (SO_4^{2-}) in separate chambers using EDM. Brines are then fed to a NF unit and then to a VMD module. The results show that the SEC of the total system was 33 kWh_e/m^3 and 154 kWh_{th}/m^3 of feed water. The ED system consumed 2 kWh_e/m^3 and the NF 29 kWh_e/m^3. Cutting the need for anti-scalant, this technology has the potential to achieve lower cost. Additionally, the combined use of DCMD and EDR for SWRO brines was studied to achieve ZLD [107]. In their pilot, pre-treated seawater was fed to a RO unit and the concentrate was fed to the DCMD system. The rejected brine was fed to the EDR system as the highly concentrated solution. Results suggest this system can reach water recovery up to 92 %. A mathematical model of a freeze desalination (FD) system combined with MDC was built for ZLD powered by renewable energies [152]. The model was designed to treat 72 kg/day of feed seawater using solar panels. Combining MD with crystallisation allows one to reduce the SEC and increase recovery. In this model, FD consists of an ice crystalliser and a filter to separate brines and ice crystals. Additionally, the higher the salt concentration, the greater the amount of salt on the ice crystals. However, FD is not economical alone, but combining FD with MDC is interesting because MD is less sensible to high concentrations than FD. In this study, the model was tested with seawater at 3.5 wt% NaCl as the feed for FD. The results suggest the FD-MDC unit can achieve 30 % and 70 % water recovery respectively, achieving 100 % ZLD. The model found that recycling the thermal energy between the hot and cold streams can save up to 18 % of the total SEC. The model can produce 2.52 kg/day of salt and recover 69.48 kg/day of water. The final SEC was 58.3 kWh_e/day of hot energy and 59.8 kWh_e/day of cold energy. To reduce SEC, the study suggests high MD feed temperature and concentration, high distillate temperature and FD recovery. But this model is very sensitive to feed and distillate flow rates [152].

The potential of using COMRO was analysed to regenerate the draw solution of FO systems to recover more water from metallurgical industry brines [262]. NaCl was used as the draw solution and the feed brine entered the system at 17 m^3/h with 41,038 ppm TDS. The brine enters the FO-COMRO process and produces fresh water and highly concentrated brines which are then further treated by an evaporative crystalliser. The results estimate that 75 % of the water can be recovered with an energy consumption of 7.4 kWh_e/m^3 at a cost of 6.05 $/$m^3$ of recovered water. The total capital cost of the FO-COMRO unit was estimated at 2.34 M$ with an OPEX of 377 k$/year. The application of ZLD technologies for steam assisted gravity drainage (SAGD) heavy oil wastewater has been recently studied [284]. The technology uses brine concentrators and evaporative crystallisers. Industrial heavy oil wastewater typically contains several salts and organic compounds which form mixed salt brines. This requires the use of specific brine crystallisers with different designs to prevent fouling and scaling. Additionally, highly concentrated mixed salt brines have higher boiling points which leads to adequate sizing. Brine concentrators and brine crystallisers can be used in SAGD to recover and reuse pure water to achieve ZLD. They can also be used to treat blowdown from steam generators or as a pre-treatment process for feed water to the steam generator if the TDS concentration is higher than 8000 ppm. In this case, the process can recover high quality water with <10 ppm TDS. Mechanical vapour recompression (MVR) can be used for the concentrator and crystalliser instead of the MVC mode in the absence of low-pressure steam. ZLD for SAGD is a proven technology that has already been implemented to >100 installations.

The ZLD technology trends have been studied for coal chemical industries in China [285]. There are different treatment configurations depending on the quality of the feed wastewater and the coal chemical process used to produce oil. For direct coal liquefaction (DCL) processes, wastewater with high organic content or containing oil have to go through a pre-treatment step before entering an anaerobic degradation tank and a MBR. A NF/RO system is then used to further process the effluent with a recovery rate of 75 %. The reject and the blowdown from the cooling tower are treated through a MF/RO unit which recovers on average 70 % of water. The rejected brine from this process is sent to an evaporator with an average recovery of 92 %. The brines are then treated with an evaporation pond. For indirect coal liquefaction (ICL), wastewater with organic content is pre-treated with an aerobic biodegradation system and an ozone and biological aerated filter followed by a UF/RO system with 75 % recovery. An evaporator and evaporation pond are then used to concentrate brines. For wastewater containing salts, a pre-treatment and a UF/RO unit are used to recover 94 % of water on average. Rejected brines are then treated with evaporators followed by either an evaporation pond or a crystalliser. A pilot study was conducted to treat palm oil mill effluent (POME) to achieve ZLD [286]. The pilot treated 5 m^3/h of feed POME. The results suggest the system can achieve 100 % ZLD, zero GHG emissions and low capital and operating costs. The system can process POME from 27,000 ppm to 20 ppm biochemical oxygen demand (BOD). The biological treatment consists of an anaerobic digestion and aerobic biodegradation system. The membrane system uses several UF and RO membranes. The produced biogas is used in a biogas engine to produce electricity.

A FO pilot for ZLD was able to concentrate brines from 73,000 to 180,000 ppm TDS [287]. FO is capable of low and reversible membrane fouling, greater salt rejection and is less susceptible to contaminants in the feed water. It consumes less energy than conventional desalination solutions and can reach high water flow rate and high recovery. FO can be used for feed water with salinities up to 218,000 ppm but requires a high SEC of around 285 kWh_e/m^3 as a result of the high concentration. However, it can be combined with MD to act as a membrane brine concentrator (MBC) to reduce energy consumption [6]. Combinations of RO and FO have shown to be able to concentrate up to 220,000 ppm using a draw solution of NH_3/CO_2 [165]. FO has the disadvantage of consuming a lot of energy for the regeneration of the draw solution [262]. This system consists of two RO chambers: a high-pressure chamber at 60–70 bar with the highly saline feed and a low-pressure chamber with a low saline solution named sweeping solution. The pressure difference between the feed and the sweeping solution is higher than the osmotic pressure which induces water flow from the feed to the sweeping solution. A concentration of the sweeping solution below 40,000–50,000 ppm NaCl allows the sweeping solution to be treated in a normal RO system for additional water recovery. But higher concentrations require the sweeping solution to be treated with OARO or COMRO [5].

5.4.2. Techno-economics of ZLD

Table 12 lists and compares the results from different techno-economic case studies. Table 13 summarises and compares the performance and techno-economics of the ZLD technologies. A system combining a brine concentrator and an evaporative brine crystalliser is the most common and usually the most economic with an average produced water cost of 0.82 $/m^3$ while a system with a brine concentrator with evaporation ponds is the second cheapest with 1.1 $/m^3$ [6]. Few studies have analysed the economics of salt recovery from ZLD systems. Panagopoulos, 2021 [162] compared the economics of a conventional thermal ZLD system consisting of a brine concentrator and an evaporative brine crystalliser applied to either a BWRO or a SWRO plant. On a basis of 100 m^3/day of feed brine, results suggest that the cost of treated brine is 0.84 $/m^3$ for the BWRO case as opposed to 1.04 $/m^3$ for the SWRO case due to the higher energy demand. Recovering salts increases profits from 2.15 $/m^3$ to 3.02 $/m^3$. A later study [288] compared the economics of the same ZLD system to a brine concentrator/WAIV set-up applied to a SWRO plant of 100 m^3/day. Results show that the water recovery, SEC and cost of treated water are respectively 99.14 %, 22.15 kWh_e/m^3 and 1 $/m^3$ for the first system as opposed to 85.75 %, 15.34 kWh_e/m^3 and 0.853 $/m^3$ for the WAIV system. The WAIV alternative consumes less energy and is cheaper but it does not allow water recovery which can be sold in the first scenario. But both options are profitable with profits ranging from 1.80 $/m^3$ without salt sale and up to 2.26 $/m^3$ with salt sale. A techno-economic comparison between AGMD and MVC for ZLD application was conducted [183]. The systems were simulated for different feed flow rates ranging between 100 and 350 kg/h and for feed salinities at 70,000 ppm and 240,000 ppm. The results show that MD can be 40 % more cost-effective than MVC and even up to 75 % more cost-effective if MD uses waste heat.

5.4.3. Value added minerals extraction

Recovered salts can be sold, reused on site or disposed ecologically. Salts are widely used in chemical industries consuming about 11.5 million tons per year [98]. Desalination brines usually have major quantities of Cl, Na, SO_4, Mg, Ca and K as well as minor quantities below 1 ppm of Li, Rb, B, Sr, In, Ba, Ni, U, Cs and Ge. The different salts that can be recovered from brines include sodium chloride, calcium carbonate, gypsum, sodium sulphates, sodium hydroxide, calcium sulphates, calcium chloride, magnesium sulphate, magnesium hydroxide, magnesium oxide, bromine, rubidium, uranium, potassium, lithium, cesium, nickel and vanadium [5,155]. Technologies for salt recovery from brines include mostly crystallisers but also solar evaporation ponds via evaporitic extraction, MDC, ED/EDR, ion-exchange as well as direct metal extraction methods such as adsorption, electrochemical methods, solvent extraction, reactive crystallisation, and selectrodialysis (SED) [98]. Combining different ZLD technologies is recommended to lower costs and energy consumptions and to increase resource recovery [5]. Figs. 23–25 show different recent systems to recover salts. The advantages of salt and metal recovery from brines include reduced cost of water, increased profit, avoiding the environmental impacts of brine discharge and increasing sustainability by responding to the raising demand for rare salts and metals like lithium. However, such technologies are still at a R&D phase and require further development to increase their commercial feasibility and profitability for industrial scales. Sodium, magnesium, potassium and bromide extraction techniques are well-known as precipitation, ion-exchange, adsorption and membrane separation. However, metals present in trace amounts in brines like rubidium, uranium, cesium, nickel, vanadium and lithium are currently difficult to extract due to their low concentration. The separation of monovalent and multivalent ions is important for resource recovery and can be done through NF or SED. NF can reach high calcium retention

Table 12
List of the summarized results from different studies on ZLD. *The value is expressed per cubic meter of feed water. Subscripts: th: thermal; e: electric.

Feed water type	ZLD system	Initial TDS (ppm)	Final TDS (ppm)	Water recovery	Energy consumption (kWh/m^3)	Specific recovered water cost ($/m^3)	References
Industrial wastewater	Brine concentrator + evaporative crystalliser	42,000	70,000	40 %		3.5	[266]
RO brines	MD	70,000	250,000	72 %			[183]
RO brines	MVC	70,000	250,000	72 %			[183]
Metallurgical industry brines	FO-COMRO	41,038	164,152	75 %	24.67th	6.05	[273]
Desalination brines	MED + evaporative crystalliser	70,000	260,000	73 %	167-306th	4.17	[267]
Industrial wastewater	Falling film brine concentrator	90,000	243,243	63 %			[256]
Oil & gas wastewater	SCWD	75,000–270,000		40 %–60 %		21.95–108.69	[259]
Concentrated brines	Cascaded fluidised bed crystalliser	77,000			168.33th*	7.6	[260]
Oil & gas wastewater	ED-NF-MD	2430	373,000	99.80 %	154th*		[107]
SWRO brines	MD + RO			92 %			[152]
Flue gas desulphurisation wastewater	Forced circulation 3-effect MED and crystalliser	50,000	250,000	84.2 %	212th +15.4e	5.60–10.24	[289]
Seawater	Low-salt rejection RO	35,000	234,000	50–75 %	2.4–8.0e*		[290]
Ultra-high salinity brines	Temperature swing solvent extraction	295,000	33,100	91.2–95.9 %	172th*		[291]

Table 13
Techno-economic comparison of the different ZLD technologies. Subscripts: th: thermal; e: electric. Results are expressed per cubic meter of produced water.

Technology	SEC (kWh/m^3)	LCOW ($/$m^3$)	SIC ($/($m^3$/day))	Salinity limit (ppm)	Water recovery	Land footprint ($m^2/(m^3/h)$)	Recovery	Advantages	Disadvantages	References
MSF	69.4–83.3th + 2.5-5e or total equivalent 12.2–27.3e	0.56–1.75	1230–2800	70,000–180,000	85–90 %	4.5–5	Water	High salinity limit; low temperature; high-quality freshwater; large scale; low pre- and post-treatment required.	High SEC and SIC; sensible to scaling, fouling and corrosion.	[4,5,164,170,292,293]
MED	41.7–61.1th + 0.5–2.5e or total equivalent 7.7–21.35e	0.52–1.10	1230–2800	70,000–180,000	93 %	4.5–7	Water	High salinity limit; low temperature; high-quality freshwater; large scale; low pre- and post-treatment required.	High SEC and SIC; sensible to scaling, fouling and corrosion.	[4,5,164,169,170,292–294]
VCD	10–55.6e for TVC and 7-25e for MVC	2.0–2.6		High	92 %		Water	High salinity limit; high-quality freshwater; low pre- and post-treatment required.	Limited to small scales; high investment and operating costs; risk of scaling, fouling and corrosion on compressor.	[5,6,165,170]
Brine concentrator	15.9–26.5e	1.11	1800–4400	250,000	60–99 %		Water	High salinity limit; high-quality freshwater; high concentration; large scale.	High investment and operating costs; risk of scaling, fouling and corrosion; high SEC.	[4–6,21,165,183]
Evaporative brine crystalliser	50-70e	1.22	500–2000	300,000–350,000	97–99 %		Water and salts	High salinity limit; high-quality freshwater; high concentration; large scale; salt recovery.	High SEC and investment and operating costs.	[5,6,165,183]
Solar crystalliser	413.2-621th			250,000	88.4–94.3 %		Salts	Simple design; free energy; salt recovery; modular design; easy scale-up.	Large land area; low efficiency; difficult to control crystal growth; slow process; no water recovery; low evaporate rate between 1.36 and 2.42 L/(m^2/h).	[255,268]
EFC	43.5-85th	1.42		250,000	98 %		Water and salts	High salinity limit; salt recovery; theoretical energy consumption is lower; can recovery different salts separately.	High investment cost; ice crystals must be washed off with freshwater; low efficiency.	[4,5,269,263]
SCWD	125–555.6th	1.16–108.7	22,150	250,000	93 %		Water and salts	High salinity limit; water and salt recovery; energy consumption decreases with higher feed concentrations.	High SEC and high investment and operating costs.	[258,261]
Evaporation pond	559.4–895.2th	3.28–10.04		High	99 %	8000–32,000	Salts	High salinity limit; free energy; low investment and operating costs; easy to build; low maintenance required; salt recovery.	Large land area; low efficiency; slow process; no water recovery; risk of brine leaching; low evaporation rate between 0.25 and 2 L/(m^2/day) and up to 14.3 L/(m^2/day) with enhanced umbrella.	[4,5,273,276,263]
Passive solar stills		1.20–21.13		High	99 %	1333–4000	Water and salts	High salinity limit; free energy; low investment and operating costs; easy to build; low maintenance required; water and salt recovery; high-quality freshwater.	Large land area; low efficiency; slow process; low freshwater production between 2–6 L/(m^2/day).	[5,276]
WAIV	0.3–1.5e	1.37		100,000–200,000	50–90 %		Salts	Free energy; low investment and operating costs; easy to build; salt recovery.	Low efficiency; no water recovery; slow process; risk of brine leaching.	[4,5,279,263]
Spray dryers	52-64th	0.09$/kg of salt		250,000	99 %		Salts	Easy to control salt growth; salt recovery.	High energy consumption; limited to small-medium scales; no water recovery; pretreatment required to remove impurities.	[4,5]
Ohmic evaporators				80,000	81–93.5 %		Water	Reduction of brine volumes; water recovery; high-quality freshwater.	No salt recovery; limited to small scales.	[5]
RO	2-6e	0.26–0.75	1000–2500	70,000–75,000	75–85 %	3.5–5	Water	Low energy consumption; low investment and operating cost; low LCOW; high water recovery.	No salt recovery; low salinity limit; sensible to scaling and fouling; short membrane life; lower quality freshwater.	[4–6,164,165]

(*continued on next page*)

Table 13 (*continued*)

Technology	SEC (kWh/m^3)	LCOW ($/m^3)	SIC ($/(m^3/day))	Salinity limit (ppm)	Water recovery	Land footprint (m^2/(m^3/h))	Recovery	Advantages	Disadvantages	References
HPRO	3-12e	0.79		120,000–130,000	40–70 %	3.5–5	Water	Low energy consumption; low cost of water; water recovery; higher salinity limit than RO.	No salt recovery; low salinity limit; sensible to scaling and fouling; short membrane life; lower quality freshwater.	[4,5]
OARO	3.16-19e	2.4–6.6		100,000–140,000	35–72 %	3.5–5	Water	Low SEC, higher salinity limit and lower cost than HPRO; water recovery.	No salt recovery; low salinity limit; sensible to scaling and fouling; short membrane life; lower quality freshwater.	[4,5,262]
MD	39-67e	0.26–130	1000–1500	200,000–350,000	50–90 %		Water	High salinity limit; can use waste heat; high-quality freshwater; water recovery.	High SEC; risk of membrane wetting, scaling and fouling, short membrane life.	[4–6,165,183,193,194]
MDC	39-73e	1.24–2.7	6500	350,000	50–90 %		Water and salts	High salinity limit; can use waste heat; high-quality freshwater; water and salt recovery.	High SEC; risk of membrane wetting, scaling and fouling; short membrane life.	[4–6]
FO	0.8–16.7e or up to 285e	0.55–0.63	1000	200,000	50–98 %		Water	Low pressure; low cost; water recovery	Risk of scaling and fouling; no salt recovery.	[4–6,262,287]
ED/EDR	0.7-850e	0.85–10	500	100,000–150,000	85 %		Water	Low pressure; low cost; water recovery; scaling and fouling are reduced with EDR.	Energy consumption depends heavily on feed concentration; risk of scaling and fouling; no salt recovery.	[4–6,165,170]
EDM	0.6-8e	0.60		150,000	90–92 %		Water and salts	Low pressure; water and salt recovery.	Risk of scaling and fouling; no salt recovery.	[4–6,263]

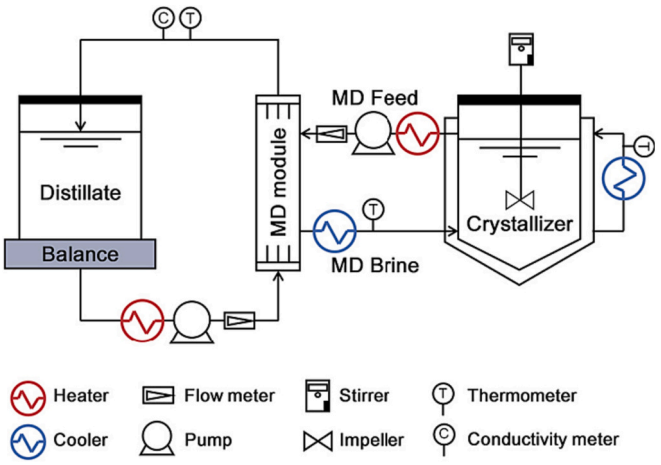

Fig. 23. Schematic diagram of a MDC system used to recover salts from SGPW. Reprinted from [296] with permission from Elsevier.

over 98 % and sulphate retention above 85 %. SED is a form of ED which uses monovalent ion-selective exchange membranes to fractionate monovalent ions from multivalent ones [98]. Brines also contain rare earth elements such as tellurium, neodymium, dysprosium, cobalt, platinum, yttrium, lanthanum or cerium which can be used in many different industries including the manufacturing of solar panels and wind turbines. Nonetheless, their low concentrations and the presence of other ions makes them difficult to recover and requires highly selective methods. Recovery treatments often require removal of competing ions before the targeted metal can be extracted. For example, recovery of platinum-group metals requires removal of cobalt, copper and nickel and recovery of lithium requires removal of magnesium [193]. Moreover, the presence of pollutants in brines such as iron, chromium, zinc, copper, cadmium, nickel, lead, mercury or molybdenum requires adequate brine treatment such as adsorption, ion-exchange, membrane separation, flocculation, oxidation-reduction or chemical precipitation. Adsorption is the most adopted method because it is easy to apply and cost-effective [155]. Additionally, the production of hydrogen from seawater and other water streams by electrolysis has been recently reviewed [295]. Table 14 shows results from recent studies on ZLD systems aiming at recovering salts from waste brines. Although several novel ZLD systems have been suggested in recent literature, few of them have looked at the associated economics and potential revenue generated from recovering water and minerals. The combination of MD with MSF crystallisation applied to SWRO brines was able to recover 89 % of water and achieve a low LCOW of 0.35 $/m^3 by extracting $Na_2SO_4{\cdot}10H_2O$ [265]. Similarly, using a brine concentrator with WAIV was able to recover NaCl, 86 % of water and achieve a low LCOW of 0.85 $/m^3 from SWRO against 99 % water recovery and a LCOW of 1 $/m^3 for a conventional concentrator-crystalliser system [288]. Poirier et al. [13] have run a techno-economic analysis of brine treatment by multi-crystallisation to separately recover $CaCO_3$, $CaSO_4$, NaCl and $MgSO_4{\cdot}7H_2O$ at high purity. The results demonstrate that the energy consumption was reduced from 690 kWh_{th} to 125.90 kWh_{th} per ton of feed brine. The system recovers 99.2 % of the water and reduces the mass of the discharged brine by 98.9 %. NaCl and water represent the main revenue sources due to their high amount and high purity while epsomite's poor purity prevents it commercialization due to co-precipitation of other crystals such as $MgCl_2$. Nevertheless, although this system has a LCOW at 13.79 $/m^3 which is higher than the LCOW of the conventional ZLD system at 7.85 $/m^3, it has potential for optimization and scale-up. Also, it is expected that using renewable energies could reduce the high electricity cost of the system and thus the LCOW. As a result, it is thought that achieving high purity crystals is essential to economic profitability and commercialisation. Thus, separation of the

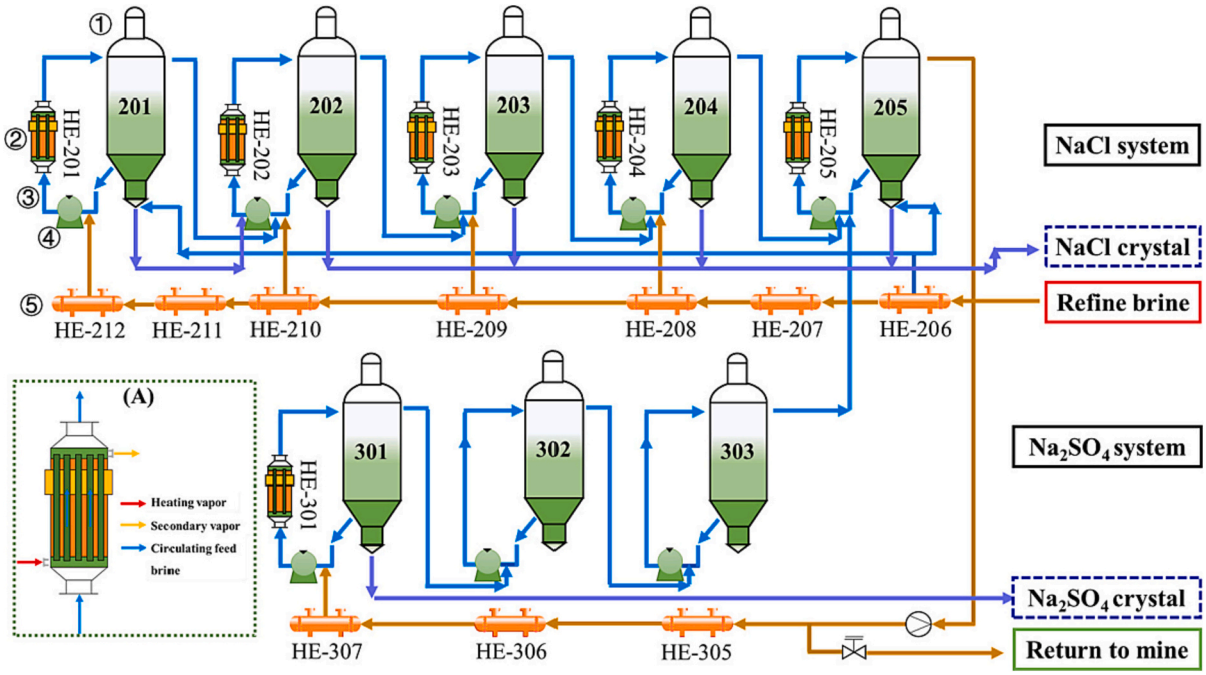

Fig. 24. Schematic diagram of a MED system used to recover NaCl and Na_2SO_4 from highly saline brines. Reprinted from [297] with permission from Elsevier.

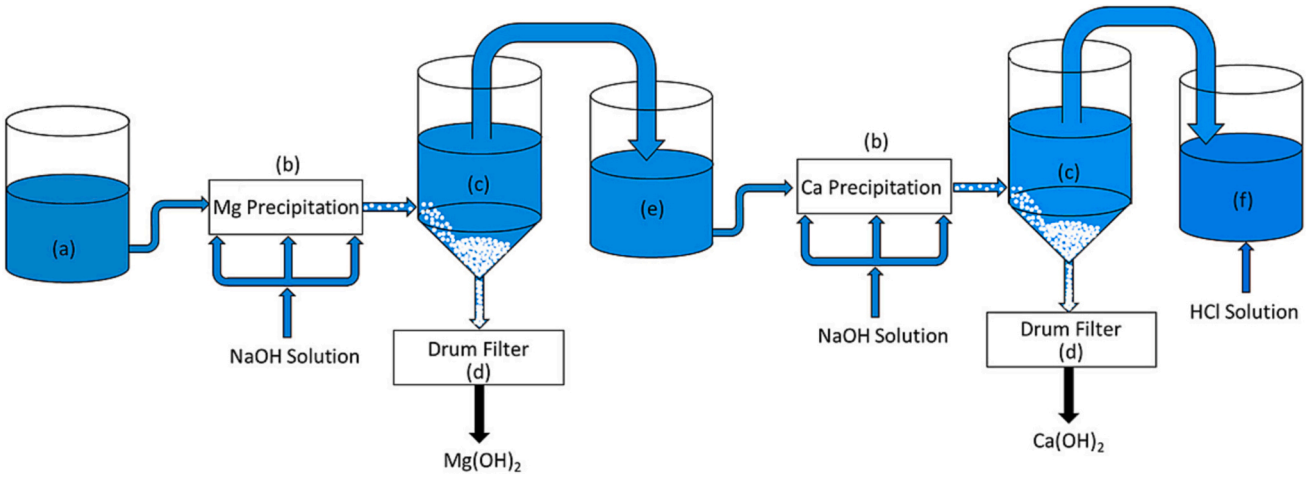

Fig. 25. Schematic diagram of a multi-crystallisation pilot for selective recovery of magnesium and calcium by pH swing. Reprinted from [298] with permission from Elsevier.

different minerals is important and would allow to create several revenue sources other than water and/or NaCl alone. More research is therefore required to explore the economic feasibility of such systems, such as multi-crystallisation, to evaluate profitability at different scales. Brine evaporation remains the main solution to separate pure water from crystals but the combination of adsorption or electrochemical ion separation holds potential to produce high purity products which could be sold at higher prices.

5.4.4. Future prospects of lithium extraction

The recovery of lithium from waste brines has sparked much interest in the research community due to its high value and increasing demand in batteries. The global production of lithium carbonate equivalent (LCE) in 2019 was 325,000 t/year LCE [310] with its demand expected to increase exponentially, promoted by the development of electric vehicles (EVs) and renewable energies, making lithium an important resource for sustainability. But current lithium production methods from salt lake brines (salars) and hard-rock (spodumene) struggle to meet the demand which poses risks of shortage. About 2/3 of the global lithium production comes from salt lake brines containing 100–1500 ppm Li in Chile, Argentina, Bolivia and Australia using an evaporitic extraction method which poses concerns over the security of this resource [15,16]. Currently, only highly lithium-concentrated brines containing at least 100–500 ppm are commercially exploited using evaporation ponds that remove other ions by precipitation to produce a concentrated solution of LiCl which can be post-treated by carbonation with Na_2CO_3 to produce Li_2CO_3 (Fig. 26) [15,16]. However, this is a slow process that takes 1–2 years to concentrate Li to 5000–6000 ppm before carbonation is possible, and it consumes on average 5–50 m^3 of water per ton of Li_2CO_3 produced with no water recovery [15]. As a result, this process causes concerns about its environmental impact for communities living near extraction sites.

Oil & gas produced water, geothermal brines, seawater desalination brines and seawater have been suggested as alternative sources of

Table 14
Results from different studies on ZLD systems for salt recovery.

Feed water	System	Conditions	Salts recovered	Water recovery	LCOW ($/m^3)	Reference
Artificial NaCl, KCl and $NaNO_3$ solutions	MDC with cascaded crystalliser.	50 °C	NaCl: 0.931 kg/m^2/h KCl: 0.437 kg/m^2/h $NaNO_3$: 1.141 kg/m^2/h			[299]
200,000 ppm NaCl brines	MDC with ceramic membrane-promoted crystallisation.	50 °C	NaCl needles: 0.194 kg/m^2	0.790 kg/m^2		[300]
150,000 ppm KCl brines	MDC with ceramic membrane-promoted crystallisation.	60 °C	KCl needles: 0.134 kg/m^2	0.739 kg/m^2		[301]
Desalination brine	MDC with anion-exchange membrane.	Precipitation with $Ca(OH)_2$.	$Mg(OH)_2$			[302]
Desalination brine	MDC with membranes modified with acetone or LiCl.	60–70 °C	NaCl: 0.5–0.7 kg/m^2/h	1–1.8 kg/m^2/h		[303]
Sub-soil brines	Vacuum-assisted MDC.	Vacuum	100 % of $CaSO_4$ and NaCl	14.40 kg/m^2/h		[304]
73,050 ppm SWRO brines	Fractional submerged MDC.	Addition of $(NH_4)_2SO_4$ to create a sulphate-rich environment and prevent $CaSO_4$ scaling.	Na_2SO_4: 0.224 kg	72 %		[305]
255,300 ppm salt lake brines with 2500 ppm Li^+	Crystallisation-precipitation.	Mg removal by solvent evaporation at 40 °C and precipitation into carnallite and $MgHPO_4$ by KCl and Na_2HPO_4 addition.	93.2 % of lithium recovered and 99.6 % of Mg removed.			[306]
200,000 ppm salt lake brines with 300 ppm Li^+	Graphene oxide composite pervaporation MDC.	MD concentrates Li^+ to 1270 ppm and precipitation of LiOH in the crystalliser along other salts.	LiOH	11 kg/m^2/h	36.6	[307]
Ion-exchange brines	NF + selective crystallisation.	Addition of NaOH to precipitate $Mg(OH)_2$ at pH 9.8–10.4 and then $Ca(OH)_2$ at pH 11.75–12.4.	100 % recovery of Mg at 90 % purity and 97 % recovery of Ca at 96 % purity.			[298]
18,436 ppm tannery wastewater	Vacuum MDC with TiO_2-coated membrane.	60 °C	99.97 % recovery of NaCl and Na_2SO_4.	5.9 kg/m^2/h		[308]
30,000 ppm SGPW	MDC	SEC: 28.2 kWh/m^3	84 % recovery of NaCl and $CaCO_3$ at 2.72 kg/m^2/h.			[296]
282,600 ppm SWRO brines	MD pre-treatment + MSF crystalliser	40 stages to achieve a GOR of 4.	$Na_2SO_4{\cdot}10H_2O$: 25.05 kg/h	89 %	0.35[a]	[265]
306,000 ppm NaCl brine	MED with 8 effects	Pre-treatment removes 97.88 % of Ca and 94.1 % of Mg by precipitation with NaOH and Na_2CO_3 to avoid scaling. Operating temperature of the MED ranges from 130 to 15 °C.	Separate recovery of NaCl and Na_2SO_4.			[297]
Waste brine	Crystallisation	Injection of $Mg(OH)_2$ to create a $MgSO_4$-rich environment and injection of lime in a second crystalliser.	$Mg(OH)_2$ and gypsum.			[309]
Desalination brines	Multi-crystallisation	Successive crystallising temperatures: 35, 125, 80, 29 °C. SEC: 60.72 kWh_e/m^3[a].	$CaCO_3$: 0.098 k/h, 53.8 % recovery, 100 % pure. $CaSO_4$: 2.14 kg/h, 96.4 % recovery, 97.7 % pure. NaCl: 37.20 kg/h, 91.6 % recovery, 100 % pure. Epsomite: 4.63 kg/h, 71.1 % recovery, 40.7 % pure.	99.2 %	13.79[a]	[13]
250,000 ppm SWRO brine	Brine concentrator + evaporative brine crystalliser	SEC: 22.15 kWh_e/m^3	NaCl	99.14 %	1.005[a]	[288]
200,000 ppm SWRO brine	Brine concentrator + WAIV	SEC: 15.34 kWh_e/m^3	NaCl	85.75 %	0.853[a]	[288]

[a] The value is expressed per cubic meter of feed water.

lithium due to their high concentration of lithium at respectively 4.6–572 ppm [16], 1–100 ppm [311], 0.29 ppm and 0.17 ppm [311–313]. Lithium extraction from those water streams can create a circular economy that promotes the development of Li-ion batteries for EVs and intermittent renewable energies (Fig. 27). This approach also serves as an alternative and sustainable way of producing lithium instead of conventional extraction methods from hard-rock or salars which consume large volumes of water and contribute to air, water and soil pollution. Additionally, seawater being an infinite resource makes this approach sustainable for meeting increasing lithium demand. Indeed, the estimated reserve of lithium in oceans is 230,000–250,000 Megatons Li^+ which is the equivalent of 1200–1300 billion tons LCE [314].

New techniques called direct lithium extraction (DLE) methods have emerged to extract lithium from seawater or brines more sustainably. These methods include adsorption, ED, ion exchange, electrochemical extraction, solvent extraction and selective NF which have gained popularity due to their high selectivity [15,16]. Table 15 lists the key aspects of the different lithium recovery methods. All those technologies aim at producing a highly-concentrated solution of LiCl. Once sufficient concentration has been reached, carbonation is possible to produce Li_2CO_3 crystals which is commonly used in the manufacturing of lithium-ion batteries and others. Lithium carbonate is also a precursor to different chemicals used in industries such as lithium hydroxide monohydrate which is also used for the manufacturing of cathodes for high-power lithium-ion batteries [315,316]. Another novel alternative is to produce Li_3PO_4 by reaction with H_3PO_4 which can be used for the manufacturing of lithium iron phosphate batteries. This approach can reduce process time and operate at lower lithium concentration due to the lower solubility of lithium phosphate compared to lithium carbonate

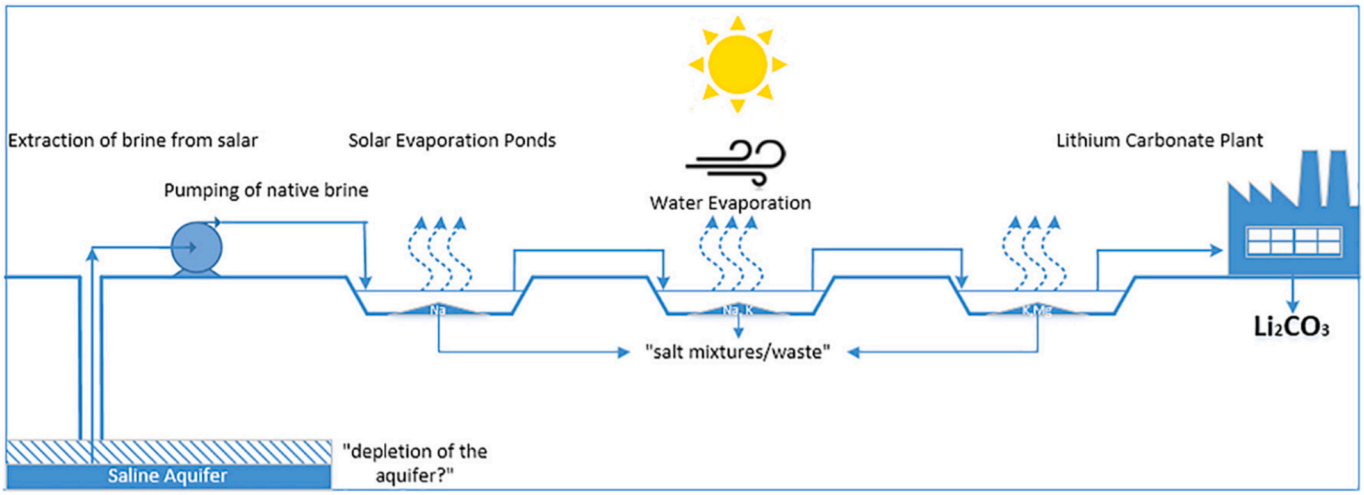

Fig. 26. Schematic of the traditional evaporitic extraction of lithium from salt lake brines. Reprinted from [15] with permission from Elsevier.

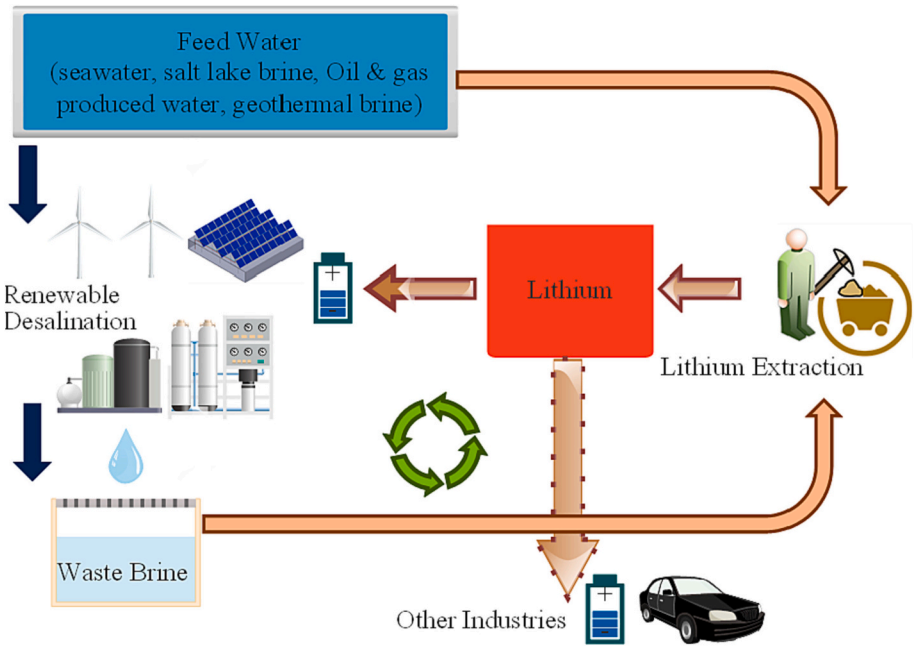

Fig. 27. Circular economy approach for lithium recovery from waste brines.

[16]. But the main issue faced by all methods is the presence of impurities, especially magnesium which has very similar physical properties to lithium which leads to co-precipitation during carbonation. Battery-grade lithium carbonate corresponds to 99.5 % purity minimum while tech-grade lithium carbonate corresponds to 99 % purity minimum [317]. Hence lithium extraction requires pre-removal of impurities and magnesium to reach sufficiently low lithium-to-magnesium ratio before carbonation [15,313].

Lithium recovery from desalination brines has sparked a lot of interest using DLE methods. Electrochemical recovery using λ-MnO_2/Ag electrodes on brines containing 0.43 ppm Li was able to produce a concentrated solution of 1319 mg/L Li at 99 % purity using a low energy consumption of 3.07 Wh/g-Li for a recovery rate of 10.1 mg-Li/g-adsorbent/day compared to 1–3.2 mg-Li/g-adsorbent/day for adsorption methods [320]. Different ion-exchange resins proved suitable for brine containing 0.60 ppm Li, reaching high retention efficiency >95 % for artificial solutions and high desorption recovery between 73.8 and 89.8 % [319]. But the presence of other ions reduces recovery and purity. The extraction of lithium from Dead Sea end brines containing 30–40 ppm Li by chemical precipitation was studied [321]. Tri-sodium phosphate (TSP) showed promising results as a reagent for the precipitation of Li_2PO_4. This process was able to increase Li concentration to 1000–1700 ppm and recover >40 % of Li from real brine and up to 55 % from artificial brine.

DLE methods have been largely tested on salt lake brines as alternative methods to traditional evaporitic extraction to improve recovery time and water consumption. Electrochemical recovery using activated carbon anode and graphene gauze modified cathode made of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ was able to extract 13.84 mg-Li/g-adsorbent/cycle with an energy consumption of 1.4 Wh/mol-Li at 93.4 % purity from salt lake brine containing 163 ppm Li [322]. Desalination of salt lake brines was suggested as a novel method to recover lithium and water and replace conventional evaporation ponds (Fig. 28) [318]. Simulations carried out on eight different salt lake brine compositions varying between 230 and 1570 ppm Li showed that 40 % water recovery before lithium extraction is possible. Although results depend heavily on brine composition and

Table 15
List of the different lithium extraction methods from brines [15,16,313,318–320].

Methods	Characteristics
Evaporitic extraction	Most common method for salt lake brines. Combination of several evaporation ponds that gradually precipitate and remove unwanted salts. Evaporation ponds require 1–2 years to concentrate Li to 5000–6000 ppm before chemical reaction is possible. Slow process affected by weather fluctuation. Other salts are extracted separately. Mg ions must be removed before chemical treatment to avoid co-precipitation. High consumption of water of 5–50 m^3 per ton of Li_2CO_3 produced. No water recovery.
Adsorption	Highly selective adsorbents. Examples of adsorbents: manganese oxide-based (λ-MnO_2, $Li_{1.6}Mn_{1.6}O_4$, HMnO) titanium-based (H_2TiO_3), activated alumina and aluminium-based, zirconium phosphate and zirconium oxide-based, modified resins. Adsorbents are used in the form of granules or membranes. Desorption creates a highly concentrated solution of Li^+ but usually requires acid HCl or water as desorbents.
Ion-exchange	Ion-exchange resins adsorb Li^+ ions by swapping places with H^+ ions. Then Li^+ ions are desorbed through backwash.
Electrochemical extraction	Similar principle to battery charging. Electrodes are plunged in the brine to capture Li^+ ions. The cathode captures the Li^+ ions while the anode captures the complementary negative ions. Several cathode/anode materials exist. Cathode materials are $LiFePO_4$-based or $LiMn_2O_4$-based because of their high selectivity to Li^+ ions. Anode materials include $FePO_4$, Ag, Zn, activated carbon, $Li_{1-x}Mn_2O_4$, polypyrrole. Once saturated with Li^+ ions, the cathode is plunged into a LiCl solution to reverse electrode polarity to liberate Li^+ ions.
Electrodialysis	Uses Li^+-selective membranes with electrodes to extract Li^+ ions. Once saturated with Li^+ ions, the cathode is plunged into a LiCl solution to reverse electrode polarity to liberate Li^+ ions.
Solvent extraction	Examples of organic solvents include β-diketone, n-butanol, neutral organophosphorus extractants, ionic liquids or kerosene.
Selective NF	Uses Li^+-selective membranes. Pure lithium extraction is difficult due to the similar properties of other metals present in the brine.

divalent ions (Mg^{2+}, Ca^{2+}, SO_4^{2-}), it may economically compare to evaporitic extraction as its competitive potential lies in faster process and ability to sell recovered water but would require significant energy. A double-slope solar still was also tested as a desalination approach to brines (510 ppm Li and 265,880 ppm TDS) which was able to produce 2 L/m^2/day of freshwater but achieved 3–4 times lower evaporation rate than the evaporation pond [276]. Graphene oxide pervaporation membrane crystallisation showed reduced membrane wetting and fouling at 70 °C when applied to brine containing 200,000 ppm TDS and 300 ppm Li [307]. High water flux of 11 L/m^2/h was achieved as opposed to 0.5 L/m^2/h for a traditional solar pond with a lower footprint. For a capacity of 10 m^3/day, the system is economically viable with a payback period of 3.6–27 years if both water and lithium hydroxide are sold. Electrochemical ion pumping flow-through-electrodes reactor consists an innovative electrochemical method which was able to produce a LiCl solution at 42.4 ppm Li at 94 % purity from brine at 6.9 ppm Li with a total energy consumption of 1.72 kWh/mol-Li [323]. Pulsed electrochemical intercalation is another innovative DLE method to extract lithium from seawater (0.18 ppm Li) and salt lake water (21.4 ppm Li) [312]. $FePO_4$ electrodes are coated with a layer of TiO_2 to increase selectivity to Li + over Na+. The pulse-rest steps increase the lifetime of electrodes by promoting structure stability. High selectivity was achieved but repeated cycles would require filtering pre-treatment to avoid fouling on electrodes from other impurities. A novel sequential crystallisation process was suggested to recover lithium from highly-concentrated brines (2500 ppm Li and 255,300 ppm TDS) with high Mg/Li ratio > 20 [306]. Solvent evaporation at 40 °C coupled with the injection of KCl to produce carnallite $KMgCl_3{\cdot}6(H_2O)$ was able to remove 53.1 % of Mg. Then Na_2HPO_4 injection precipitated the remaining Mg into $MgHPO_4$. This reduced Mg/Li ratio to 0.16 which can be post-treated to produce Li_2CO_3. 99.6 % Mg removal and 93.2 % lithium recovery were achieved and reagents can be recycled. Different MDC configurations tested on artificial brine containing 41,646–55,528 ppm Li showed that VDC is the only configuration that reaches supersaturation because it counters the high osmotic pressure of the feed brine and recovered 8.3 % of water, 15.1 kg/h of LiCl from 1 m^3/h of feed and reached a levelized cost of LiCl of 2.18 $/kg [324]. Direct crystallisation of lithium sulphate monohydrate $Li_2SO_4{\cdot}H_2O$ from salt lake brine containing 9717 ppm Li using adsorption on colloidal silica-granulated spinel-type manganese oxide adsorbent was able to achieve a yield of 83 % $Li_2SO_4{\cdot}H_2O$ at 84 % purity [325].

Shale gas produced water (SGPW) and flowback produced water (FPW) have been studied as interesting sources of lithium due to their high concentration and their need for ZLD treatment. Titanium-based adsorbent H_2TiO_3 was able to recover up to 17.9 mg-Li/g-adsorbent from SGPW containing 157,000 ppm TDS and 95 ppm Li [326]. Pre-treatment with Na_2CO_3 removed 96 % of divalent ions (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}) by precipitating them into carbonates. This improved adsorption capacity to 25.1 mg-Li/g-adsorbent. It was also shown that higher concentrations of alkanes, especially n-hexane, decreases the recovery of lithium and should therefore be pre-removed before adsorption [327]. Similarly, $H_{1.33}Mn_{1.67}O_4$ adsorption with Na_2CO_3 pre-treatment showed recovery of 16.24 mg-Li/g-adsorbent with pre-treatment as opposed to 13.27 mg-Li/g-adsorbent without it when applied to SGPW with 33 ppm Li [328]. Solvent extraction using di-(2-ethlhexyl)phosphoric acid (D2EHPA) is interesting due to the low affinity with lithium compared to other ions [329]. But the presence of organics, especially long chain alkanes like n-hexane, negatively impact

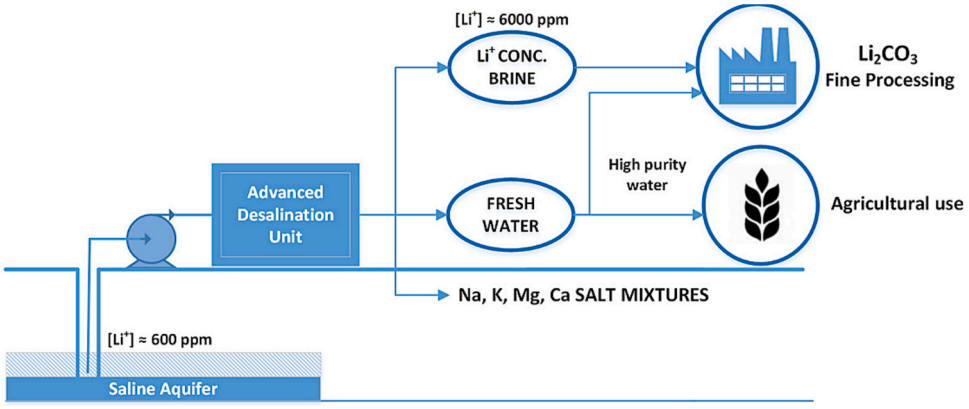

Fig. 28. Schematic of the suggested application of desalination for water and lithium recovery from salt lake brine. Reprinted from [318] with permission from Elsevier.

lithium recovery efficiency and requires their pre-removal. Manganese-based ion-exchange adsorbents applied to hydraulic fracturing FPW (100,000 ppm TDS and 100 ppm Li) were able to recover 18 mg-Li/g-adsorbent and > 80 % Li recovery [330]. The presence of organics reduce recovery and should be pre-removed by NF. A techno-economic analysis of Li recovery from oilfield brine by adsorption showed that this can be a profitable option for a minimum lithium concentration of 190 ppm Li and a volume of feed water of at least 1.2 Mm^3/year [331].

The traditional production of Li_2CO_3 is done by spontaneous reactive crystallisation of a LiCl solution with Na_2CO_3 which is difficult to control and can lead to inadequate particle size distribution unfit for battery grade usage. Alternatively, carbon capture was tested to extract lithium from salt lake brines by a method called CO_2 gas-liquid reactive crystallisation to produce Li_2CO_3 [332]. This method was tested by injecting CO_2 microbubbles inside a crystalliser containing a purified LiCl solution with 20 g/L of Li^+. $NH_3{\cdot}H_2O$ was added to create a mild alkaline environment by forming NH_4^+ and OH^- in solution to improve CO_2 absorption and control crystallisation. This method avoids the addition of Na^+ ions which reduces impurities, increases conversion due to a higher Gibbs free energy of reaction, and utilizes free CO_2 for carbon capture. Microbubbles help control and maintain the crystal size to meet battery-grade needs. The produced battery-grade Li_2CO_3 was successfully tested to synthetize a functional $LiFePO_4$ cathode.

5.4.5. Carbon mineralisation

CO_2 sequestration in desalination brines has been studied extensively [254,333–340] as a way to post-treat waste brines and produce mineral carbonates from calcium and magnesium to reduce carbon emissions and create a circular economy for carbon mineralisation with waste brines to achieve ZLD (Fig. 29). These carbonates can then be sold to different industries. These studies [254,333,334,336,337,339,340] often use the pH swing method (Fig. 25) to separate Mg and Ca ions by precipitation of $Mg(OH)_2$ at pH between 7 and 11 followed by $Ca(OH)_2$ at pH between 11 and 13 [335,336]. Those hydroxides then separately react with CO_2 to form magnesium carbonates and calcite $CaCO_3$ at ambient conditions. CO_2 dissolution in water in Reaction (1) is enhanced at lower temperature and higher pressure after which it is converted into bicarbonate and then into carbonate in Reactions (2) and (3) respectively. Thus, an alkaline environment is required which is usually done by addition of NaOH before CO_2 microbubble injection (direct method) or using amine-based CO_2 adsorbents (indirect method). Multivalent cations like Ca and Mg or monovalent cations like Na, K and Li then spontaneously react with carbonate ions to form carbonate salts in Reaction (4) and (5) respectively.

$$CO_{2\,(g)} \leftrightarrow CO_{2\,(aq)} \tag{1}$$

$$CO_{2\,(aq)} + OH^- \leftrightarrow HCO_3^- \tag{2}$$

$$HCO_3^- + OH^- \leftrightarrow H_2O + CO_3^{2-} \tag{3}$$

$$Ca^{2+} or\ Mg^{2+} + CO_3^{2-} \rightarrow CaCO_3\ or\ MgCO_3 + heat \tag{4}$$

$$2Na^+ or\ 2K^+\ or\ 2Li^+ + CO_3^{2-} \rightarrow Na_2CO_3\ or\ K_2CO_3\ or\ Li_2CO_3 + heat \tag{5}$$

Direct CO_2 mineralisation in desalination brines was tested to produce calcite and hydromagnesite $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ [333]. The process consists of alkalinisation with NaOH followed by the injection of CO_2 microbubbles and then filtration of the crystals. Results showed that 99 % of Ca and 86 % of Mg precipitated. In a later study, Bang et al., [334] improved their approach by suggesting a sequential CO_2 mineralisation system to produce separately calcite and hydromagnesite using CO_2 injection into desalination brines. Results showed that 99 % of Ca, 69 % of Mg ions and 69 % of the injected CO_2 were precipitated as carbonates. This method also reduced the consumption of NaOH by 76 % compared to the previous study. Using this method, the total conversion ratio of CO_2 was increased from 12 % to 57 %. Experiments were carried out using either 99.9 %vol or 15%vol CO_2 (mixed with N_2). Using 99.9 %vol CO_2 showed higher precipitation ratio of Ca and Mg but lower total CO_2 conversion ratio than when using 15%vol CO_2. This system was then optimised and tested under different agitation conditions, ion concentration and CO_2 injection rates [254]. Stirring improved conversion ratio of Mg from 69 % to 90 % during Mg carbonation and that of CO_2 to 99 % in total. Increased CO_2 injection rate reduced Ca conversion rate and increased Mg conversion rate during Ca carbonation. Reducing CO_2 injection rate increased Mg conversion and increased overall CO_2 conversion rate. Additionally, suspending the separated $Mg(OH)_2$ in a deionised solution allowed to increase hydromagnesite purity to 98 %.

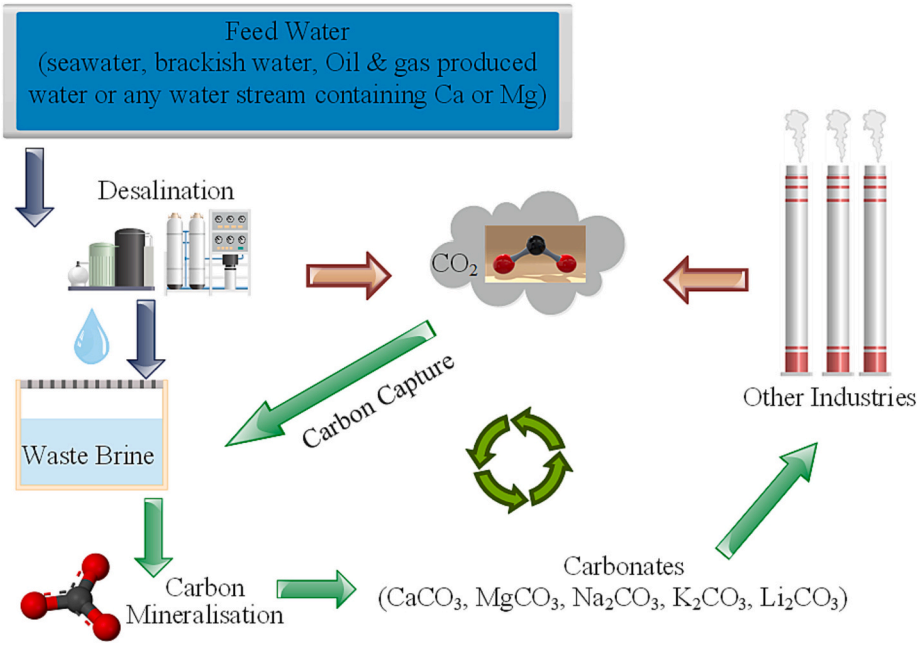

Fig. 29. Circular economy approach for carbon mineralisation with waste brines.

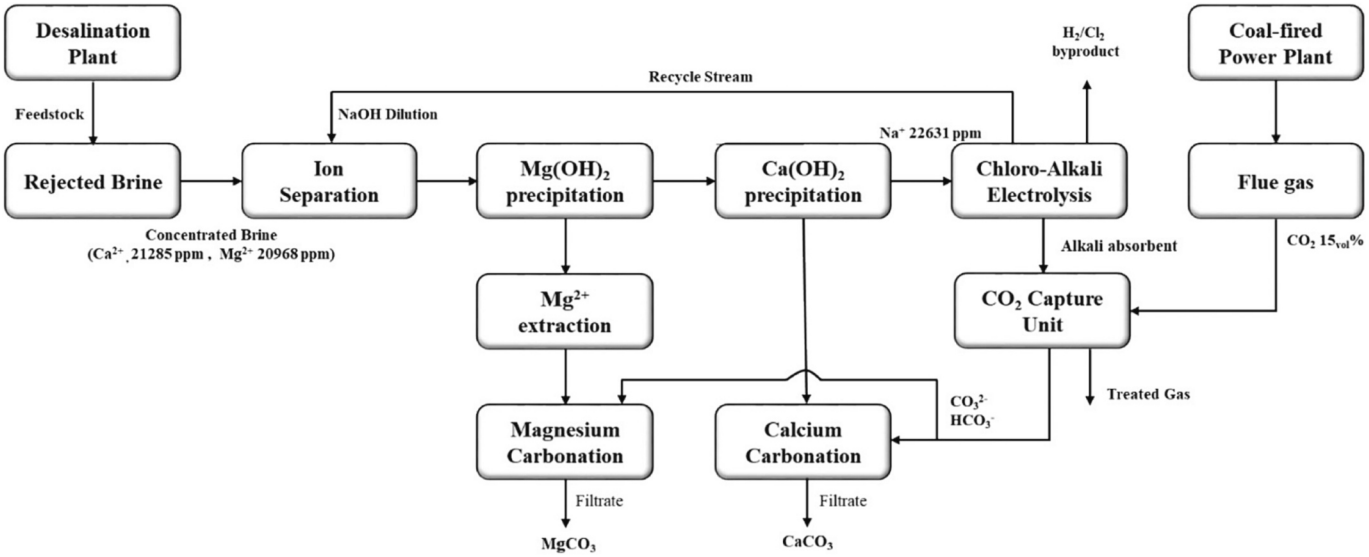

Fig. 30. Schematic of the carbon mineralisation process from desalination brines using chloro-alkali electrodialysis to produce NaOH and using amine-based CO_2 adsorption. Reprinted from [336] with permission from Elsevier.

A carbon mineralisation system combining pH swing with chloro-alkali electrodialysis and amine-based CO_2 adsorption was modelled on Aspen Plus (Fig. 30) [336]. Chloro-alkali electrodialysis is used on the rejected brine to produce the needed NaOH solution continuously. CO_2 is captured directly from flue gas using amine-based adsorbent. Then, the CO_2-saturated amine-based adsorption solution is mixed separately with $Mg(OH)_2$ and $Ca(OH)_2$ to produce $CaCO_3$ and $MgCO_3$. Results estimate conversion yields for Ca into $CaCO_3$ at 98.5 % and for Mg into $MgCO_3$ at 61.4 % and an energy consumption of 16.55 kWh/kg CO_2. Economic results show that the system can be profitable. This system was then improved to integrate sequestration of NO_x, SO_2 and CO_2 [340]. SO_2 and NO_x react with $Ca(OH)_2$ to produce $CaSO_4$ and $Ca(NO_3)_2$. NO_x, SO_2 and CO_2 capture reached 90 %, 99 % and 91 % respectively. The economic results show that the proposed system is between 7.9 and 14 % cheaper than using traditional methods of selective catalytic reduction for NO_x treatment, wet flue gas desulphurisation for SO_2 treatment and amine-based absorption for CO_2 capture. Although chloro-alkali electrolysis allows free and continuous supply of NaOH and useful H_2, it produces toxic Cl_2 gas which must be post-treated carefully.

Several studies [339,341] have looked at the application of a modified Solvay process to produce sodium carbonates. The Solvay process is commonly used to produce Na_2CO_3 or $NaHCO_3$ from saline solutions of NaCl by reaction with CO_2 in the presence of ammonia NH_3. Ammonia increases pH at low temperature between 10 and 20 °C to increase CO_2 solubility and dissolution. However, the use of NH_3 is hazardous and costly. As a result, NH_3 can be replaced by $Ca(OH)_2$ which was shown to increase carbon capture and Na removal while reducing energy need. But desalination brines are usually rejected at 40–55 °C which reduces CO_2 solubility. To answer these issues, a modified Solvay process based on the use of KOH instead of $Ca(OH)_2$ was suggested [341]. KOH has a higher solubility at higher temperature and can maintain high pH around 13.6 which promotes carbon capture and cuts the need for cooling. Experiments were conducted with KOH on desalination brine containing 70,570 ppm TDS at 10–60 °C and 1–3 bar using 10%vol CO_2 or 90%vol CO_2. Carbon capture stays relatively constant between 10 and 50 °C and increasing pressure linearly increases carbon capture because more CO_2 can be dissolved. Lower CO_2 flow rate also increased carbon capture due to higher residence time. Removal of 45.6 % Na, 29.8 % Cl, 91.2 % Mg and 100 % Ca was achieved.

6. Modern evaluation and optimisation methods

In the conclusion, the authors would like to provide readers a modern evaluation of the optimization methods applied to the desalination systems. In order to have a comprehensive review of applied methods, a Scopus search using the keyword “desalination” [342] was used. Among 40,374 documents (37,622 in English), the following evaluation methods were mentioned:

- Energy efficiency was discussed in 1788 papers,
- Economic analysis was reported in 803 papers,
- Exergy concept as a thermodynamic analysis was applied in 762 papers.

More detailed evaluation demonstrated that the concept of energy efficiency and exergy has been applied mainly to the desalination technology but not to the pre- and post-treatment of seawater. Very often, only specific power consumption for the selected desalination process was reported. However, the economic analysis has been applied to the entire technological process. This is confirmed by data reported in Tables 10–14.

The exergy analysis (as the combination of the first and the second laws of thermodynamics) became very popular for application to different energy-conversion and chemical-intensive processes. Many papers report its application to evaluate desalination technologies. However, the pre- and post-treatment of seawater is not included. The same situation is applied to the optimization, including the application of mathematical methods or the so-called exergy-based methods (exergo-economic, exergo-environmental analyses etc.) [343]. Some successful applications can be found in the literature [211,215,344]. The reason that the exergy analysis has not been widely applied to the pre- and post-treatment of seawater is the exergy calculation procedure. The exergy streams consist of the physical and chemical exergy at assumption that potential and kinetic exergies are not considered [345,346]. According to the definition, the physical exergy depends on temperature and pressure and their deviations from the selected thermodynamic environment. The definition of the chemical exergy is more abstract because different thermodynamic environments are involved: gases, liquids and solids. For liquids, it is “ionic and non-ionic substances from the oceans”. Therefore, there are two possibilities to calculate the exergy of the seawater streams:

- As a mixture of pure water with other substances where both physical and chemical exergies must be considered. However, the contribution of the chemical exergy is very small.
- As a complex substance of "ionic and non-ionic substances from the oceans" where only physical exergy is required.

For the proper energy analysis, the chemical composition of the seawater plays an important role. It is obvious that the selection of the desalination process, evaluation of the energy consumption and costs depend on a desalination plant location i.e. properties of the seawater. Very detailed calculations of the physical and chemical exergy for the seawater can be found in the literature [347]. The application of different optimization strategies can be found, for example, in [206,348]. The comparison analysis of reported results is not meaningful because it required the consideration of the applied evaluation methodology review and assumptions.

7. Conclusion

The review of the different pre-treatment, desalination and post-treatment methods for different water streams has been conducted. The pre-treatment of the feed water depends upon several factors including its composition, the chosen desalination system and its sensitivity to fouling and scaling. Conventional pre-treatment methods are still widespread, but researchers are moving towards novel membrane pre-treatment methods due to their high retention performance, low cost and flexibility. UF is seen as an attractive step prior to RO due to its intermediate performance and cost compared to MF and NF.

RO is the most commercially available desalination technology at the moment because it achieves the lowest cost, lowest energy consumption, high efficiency, high reliability and a flexible modular design, while fit-for-purpose adaptations to further reduce power consumption by employing a batch process are under consideration. Degradation of membranes and equipment can increase maintenance and replacement costs and lead to system failure. Operating at lower temperature slows down degradation and allows the use of cheaper materials. Tools such as system reliability analyses can be used to predict and reduce degradation using modelling and experimental results to identify causes of failure. Future development on the relationship between materials and failure probability should be conducted. It is important to note that thermal desalination technologies, especially MSF and MED are still common due to their low cost and are continuously being improved to increase their performance. MSF is slowly being replaced by MED systems due to its higher energy performance thanks to its latent heat recovery. Heat and mechanical energy recovery are important systems used to lower energy consumption. RO and MED are seen as the most feasible technologies for large-scale applications and are often seen as competitors. The other desalination technologies including FO, MD, HDH, FM and ED/EDR are still at a research stage and require further technical development to analyse their commercial feasibility. Emerging technologies like hybrid systems, hydrate-based and nuclear desalination are gaining interest due to their increased efficiency. However, to compete with established processes like RO, developing technologies must reach greater levels of technological maturity through innovation in research and through scale-up applications. Recent research focuses on the use of renewable energies to power desalination systems to achieve carbon neutrality. Technological advancements in renewable energies along with cheaper equipment, rising environmental concerns and the need for energy independence encourages the use of renewable energies. Intermittency can be reduced using energy storage or diverse energy sources. Desalination from the dissociation of hydrates through heating or depressurisation has sparked interest because of the possibility to recover hydrate crystals from concentrated brines and dissolved hydrate former gas from recovered water. Moreover, nuclear desalination is gaining attention due to its flexibility in powering both membrane or thermal technologies under constant operation. SMRs hold the most potential because of their smaller land area, faster construction, lower investment costs and safer operation. Additionally, the recovery of uranium from brines would allow the creation of a circular economy where it could be directly used as fuel and promote energy independence. However, nuclear desalination poses safety concerns related to nuclear accidents and will face public opposition.

The brine post-treatment plays a crucial role in environmental preservation and the development of a circular economy by treating waste brines as a resource. Different ZLD technologies exist but thermal-based ones, especially brine concentrators and evaporative crystallisers, are currently the most appropriate for water and salt recovery due to their high salinity limit, high recovery rates and low cost. Membrane technologies for ZLD are still at a research stage and cannot recover salts due to their high scaling sensitivity which limits them to pre-concentration. However, they achieve lower costs, especially RO, and can be combined with thermal methods to lower costs and energy demand as pre-concentration techniques. Moreover, combing thermal desalination technologies with thermal ZLD technologies would allow additional heat recovery between those two stages to reduce energy consumption. MDC is currently the most studied approach for water and salt recovery due to its low operating temperature but still faces challenges mainly high cost, scaling and low flow rates.

Carbon sequestration in brines can be used to both reduce carbon emissions and recover valuable carbonates. The extraction of lithium from seawater, salt lake brines, geothermal brines and oil field produced water has sparked a lot interest as a way to supply to increasing demand and achieve ZLD. Different lithium extraction techniques are available but are still at a research stage as well and are only feasible for brines containing large concentrations of metals and require selective separation of ions and crystals to reach high purity.

ZLD technologies require further development to allow their commercial application on large-scale systems for the recovery of salts and metals. But recent studies showed their capability to increase profitability by selling salts and water from waste brines. The main challenge is the separation of minerals like Na, K, Ca, Mg, Cl, SO_4, and Li to produce high-purity industrial-grade salts. Multi-crystallisation is seen as a promising method for separating salts by playing on temperature-solubility behaviour differences as well as thermal energy recovery to reduce the SEC. The economic value for doing mineral recovery is crucial to allow ZLD systems to be profitable by offsetting the investment and operating costs and has potential to reduce the LCOW of desalination plants by increasing water recovery and by generating new income streams. It also serves as a sustainable way of producing minerals as opposed to traditional mining activities. Simulation of different approaches and running sensitivity study may help in predicting the most effective and economical ZLD methods. Additionally, exergy analysis tools could be applied to pre- and post-treatment design for optimisation.

CRediT authorship contribution statement

Kristofer Poirier: Investigation, Writing – Original Draft. Mohsen Lotfi: Investigation, Writing – Original Draft. Kapil Garg: Investigation. Kumar Patchigolla: Conceptualization, Methodology, Supervision, Project administration, Writing – Review & Editing, Funding acquisition. E.J. Anthony: Writing – Review & Editing. Nadimul Haque Faisal: Writing – Review & Editing. Vinay Mulgundmath: Writing – Review & Editing. Jai Krishna Sahith: Writing – Review & Editing. Prashant Jadhawar: Writing – Review & Editing. Liam Koh: Writing – Review & Editing, Funding acquisition. Tatiana Morosuk: Writing – Review & Editing. Najah Al Mhanna: Supervision, Project administration.

Kristofer Poirier and Mohsen Lotfi contributed equally to this work.

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Declaration of competing interest

The authors declare no conflict of interest.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

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