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Concentrate management technologies for desalination processes leading to zero liquid discharge: technologies, recent trends and future outlook

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ABSTRACT

In order to equilibrate the global clean water supply and demand stress, the application of both thermal and pressure-driven membrane processes results in the generation of an enormous volume of concentrated waste stream as a by-product. This waste stream which is known as brine or concentrate needs to be disposed of. Owing to the massive volume of concentrate, and stringent discharge regulations, the desalination plant operators are facing unprecedented challenges that call for adopting different approaches to brine concentrate management. This article presents a comprehensive literature review on the zero liquid discharge (ZLD) systems for desalination industry. Major components of both high-recovery and ZLD technologies have been reviewed and presented based on their advantages, disadvantages, capital investment, operation and maintenance costs to help enable industrialists, researchers, engineers and technicians to compare and identify the appropriate concentrate management technology. In addition, beneficial uses and final disposal technologies for brine have been briefly described. Finally, current and future research trends related to concentrate management strategies and possible improvements in ZLD technologies are highlighted.

Keywords: Concentrate management; Zero liquid discharge technologies; High-recovery processes; Brackish water RO desalination, Membrane-based desalination; Environment

1. Introduction

Because of recent global mega trends (increasing population, urbanization, economic growth, global warming and rapid industrialization) drinking water supply is under severe stress worldwide and this has a direct consequence on the scarcity of clean water resources globally [1–3]. Careful statistics indicate that every third person in this world is deprived of clean drinking water [4,5]. In the past few decades, clean water supply has become very critical due to excessive water demand and contamination of the existing clean water sources. Dirach et al. [6] pointed out that for the entire Mediterranean region, conservative estimates indicate a water shortage of about 10 million m^3/d by the year 2020. Furthermore, Shannon and co-workers [7] stressed that

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global water consumption is increasing and quality regulations on drinking water have become more severe. To cope up the ever-increasing global clean water demand while keeping the conventional energy resources reserved, several innovative approaches have been attempted, e.g., the two studies by Gude and Narayan et al. [8,9] emphasized the utilization of renewable energy for sustainable desalination have been published. Similarly, Buonomenna and Plappally [10,11] stressed efficient utilization of energy for water treatment, end use, reuse, reclamation, and disposal.

The fact that almost 98% of the world's water supply comes from seawater or brackish water has made desalination to be an important method to solve the global scarcity of fresh water. Elimelech et al. [12] identified that due to recent development of advanced membrane materials and energy recovery devices, membranes-based desalination is proving as a major technology for overcoming the stress on the global fresh water supply. As quantified by Mane [13] and Greenlee et al. [14], currently, reverse osmosis (RO) is the leading technology for new desalination installations with a 44% share in world desalting production capacity and an 80% share in the over 15,000 desalination plants installed worldwide.

1.1. Major concerns of desalination plants

Currently, there are two major methods of desalination, namely, thermal-based and pressure-driven, the later include membranes-based processes such as micro filtration (MF), ultra filtration (UF), nano filtration (NF), and reverse osmosis (RO). World's total desalination capacity was reported to be 86.8 million m^3/d in June, 2015 [15], whereas in 2013, seawater RO (SWRO) and brackish water RO (BWRO), respectively, constituted 59% and 22% of the global RO desalination capacity [16]. This increased interest in RO desalination has resulted in potential environmental problems. RO desalination plants extract enormous volumes of water globally producing two streams; permeate (or fresh water) and reject (or brine/concentrate). Del Bene et al. [17] specified that the dense concentrate thus produced is discharged back into the environment and has been pointed out to be the major cause of detrimental impact for both physico chemical and ecological attributes of receiving environments as explained by Roberts and Lamei et al. [18, 19]. In addition, as demonstrated by Mickley and Truesdall et al. [20–22], brine disposal and management is becoming an increasing challenge and is very expensive nowadays, ranging from 5 to 33% of total desalination cost, complicating implementation of concentrate management [23].

Arnal et al. [24], pointed out that disposal costs for inland desalination plants are even higher than those for plants discharging brine into the sea. The following three studies by Arnal [24–26], Gabelich [24–26] and Ahmed et al. [24–26] specified that major factors affecting the disposal costs are: the quality of the concentrate, treatment level prior to disposal, disposal technique and the volume of the concentrate. Furthermore, discharge regulations have become more stringent for the desalination industry worldwide. Owing to strict discharge guidelines, environmental impacts that concentrate disposal can cause and increased disposal cost, concentrate mangers are faced with unprecedented problems that call for different approach to concentrate management in various industries including desalination, municipal, wastewater treatment, water reuse and reclamation. In order to address these issues, many technologies have been developed: e.g., Ahmed et al. [27] emphasized the need for the advancement of higher recovery systems, Einav et al. [28] stressed the development of systems for reducing environmental impact by dilution and Jegatheesan et al. [29] highlighted the importance of salt recovery systems. However, more focused research and examination is needed to reduce concentrate quantity and to allow more recovery and reuse of concentrate.

As pointed out earlier that concentrate management is much more serious issue for inland desalination facilities compared to seawater desalination installations. Because, BWROs are inland plants and disposal of the concentrate brine is a serious and challenging issue. Especially in winter season the water disposed in the adjacent land does not evaporate in a timely manner and becomes a kind of lake and due to prolonged storage bacteria develop and start smelling and becomes nuisance for the neighboring land owners. The other problem is removal of dried concentrate in the form of salt on the ground which has to be scrapped and dumped at waste dumping areas with additional cost (freight charges). Also in BWRO, the ground water is very costly; and with 70% recovery generally practiced, about 30% ground water has to be discarded to the waste stream. Therefore, it is always desired to extract as much as possible to save the valuable water resource in inland areas. In case of seawater RO the recovery ratio is around 35–40% and the concentrate volume is large. Given the fact that most of the SWRO plants are installed near the seashore with the nearby disposal site (that is sea), thus SWROs need entirely different approach of concentrate management and can be dealt separately. Therefore, the scope of this article is restricted primarily to the recovery enhancement, concentrate minimization systems and techniques developed for brackish water desalination processes.

With the goal of achieving ZLD/near-ZLD goal, we are currently establishing Research & Development facilities for increasing water recovery of brackish water RO (BWRO) plants installed at KFUPM, Dhahran, Saudi Arabia. As a stepping stone towards establishing ZLD systems, we are currently conducting state-of-science reviews, technical evaluation of desalination configurations and technologies with the focus on water recovery enhancement techniques and thereby concentrate minimization of BWRO plants installed at KFUPM.

In this paper, we present a comprehensive literature review on high-recovery/volume reduction technologies (VRTs), zero liquid discharge (ZLD) technologies and advantageous uses and final disposal options for the concentrate generated during desalination. The article is unique in its depth and breadth. To the end of breadth, it contains comprehensive review of VRTs, ZLDs, hybrid processes developed for higher water recovery and concentrate management, brief discussion of beneficial uses of brines generated during desalination processes and final disposal options for the concentrate generated during desalination. The abstract of the intensive literature review conducted is provided in the form of figures, tables, as well as text in this article, e.g., the depth of the article provides salient features (advantages, disadvantages, capital, operation and maintenance (O&M) costs) of VRTs, ZLDs, hybrid processes in tabular form as well as in text, such that figures and tables present a quick review of the aforesaid technologies, however, for detailed discussion, a researcher may read the relevant text and references. In addition, current status and limitations/room for further improvement are given at the end of each section for each technology discussed. Furthermore, future market value of high recovery and ZLD systems and components has been highlighted. Finally, all the relevant recovery enhancement and ZLD technologies are summarized and compared in terms of applicability and certain set of performance evaluation criteria.

2. Reverse osmosis concentrate management

EI-Manharawy [30] emphasized that water type is the cornerstone in RO system planning and designing. With the fact that all natural waters are classified into two main groups, namely, brackish water and seawater with total dissolved solids (TDS) of 1000–15000 mg/L and >15,000 mg/L respectively, the systematic identification and differentiation of all natural water is almost missing. This study demonstrated that based on their ions molar concentrations and ratios, natural waters could be classified into four major chemical classes and ten water types as based on their ion molar concentrations and ratios. The proposed "Water Molar Classification" was proved to be useful in understanding the chemical nature of the investigated water type and its possible behavior under the pressure-driven (membranes-based) desalination technologies.

Pontius et al. [31] stated that the characteristics of concentrate strongly depend on the pretreatment method adopted, the feed water characteristics (both composition and concentration), the membrane process used, the recovery, and the additional chemicals used. Pressure-driven desalination processes (such as MF, UF, NF and RO) take feed water as the intake and produce two streams, namely, permeate (the product) and reject/brine/concentrate (a byproduct to be recycled or needing further treatment). Van der Bruggen at al. [32] mentioned that concentrates originating from MF or UF comprise of colloidal particles, suspended solids and larger organic molecules, in contrast, NF and RO generate concentrates containing higher concentrations of ions of minerals salts, small organic compounds with no suspended solids and colloids provided a proper pretreatment is applied. In contrast to thermal desalination plants, design of an RO plant is seriously influenced by the site-specific water composition, e.g., pre-treatment design. This site-specific water composition necessitates a comprehensive and precise analysis of feed water composition that must be performed together with the historical data before the design commences.

2.1. Concentrate management options

As specified by Mohsen et al. [33], the energy requirement of an RO system is controlled by two major factors, namely, salinity of the feed water and membrane properties. Qiu et al. [34] stated that reduction in the specific energy consumption (SEC) of a BWRO unit can be achieved by: (i) use of additional membrane elements to recycle brine, (ii) increasing number of stages (with or without energy recovery device (ERD)), or (iii) operating the BWRO in closed circuit mode or batch mode. The overall product water recovery of the RO process is nearly a linear function of the energy cost. Therefore, recovery of the RO process is considered as the most important factor controlling the economics of desalination as mentioned by Wilf et al. [35]. A high recovery process not only aims to maximize the volume of the desired product (the fresh water) but also minimizes waste fraction (RO concentrate) generation and disposal costs.

2.1.1. Multi-staging

Conventional BWRO plants consist of a single stage RO module as shown in Fig. 1. Presenting the example of such a system in Saja'a UAE, Almulla et al. [36] achieved an average water recovery of 68%, pressurizing feed of TDS 3261 mg/L at 18–20 bar. Later, an overall permeate recovery of ~80.8% was achieved by employing an additional seawater RO unit connected to the reject of the above mentioned RO system. However, the addition of second RO module caused an increased osmotic pressure at the exit of second RO module that required application of feed pressure high enough to overcome the increased osmotic pressure. Therefore, it is important to use the second RO module with specific properties such as low operating pressure, high salt rejection and high permeate flux.

The studies by Mane [13,37] and Maskan et al. [13,37] demonstrated that double-stage RO configurations are more energy-efficient and can yield more product water recovery than a single-stage RO system. Several authors [36,38,39] have increased the global water recovery by tandem RO (primary RO + secondary RO), in addition, Wazzan et al. [38] reported 37% reduction in SEC that was achieved by utilizing tandem RO system. An optimum design of BWRO system was proposed by Nemeth [39], the design incorporated inter-stage pressure boosting or employing permeate throttling at the first stage; the designed systems resulted

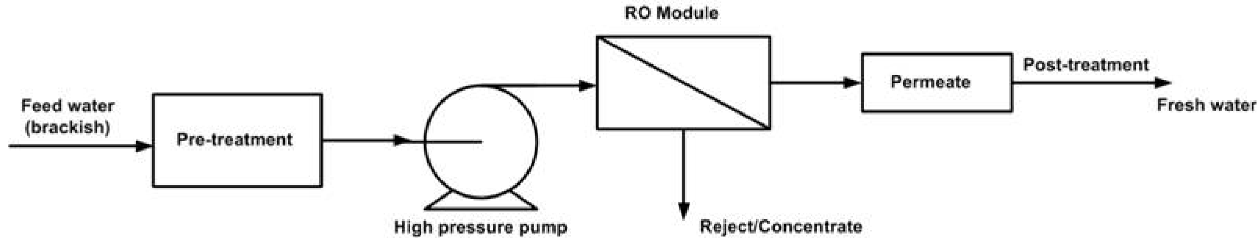


Fig. 1. Conventional single stage BWRO system.

in an enhancement of 40% and 37% permeate flux through the second module, respectively. As described by Vince et al. [40], the installation of inter-stage booster pumps also seems to be a good choice from an economic and environmental viewpoint. A double-stage BWRO system without inter-stage booster pump is depicted in Fig. 2.

Typically, a BWRO plant is configured in a staged array; that is the next stage contains half as many membrane modules as the previous one, i.e., 2:1 array. However, it should be noted that in order to keep the capital cost down, most of the small-scale RO systems were built without an ERD; but, had to pay a heavy penalty on energy costs. In general, BWRO systems, are operated at higher recovery ratios; making energy recovery less critical. Moreover, a BWRO system may be operated in a batch mode and without an ERD. Laborde et al. [41] demonstrated that for small scale RO system, a serial arrangement is more energy-efficient than a parallel one. However, in a serial arrangement, as fresh water is removed continuously salt concentration along the length of feed channel may increase to a value as high as twice (for SWRO) or thrice (for BWRO) at the outlet of RO module as compared to its value at the inlet of module. Elimelech et al. [12] explained that to maintain a uniform permeate flux along the entire feed channel, this necessitates the operating pressure to be determined by the concentration at the outlet rather than the inlet, as depicted in Fig. 3a. Thus, the longitudinal concentration gradient results in the loss of a part of the feed energy. Fig. 3b illustrates the energy savings accomplished (pink area) by the 3-stage RO system with the three pumps providing pressure P_1, P_2 and P_3.

Qui et al. [34] emphasized that multi-staging along with inter-stage booster pump(s) is an example of a system design to eradicate this energy loss caused by the longitudinal concentration gradient. In a multi-stage configuration, RO elements are arranged in series such that first RO module is operated at lower pressure and reject of first stage is then fed to the 2nd stage RO module and the reject of the 2nd stage may then be fed to the 3rd RO (3-stage RO system) as shown in Fig. 4. It is important to emphasize that utilization of more stages not only reduces SEC but also

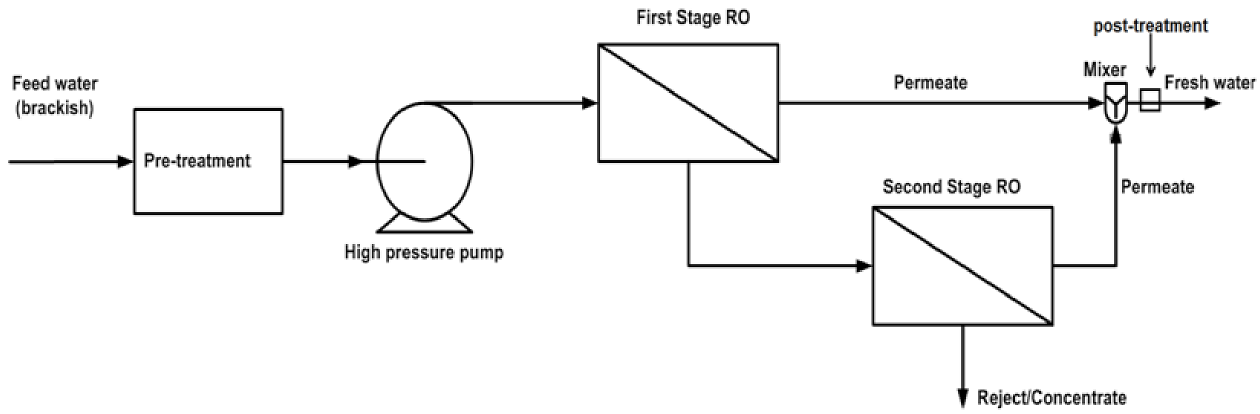


Fig. 2. A double-stage (reject staging) BWRO system configuration.

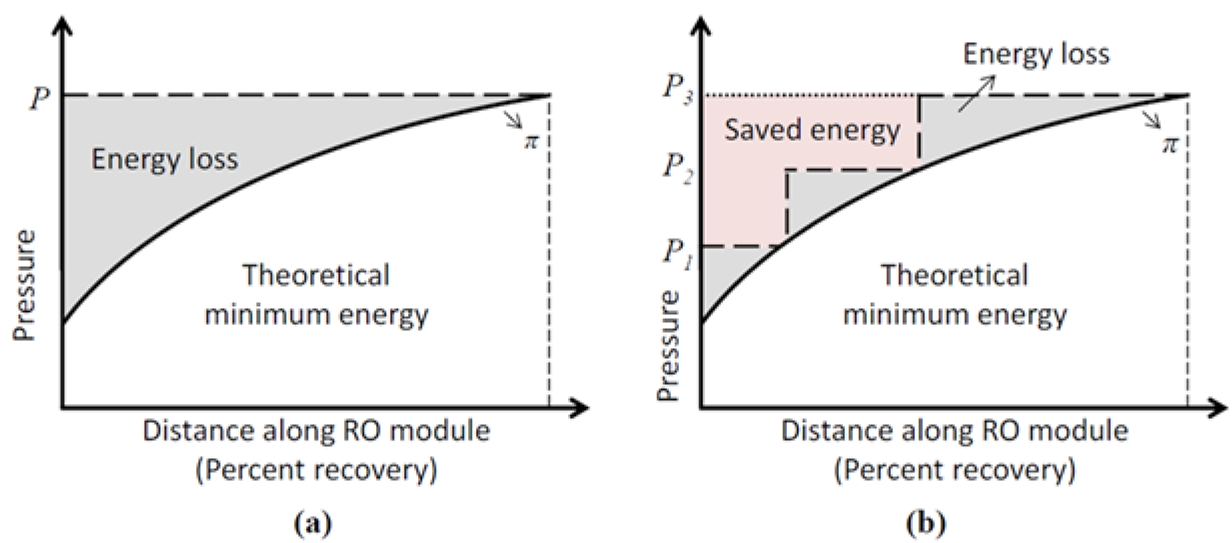


Fig. 3. Energy consumption of an RO system as a function of longitudinal concentration gradient. (a) For single-stage system, the operation pressure P must be at least equal to the osmotic pressure π of the solution at the outlet of membrane module, (b) for 3-stage system, by providing appropriate pressure for each stage, the energy loss (gray area) is reduced, and some of the extra energy is saved (pink area). Adapted from [12], reprinted with permission from AAAS.

improves water recovery. Nonetheless, this improvement is not significant when the number of stages surpasses four. Nevertheless, Vince et al. [40] reported that 3-stage designs with module connected to the reject along with intermediate booster pumps, are in principle, to minimize electrical energy consumption, but, Lu et al. [42] demonstrated that the optimal design (for feed of low TDS (~3000 mg/L)) is with the addition of an ERD for a 3-stage system for enhanced recovery ratio. However, in practice, despite their relatively poor energy efficiency, single-stage systems without ERD have often been favored because of their lower capital cost as stated by Alghoul [43]. Thus, the selection of one- or multi-stage configuration requires careful attention.

Two comprehensive reviews have been published describing various designs, configurations and economic and technical aspects of BWRO systems [34,43].

McCool et al. [44] performed an analysis of upper and lower limits for RO desalination recovery. Mathematical equations were developed, saturation indices of the mineral scalants and osmotic pressure were calculated using simulation software. In addition, an experimental study was performed on a laboratory-scale plate-and-frame RO (PFRO) plant to estimate the upper and lower recovery limits (that were reported to correspond, respectively, to a desired concentration factor) and concentration polarization) to simulate recovery constraints in an actual brackish RO plants.

Several other authors studied the use of tandem RO [45–47], who stressed that there is a need of intermediate treatment prior to SRO desalting step to enhance the water recovery and avoid fouling (by mineral scalants) and precipitation. The tandem RO processes employing various intermediate chemical treatments have been discussed in section 2.1.3.

2.1.2. Batch processes

Multi-staging techniques rely on spatial separation to overcome the problem of longitudinal concentration gradient. However, another contrasting temporal separation technique (i.e. time-varying or non-steady approach) has been adopted recently for higher product water recovery and reduced concentrate discharge [48,49]. This technique relies on time-varying pressure which is applied on a single RO module as the concentration and the osmotic pressure increase. As explained by Qui et al. [48] and Davies [49], an advantage of time-varying method is that in principle theoretical minimum energy of desalination can be reached; whereas in multi-staging, one would need infinite stages to be employed to reach this energy level which is not realistic in practice. Batch mode RO operation and closed circuit desalination (CCD) mode RO operation are the two related time-varying approaches that have been reported to enable higher fresh water recovery, reduced brine discharge and minimization of specific energy consumption in BWRO. However, these two methods are still in their development stage.

The details of these systems can be found elsewhere [48–50]. Figs. 5 and 6 are presented to compare the perfor-

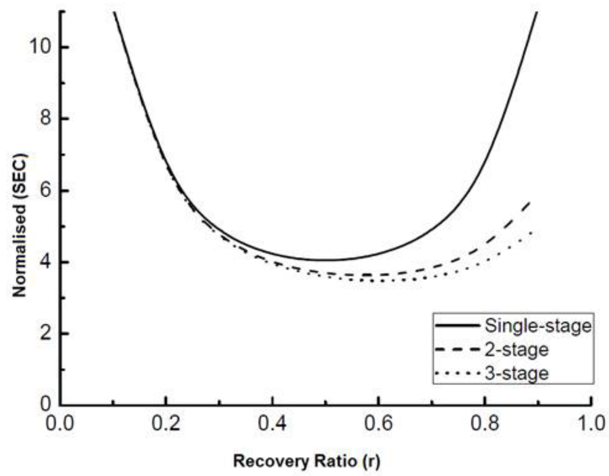


Fig. 5. Theoretical limit of normalized SEC in staged ROs without ERD. Taken from [34] and reprinted with permission from MDPI.

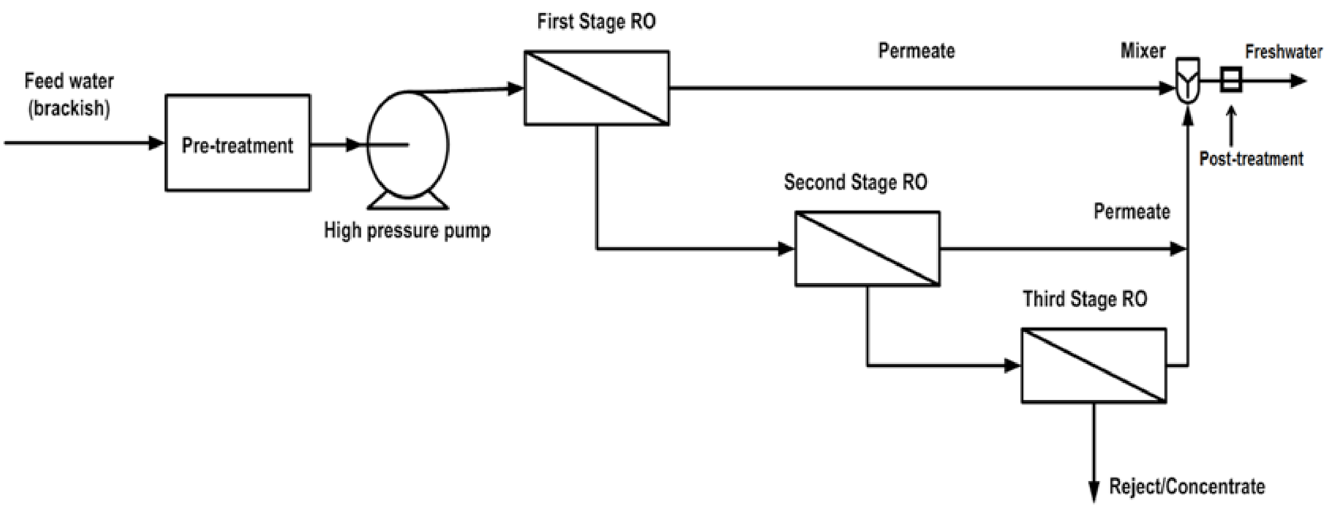


Fig. 4. Three-stage BWRO system with inter-stage booster pumps.

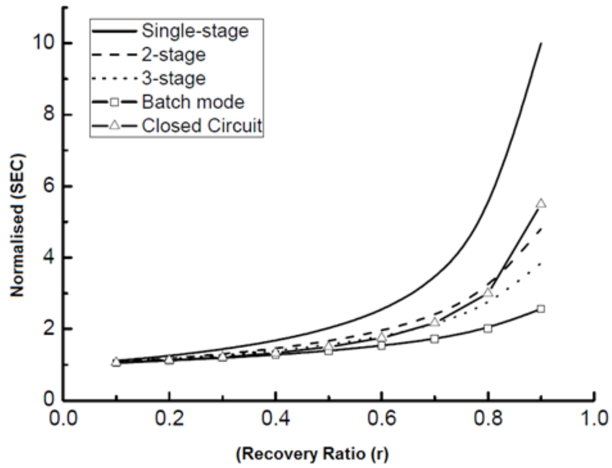


Fig. 6. Theoretical limit of normalized SEC in different multi-stage BWRO with energy recovery devices and batch-mode BWRO systems. Taken from [34] and reprinted with permission from MDPI.

mance of BWRO systems with different system configurations, where the normalized SEC is defined as SEC/P_{osm}.

It is important to note that there is a trade-off between economic and environmental objectives for a given BWRO plant which is identified by the definition of permeate flux. Higher permeate flux leads to the reduction in total cost but will increase consumption of electricity and desalination environmental impacts. Conversely, electricity consumption can be reduced by low permeate flux; however, this has to be compensated by larger membrane area and higher costs. Vince et al. [40] pointed out that the two major impacts of desalination (brine discharges and electricity consumption) identify a second trade-off. Indeed reduction of brine discharge can only be achieved with higher electricity consumption.

2.1.3. Intermediate precipitation treatment

Fouling and scaling are the most serious problems faced for the secondary desalting by RO of the concentrate obtained by the primary reverse osmosis (PRO) desalting step. With the aim of increasing the overall recovery of RO process, several authors [51–54] combined RO process with an intermediate treatment process to eliminate the precursors for the most problematic foulants and scalants.

Rahardianto et al. [53] conducted a study with the aim of achieving high product water recovery (>95%) of a mildly brackish water source by integrating the accelerated precipitation softening (APS) technique as an intermediate step between primary PRO and secondary RO desalination steps. Laboratory scale experiments were performed to investigate membrane scaling diagnostic and mineral solubility analysis were performed and evaluated to develop an effective strategy to reduce the concentration of scale-forming ions in primary RO concentrate. The study concluded that high recovery desalination of up to 98% for the Colorado River was feasible with the PRO-APS-SRO sequence with the use of antiscalant makeup in a SRO desalting stage.

The developed inter-stage demineralization strategy was found to be effective to control the concentration of scalant ions, which was not possible with traditional strategies (e.g., antiscalant addition and pH reduction). Later, by the similar authors, the study was extended to an RO desalting plant of agricultural drainage water of high mineral scaling tendency [55] and to a pilot scale brackish water RO unit. For the latter case, it was found that high recovery (~95%) is feasible despite significant process variations by the PRO-APS-SRO method over extended periods of time [54]. However, the authors suggested long-term implementation of the process would require robust on-line pH control strategy (for the effluent produced by precipitation step), careful selection and use of make-up antiscalant for the SRO desalting step, principally to inhibit membrane scaling by silicates and gypsum.

Another study carried out by Gabelich et al. [54] was conducted to enhance the recovery of a pilot-scale BWRO plant. This was accomplished by a two-stage process employing an inter-stage chemical demineralization (ICD) of the concentrate stream from PRO process followed by SRO desalting (i.e. PRO-ICD-SRO processes). Scaling propensity of the concentrate obtained from PRO desalting step was significantly reduced by alkaline-induced precipitation in a pilot-scale solids contact reactor prior to SRO step allowing an overall water recovery up to 95% of the PRO-ICD-SRO process.

Although, the processes discussed in this section have shown accomplishment for higher water recovery, their success entirely depend on the success and efficiency of intermediated chemical treatment step. It is important to point out that this step involves extensive use of chemicals and thus can increase the cost of the desalination. In addition, enormous volume of sludge is produced as a by-product that requires additional space for handling and storage and may pose serious disposal issues.

2.1.4. Electrodialysis (ED)

ED is a current-driven membrane-based separation process in which ions are transferred through alternating stacks of oppositely charged ion exchange membranes by a direct current voltage. ED is a mature technology with a multitude of new applications ranging from pre-treatment or pre-concentration technique before supplying the brine to evaporator/crystallizer [56–58], salt production [56,58,59], and recovery of organic acids from waste salt solutions [60]. The utilization of an ED process has shown success in brackish water desalination [61–66] and wastewater treatment and recycling of processed water streams applications [67–69] for low to medium feed water salinity.

Rautenbach et al. [70] adopted seeding technique in combination with electro dialysis reversal (EDR) process to achieve zero discharge from desalination of cooling tower effluent. The study concluded that although the technique showed some potential seeding/EDR operation for zero discharge, however, the process was found to be complex and expensive, since seeding crystals need to be prevented from entering into the narrow spaces of an ED stack.

Chakrabarty et al. [71] synthesized and tested ion-exchange membranes for brackish water desalination through ED process. Laboratory scale ED experiments were performed in recirculation mode using feed water of TDS 6000 mg/L of NaCl solution. Current efficiency and energy consumption were respectively calculated to be 80.14% and 4.29 kWh kg^{-1} under optimum operating conditions for 6000 mg/L feed water. The study concluded that the synthesized membranes were suitable for application in electro dialysis for water desalination.

As pointed out by Strathmann [72], ED technology is competing with RO for brackish water desalination, however, ED is mainly used in small to medium size plant (<100 m^3/d to >20,000 m^3/d) with feed water salinity ranging from 1000–5000 mg/L. Beyond the salinity limit of 10,000 mg/L, RO is considered to offer more economy for desalination. As demonstrated by Turek at al. [56], ED technique can minimized the concentration of Ca^{+2} or SO_4^{-2} ions to prevent crystallization during further evaporative process. However, the major problems faced by an ED process are fouling by colloidal particles, organics and growth of microbes. These problems should be addressed carefully and must be overcome for the efficient working of an ED equipment.

2.2. Hybrid techniques leading to ZLD

Several authors [73–75] have reported that water production costs can be reduced by using a hybrid system consisting of two or more desalination methods. Martinetti et al. [76] investigated a bench-scale study evaluating the potential of vacuum-enhanced direct contact membrane distillation (VEDCMD) and forward osmosis (FO) processes for the concentration of brackish water RO brines. Two RO brine streams of different TDS approximately 7,500 and 17,500 mg/L were further desalinated by VEDCMD and FO. Higher product water recoveries up to 90% and 81% were achieved, respectively, by FO and VEDCMD from the two brines. An overall recovery (recovery of RO combined with VEDCMD or FO) more than 96 and 98% total recoveries were reached for the two different brine streams. However, in both processes, water recoveries were limited by inorganic fouling (precipitation of inorganic salts on the membrane surface). Nevertheless, scale formed on the active surface of both MD and FO membranes was effectively removed by cleaning methods, restoring almost the initial flux. The study concluded that FO performs better than low- and high-temperature VEDCMD when treating a feed of low TDS and high scaling potential. However, when treating feed with higher TDS and lower scaling propensity low-temperature VEDCMD outperformed high-temperature VEDCMD and FO.

Oren et al. [77] studied a pilot-scale hybrid process combining RO, EDR, crystallizer/settler and wind assisted intensified evaporation (WAIV) to enhance the recovery of brackish water brine to near zero liquid discharge level. In this purist, an overall 97–98% recovery was achieved as product water from 1.3 to 1.8 m^3 of RO concentrate of brackish groundwater water with chloride levels of ~200 mg/L in batch experiments. Scaling propensity of ED was prevented by acidification, side loop crystallizer. In addition, in line micro filtration (MF) and side-loop UF were utilized to provide barrier for suspended solids to return to EDR unit. Preliminary economic estimate showed that the hybrid process is competitive with conventional RO and other enhanced recovery processes for brackish water desalination employing evaporation ponds.

Cath et al. [78] employed a novel osmotic dilution process (an osmotically driven membrane process), on both bench- and pilot-scales, by combining forward osmosis (FO) and seawater reverse osmosis (SWRO) processes for simultaneous desalination and production of pure water from the impaired water, using feed water from both secondary and tertiary treated effluents from wastewater treatment plant and impaired surface water to the process. The driving force for the osmotic dilution process arising from the salinity difference between seawater and impaired water was used for the dilution of seawater before desalination. The process has been reported to provide at least four salient features related to water and energy resources, such as, i) lower energy desalination of seawater, ii) multi-barrier protection of drinking water, iii) reduced RO membranes fouling propensity and iv) beneficial reuse of impaired water. Additionally, high rejection of dissolved solutes (both organic and inorganic and trace elements) was achieved via the multiple membrane barriers provided. An economic model was also developed that evaluated the process to be economical up to 63% recovery, beyond this recovery value, the capital cost associated with installing additional osmotic dilution membrane capacity seemed to be uneconomical for the reduced energy consumption of the SWRO process.

In an effort of enhancing the overall water recovery of an RO system, Zhang et al. [79] investigated the feasibility of a pilot-scale installation of ED installation to treat RO concentrate with high scaling propensity from a waste water treatment plant. The study aimed at reducing the volume of salty water discharge and to improve the impaired salinity of the coastline area(s) via ground water recharge. Scaling propensity of the RO concentrate was sufficiently reduced by the decarbonation process prior to ED step. The study concluded that an overall water recovery of ~95% can be achieved from the proposed RO-ED system.

In another study, Zhang et al. [80] performed techno-economic and environmental analysis for the treatment of RO concentrate originated by secondary effluent of a waste water treatment plant by employing ED process on the RO concentrate. The study concluded that the operational cost can be reduced to 0.19 ε/m^3 provided that the EDR concentrate is subjected to decarbonation in order to lower the scaling potential. Furthermore, it was proved that EDR is cost-effective and a feasible option to minimize RO concentrates with low to moderate salinity. Finally, it was suggested that CO^2 emission from membrane processes could be much less if renewable energy is employed as a power source compared to the conventional treatment methods.

Altaee et al. [81] proposed a tri-hybrid design comprising of NF/FO/BWRO system to enhance the recovery rate of brackish water. Three different salinities of brackish feed water (1, 1.4 and 2.4 g/L) were used to evaluate the proposed system under different operating conditions. The results of simulation demonstrated that the NF/FO/BWRO system was able to achieve an overall 90% recovery rate for the three different salinities of feed water investigated membrane yielded 75% water recovery of feed water, whereas, an additional 15% of water recovery was obtained from the NF concentrated brine by the following FO and

BWRO steps. In addition, power consumption of the proposed design was also calculated. The study concluded that the major power consumption (80%) was due to the final stage BWRO process, however, NF and FO processes consumed only 20% of the total power consumed by the proposed system.

Zhao et al. [82] experimentally explored the benefits of using a hybrid FO-NF system for brackish water desalination using a divalent draw solute. Bench-scale experiments were performed on an FO-NF system. Using real brackish feed water of TDS 3790 mg/L, an overall water recovery of 81.7% was achieved by the hybrid FO-NF system. The designed system was also compared with a stand-alone RO system for brackish water application. The study concluded that FO-NF system provides many advantages over standalone RO in brackish water desalination including less flux decline due to minimal membrane fouling, lower hydraulic pressure, better permeate quality, no pre-treatment requirement and no need of chemical cleaning.

Bamaga et al. [83] experimentally investigated a hybrid FO-RO system with the aim of evaluating osmotic energy recovery in FO driven membrane process. The results of the experimental study showed that the osmotic energy recovered ranged between 1.1 kJ and 2.2 kJ per each liter of permeate water at concentration gradients of 15 g/L and 30 g/L, respectively. At these two concentrations, the power density of the membrane was found to be 1.45 and 4.35 W/m^2, respectively. The study proved that the hybrid system could be used to extract water from an impaired sources using either seawater or RO brine as a draw solution through FO. However, the authors, pointed out the most significant challenges of FO technology are process and membrane configurations, membrane structure and chemistry.

Cath et al. [84] investigated a hybrid FO-RO system with the objective of extracting water from impaired aqueous solutions by using seawater as a draw solution. The authors proved that the designed hybrid system provides several advantages such as dilution of seawater before desalination, thus reducing the energy cost of desalination, and simultaneous removal of contaminants present in the impaired water through multi-level barriers of FO and RO membrane. In addition, a model based on the data collected on the system predicted that the designed system is economically feasible from 0 to 80% recovery of the impaired water source thus minimizing the cost of desalinated water significantly. In another study by Quintanilla et al. [85] it was pointed out that FO technology can help reduce the higher costs of desalination. In addition, FO technology can be particularly beneficial in augmenting the water supply from impaired water sources.

Thampy et al. [86] developed a domestic level hybrid ED-RO system for the desalination of ground/surface brackish water. Feed water with TDS ranging from 2000–4000 ppm was fed into a laboratory scale ED system and the treated water (the diluate with reduced TDS) was subsequently sent to an RO unit to produce potable water with TDS < 500 ppm. The basic idea of an ED-RO hybrid system is to operate the ED unit in the higher TDS region (i.e. lower system resistance and thus enhanced efficiency), and RO unit in lower TDS domain to lessen the salinity load on RO membrane. The designed hybrid system was claimed to achieve water recovery of > 50% to produce superior product water even with using brackish feed water of TDS 4000 ppm.

Turek et al. [87] combined EDR and RO processes with the aim of reducing cost of inland RO desalination and to enhance the overall product water recovery. Laboratory scale experiments were conducted on a hybrid EDR-RO system to investigate the effectiveness of the hybrid system. Brackish feed water of TDS about 4100 mg/L (with high potential of sulphate/carbonate scaling) was used, and an overall product water recovery of 91.6% was achieved despite high scaling potential of the investigated water. The projected unit EDR cost was found to be equal to $0.30/$m^3$ of EDR feed (or $0.38/$m^3$ of EDR diluate).

Sethi et al. [88] integrated RO system with an ED/EDR unit with the aim of enhancing water recovery and minimization of the total volume of concentrate. The authors performed bench-scale experiments and economic analysis of the designed hybrid system. The process employed comprised of primary desalination of brackish feed water by RO followed by the intermediate precipitation treatment of the RO concentrate (to remove potential scalants) and further desalination of the treated concentrate via ED/EDR to augment the overall product water recovery. The study concluded that the hybrid system could increase product water recovery from 10 to 20% compared to traditional RO configuration, with an overall recovery of about 95%. In addition, the results of the study showed that the hybrid RO+ED/EDR system is particularly cost-effective for plant capacities exceeding 1 mgd compared to RO+brine concentrator or RO+ZLD treatment options. Table 1 summarizes salient features of single and multi-stage ROs, tandem RO processes employing intermediate chemical treatments and hybrid processes leading to ZLD.

2.3. Current status of concentrate management technologies

Currently, two types of technologies are predominant for the concentrate/brine treatment, namely, pressure-driven (e.g., RO and NF) and current-driven (e.g., EDR) [89]. Although well-established, these processes cannot achieve higher water recovery that is mainly limited due shortening of membranes life caused by scaling and/or fouling of membranes [90]. Furthermore, the two studies [91,92] showed that energy costs of current-driven processes are proportional to the feed water salinity and the rate of salt removal, and therefore, desalination of higher TDS solutions (>5000 mg/L), e.g., RO concentrate is not economical by these techniques.

It is important to emphasize that tandem RO systems employing various intermediate chemical treatments systems as well as emerging hybrid systems described thus far can achieve higher water recoveries but the zero discharge goal is not accomplished. Recovery beyond 90% from the above mentioned systems is limited by higher osmotic pressure, fouling and precipitation of scalants onto the surface of membranes. More recent trend is to minimize the volume of brine/concentrate discharge from a desalination plant to zero or near zero level, and associated technologies are known as ZLD technologies. In the following section, some ZLD technologies are discussed in detail.

Table 1
Summary of the salient features of single- and multi-stage ROs, hybrid processes and tandem RO processes employing intermediate chemical treatments

Treatment method	Water recovery achieved (%)	Development status	Technical and economic observations	References
Single-stage RO (without ERD)	68%	Full scale	Lower capital cost. The most optimal BWRO system both economically and environmentally. Permeate production of 22,710 m^3/d was achieved with a feed water of TDS of 3261 mg/L and feed pressure 18–20 bar.	[36]
Double-stage RO (without any inter-stage chemical treatment)	80.8%	Full scale	Enhanced product water recovery. More energy-efficient than single stage RO. An additional water output of 3027 m^3/d was achieved by this system.	[39]
3-stage RO	–	Full scale		
Batch mode RO	70%	Prototype	A solar-powered desalination (of a ground water source) was performed utilizing the steam Rankine cycle coupled to an RO process. The efficiency of the crank mechanism depends on the expansion ratio of the steam and the recovery ratio. The efficiency decreases as these variables increase. It has been reported that a solar installation covering 1000 m^2 could produce 350 m^3 or more of desalinated water per d, and recovery ratios of 0.7 or higher are possible with feed salinities up to 10,000 ppm.	[48,49]
Close circuit desalination mode RO	80–88% (Depending on the feed salinity)	Pilot-scale	Desalination of brackish feed water of conductivity (6800–4000 μS cm^{-1}) was performed in a closed circuit by single stage consecutive sequential process. A variable pressure range of 11–22 bar with an average of 17.7 bar was employed. A record low RO energy saving (1.85 kWh m^{-3} with 13 LHM flux, and 85% efficiency of high pressure positive displacement pump) of ≈30% was achieved compared to larger desalination plants equipped with an ERD device.	[156,157]
RO+FO	91% (by FO alone) and 95–96% overall recovery, i.e., recovery achieved from RO and FO	Bench-scale	BWRO brine (with TDS 7500–17,500 mg/L) was further desalted. The system was found suitable for feed of low TDS and high scaling potential. An overall recovery of 96% was achieved	[76]
RO+VEDCMD	91% (by VEDCMD alone) and 89–98% overall recovery, i.e., recovery achieved from RO and VEDCMD	Bench-scale	BWRO brine (with TDS 7500–17,500 mg/L) further desalted. The system was reported to be suitable for feed of high TDS and low scaling potential. An overall recovery of 98% was achieved	
RO+EDR+WAEV	97–98%	Pilot-scale	A hybrid process (RO/EDR/WAEV) have been reported to be effective in recovering 97–98% of brackish water as product water (using feed water of conductivity 4.44 mho/cm) with chloride levels of 200 mg/L or less, and decreasing the disposed concentrate volume to minimum.	[77]

(*Continued*)

Table 1 (*Continued*)
Summary of the salient features of single- and multi-stage ROs, hybrid processes and tandem RO processes employing intermediate chemical treatments

Treatment method	Water recovery achieved (%)	Development status	Technical and economic observations	References
			The hybrid processes is competitive with RO and other inland desalination processes requiring evaporation ponds. Brackish water was desalinated at significantly lower costs (0.73 ε/m^3).	
FO+SWRO	63%	Both bench- and pilot-scales	The osmotic dilution process relies on the salinity difference between seawater and impaired water. Four salient features of the process are: i) lower energy desalination of seawater, ii) multi-barrier protection of drinking water, iii) reduced RO membranes fouling propensity and iv) beneficial reuse of impaired water. The process was found to be economical up to 63% recovery.	[78]
ED+RO	~95%	Pilot-scale	RO concentrate with high scaling propensity from a waste water treatment plan was treated by an ED system. Volume of salty water discharge was reduces, and the impaired salinity of the coastline area(s) was improved via ground water recharge. Operational cost can be reduced to 0.19 ε/m^3 provided that the EDR concentrate is subjected to decarbonation in order to lower the scaling potential. CO_2 emission from membrane processes could be much less if renewable energy is employed as a power source compared to the conventional treatment methods.	[79,80]
NF+FO+BWRO	90% (with 75% from NF and 15% from FO+RO)	Bench-scale	Three different salinities of brackish feed water (1, 1.4 and 2.4 g/L). The hybrid system was able to achieve an overall 90% recovery rate for the three different salinities of feed water investigated. An 80% power was consumed by the final stage BWRO process, however, NF and FO processes consumed only 20% of the total power consumed.	[81]
EDR+RO	91.6%	Laboratory scale	Brackish feed water of TDS about 4100 mg/L (with high potential of sulphate/carbonate scaling) was used. The cost of inland RO desalination was reduced and overall product water recovery was enhanced. The projected unit EDR cost was found to be equal to $0.30 per 1 m^3 of EDR feed (or $0.38 per 1 m^3 of EDR diluate).	[87]
PRO-APS-SRO Or PRO-ICS-SRO	>95% and up to 98% with makeup antiscalant before secondary RO step.	Both pilot- and full-scale	The process was evaluated for low-salinity water with TDS of ~1000 mg/L. Inter-stage chemical precipitation significantly reduced major scalant ions: calcium (>90%), barium (>95%), and strontium (~78%) and moderate reduction (10–20%) of magnesium and silica was also achieved.	[53–55]

3. Recent concentrate management technologies

Due to stringent discharge regulations, many industrial organizations are banned from discharging any liquid waste originating from their facilities. The other two major issues for desalination industry are: (a) difficult to-treat wastewaters, and (b) scarcity of water that demands recovery/recycle or reuse of existing water sources [93]. These urgencies necessitated the emergence and development of ZLD or near-ZLD technologies. As defined by Bond et al. [91], a ZLD system fully removes water from the concentrate/brine leaving a salt residue for disposal or reuse without leaving any liquid discharge from the plant boundary. However, Mickley [94] more strictly defined ZLD as, the term ZLD means no effluent (liquid) leaves the ground-level plant boundary.

3.1. Significance of ZLD technologies

ZLD is an emerging technology that has great potential to manage brine/concentrate produced in various industries including power plants, municipal, desalination wastewater treatment [95], water recycling and reuse etc. The application of a ZLD system is necessitated in order to: minimize enormous volume of concentrate/brine produced by desalination plants [96], reclaim/reuse wastewater to augment continuously increased global water scarcity, recover potable water and salt products from the concentrate stream, protecting the fresh water resources, meet stringent regulatory disposal issues on effluent discharge, reduce environmental impact and diminish cost of brine disposal in deep ocean (that increases exponentially with depth). It is important to emphasize here that concentrate management for inland desalination is much more serious compared to seawater desalination due to high recovery ratios in the former [34].

3.2. Various types (conventional and hybrid ZLDs) of ZLD systems

ZLD technologies are based on standalone thermal/evaporative processes, membrane processes (both current and pressure-driven), or a combination of the two, namely, hybrid systems [97]. As demonstrated by Mickley [94], general processing schemes of various types of ZLD systems are depicted in Fig. 7. As stated earlier, in a ZLD system/process water is entirely eliminated from the concentrate/brine such that no liquid is discharged from the plant boundary. A ZLD system, however, leaves a solid residue salts of precipitate as a final product that is transported to a suitable solid waste disposal facility, e.g., a landfill. ZLD processes range from technologically less complex (i.e., natural treatment systems) to highly technological/complex (e.g., complex mechanical processes) solutions. ZLD systems are employed in various industries covering vast areas of engineering disciplines including treatment and recycling of industrial waste effluents, and more recently, in tertiary treatment of municipal waste effluent and inland desalination. Various general ZLD processing schemes are presented in Table 2.

As described in a report by U.S. Department of the Interior Bureau of Reclamation [98], main ZLD systems developed and underdeveloped include: combination thermal process with zero liquid discharge, mechanical and thermal evaporation ZLD, enhanced membrane systems and thermal ZLD (EMS-ZLDs), evaporation ponds, dew vaporation, wind-aided intensified evaporation (WAIV) and salt solidification and sequestration.

Although a number of ZLD technologies have been effectively employed for industrial water treatment; nevertheless, the application of ZLD concept is rather new when implemented to the concentrate management of large-scale desalination plants. Salt solidification and sequestration, WAIV, and dew vaporation are the ZLD systems which are under development. Table 3 summarizes important features of ZLD systems described above.

Conventional ZLD systems essentially comprise of evaporators and brine crystallizers to entirely isolate dissolved salts from the water. Conventional ZLD processes are technologically complex and energy-intensive. The two published reports by Bowlin et al. [99] and Heimbigner [100] show that mechanical/thermal evaporation ZLD systems have been intensively applied in power industry where waste heat is abundant and regulations are more stringent limiting the discharge of effluent. However, Dascher et al. [101] and Rautenbach et al. [102] pointed out that a major issue with these systems was the formation of scale on the heat exchange tubes and

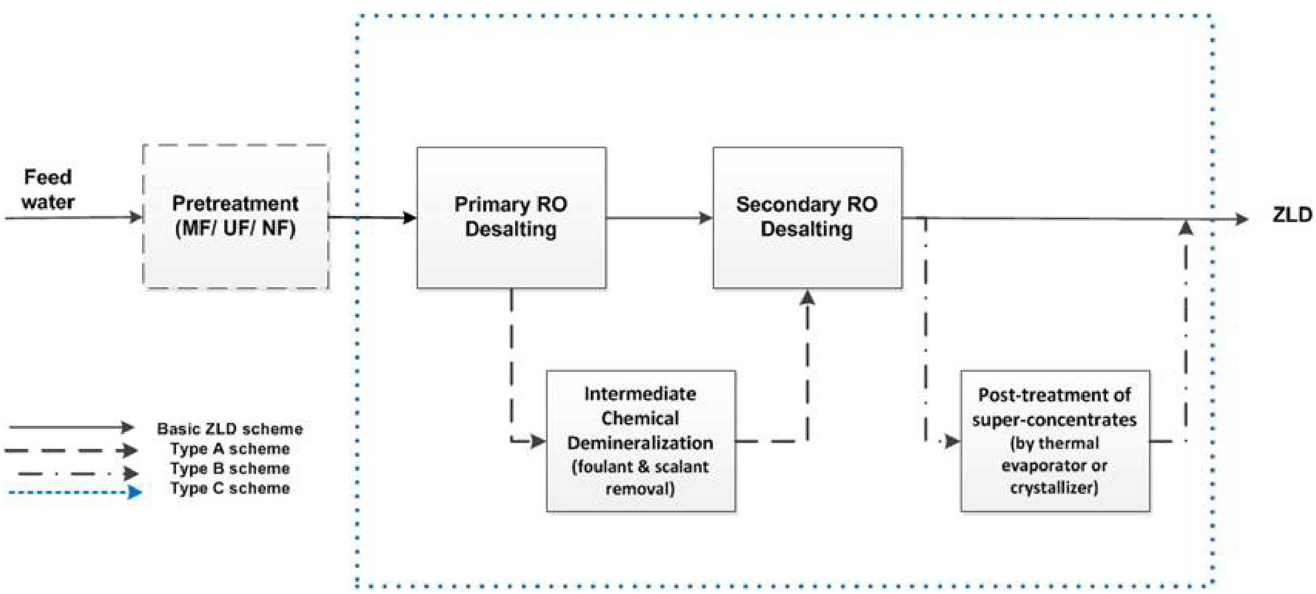
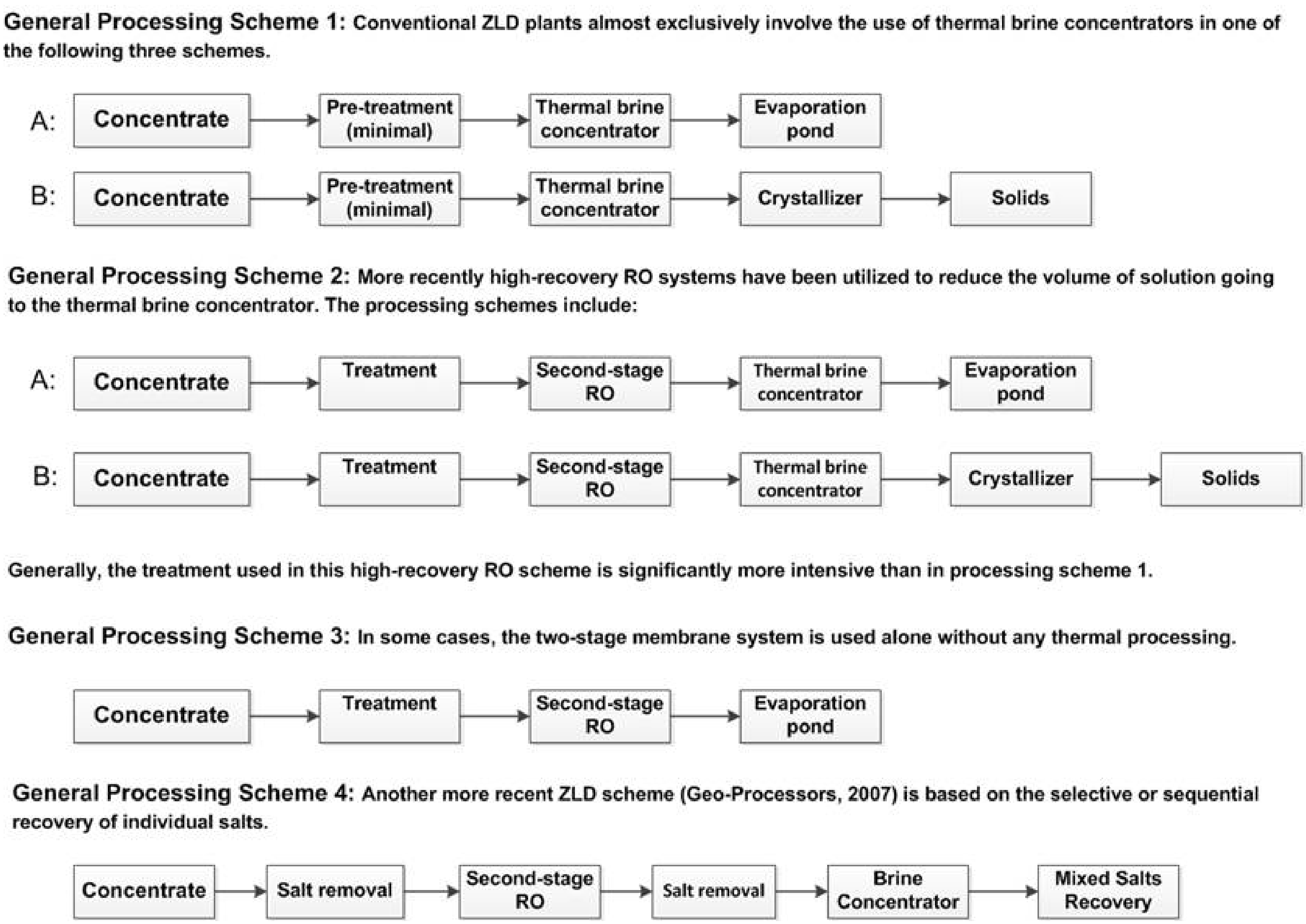


Fig. 7. Different schemes of ZLD systems.

Table 2
General processing schemes of ZLDs [94].



the problem was overcome by various special evaporators and seeded precipitation techniques. In addition, mechanical/thermal ZLDs come with their higher capital and O&M costs, and as pointed out earlier, they are energy-intensive too.

In order to minimize volume of brine that needs to be fed to the evaporators (and thereby reducing the energy demand) or to entirely replace the evaporative ZLD processing various designs of RO-incorporated ZLDs (EMS-ZLDs), namely, high-efficiency RO (HERO™), slurry precipitation and RO (SPARRO™) and advanced reject recovery of water (ARROW™) have been proposed [94].

The idea of adding membranes processes (e.g. RO and ED/EDR) is to lower the energy cost of the overall ZLD process scheme and to increase the salinity limit of the feed water to be treated, however, the utilization of membrane process is limited by the TDS of the feed water and thus the amount of fresh water to be recovered.

Although RO technology has been proven as an energy-efficient compared to thermal desalination, it has been demonstrated by Elimelech et al. [103] that the utilization of RO membrane modules is limited to a salinity limit of ~70,000 mg/L of RO exit brine. This limitation poses an upper limit on the salinity of water to be treated by RO in ZLD systems. Furthermore, the two studies by Pankratz et al. [104] and Seigworth et al. [105] have demonstrated that RO-incorporated ZLD processes have shown some degree of industrial success and are considered as emerging technologies, however, the major challenge is scaling by sparingly soluble mineral salts that limit the recoveries.

ZLD systems combined with ED have also been utilized to increase the recovery of RO in a hybrid ZLD system. It has been specified that when compared to RO, EDR and ED were able to concentrate feed waters to higher salinity of >100,000 mg/L, and were found economical (consuming 7–15 kWh_e/m^3) compared to MVC brine concentrators when treating brines of such higher salinity [77,106,107].

In order to partially desalinate feed waters, ED/EDR has also been utilized in combination with RO in some ZLD systems. The idea of designing such systems is to achieve the dual function: i) to extend the salinity limit of RO and ii) lowering energy consumption of brine concentrator. One example of such a system is presented in [Oren et al.]. In another example, Seig worth et al. [105] employed a hybrid EDR/RO/evaporation/crystallization ZLD system in order to bring down the cost of ZLD process and reuse the wastewater from Dos well combined cycle power plant. The use of ED and RO system prior to evaporator/crystallizer system, significantly reduced the volume of wastewater to be treated by thermal processes from 250 m gd to 90 m gd. The

Table 3
Summary of various ZLD systems [98]

Treatment process	Capital cost[a] (million dollars) Plant's capacity (1 mg d)	O&M Cost[b]/y (million dollars)	Advantages	Disadvantages/short- comings	Remarks
Thermal (MTE)	$17.69	$5.846	• Established technology. • Suitable for higher salinity (200,000 to 300,000 mg/L total solids). • A small site footprint. • Most organic and inorganic constituents removed and high-quality (up to TDS ~10) water produced.	• High capital and O&M costs. • Energy-intensive due to mechanical complexity. • Sound enclosures possibly needed. • Aesthetics limits: not feasible for projects with specific height limits (i.e., 50 ft. or less).	Well-established ZLD technology.
Thermal (FCC)	$20.68 Very high	$ 7.007	• Widespread industrial applications. • High-quality product water • Small site footprint when used for waste stream applications.	• High capital and O&M costs (primarily energy costs). • May require frequent cleaning when used for complex salt waste streams. • Mechanically complex. • Potential aesthetic issues associated with vertical profile.	Crystallizers are mechanically complex, energy-intensive and come with high capital and O&M costs.
Combined thermal (MTE (1 mg d) + FCC (0.05 mg d))	$20.56	$ 6.33	• Advantages and disadvantages of combined thermal ZLD systems are similar to those discussed for mechanical evaporation and crystallizers.		These ZLD systems can handle a wide range of feed water compositions while producing high-quality product water.
EMS+ZLD	Cost data is not available, however, it is expected to be similar to combined thermal ZLD		• Combined thermal ZLD systems can handle a wide range of feed water compositions while producing high-quality product water.		Proven technology for industrial brine concentrate management high in silica that requires high-quality product water.
EP	$ 43.00[c] (but cost is function of concentrate volume, geographic location, storage requirements and land cost)	$0.390[c]	• Industrially established for wastewater applications and small scale desalination plants. • Technologically simple. • Lower operating costs.	• Implementation of evaporation ponds is sensitive to land costs. • Liners are required to prevent seepage. • EPs are only suitable for arid areas with dry weather and lower humidity. • The major environmental threat is caused by the potential leakage through the lining.	EPs are optimal for arid climates with high evaporation rate.

(*Continued*)

Table 3 (*Continued*)
Summary of various ZLD systems [98]

Treatment process	Capital cost[a] (million dollars) Plant's capacity (1 mgd)	O&M Cost[b]/y (million dollars)	Advantages	Disadvantages/short- comings	Remarks
				• Social issues include: unpleasant odour, esthetics and salinization of surrounding land.	
ZLD combined with WAIV	Very low cost	Very low O&M cost	• Much reduced land requirement compared to EPs. • Lower O&M cost due to utilization of natural energy sources (solar and wind). • Operationally less complex compared to thermal based ZLD systems.	• These systems are still underdevelopment and lack full-scale performance, O&M and capital costs data. • Limited to regions with high evaporation rates. • Woven surfaces need periodic cleaning and rinsing. • Residuals has to be disposed of into landfills. • Larger footprints.	Technology is still under development and selection of suitable materials for evaporation surfaces is a critical requirement.
Dewvaportion	–	–	• Suitable for high-quality (distilled) water production. • The dew vaportion unit can be powered either by a renewable energy source (e.g., solar) or by waste heat. • Operationally lesser complex compared to thermal based ZLD systems. • Lower temperature and pressure make sure that operational cost is low. • Plastics heat transfer walls reduce capital cost and eliminate corrosion concerns.	• This technology is still in the development phase with no full-scale plant in service. • These systems lack full-scale performance, capital and O&M costs data. • The system is limited by lower water recovery (30 to 40 percent).	No capital cost, O&M cost and full-scale unit in service.
SAL-PROC™	–	–	• The process can recover marketable products.	• Not a stand-alone process brine concentration. • Not suitable for wastewater plants due to presence of toxic and hazardous materials present in wastewater.	SAL-PROC™ process involves multi-step chemical reactions and crystallization, followed by mechanical washing, dewatering and drying.

[a] Class 5 cost estimation: association for the advancement of cost estimating defines order-of-magnitude costs as class 5 cost estimates without detailed engineering data.
[b] Total capital cost (including equipment, installation and building to house the equipment in millions of dollar for a plant capacity of 1 million gallon per day (mg d)) and O&M costs (including power, labor, parts and maintenance, chemicals and consumables).
[c] This estimate is based on evaporation and rainfall data for Irvine, California. This estimate does not include land acquisition.

authors demonstrated that pre-concentrating the wastewater with EDR and/or RO resulted in 62% downsizing of the evaporator system, thus reducing the capital cost, maintenance and energy costs considerably. The authors showed that compared to straight thermal system (evaporator/crystallizer), the hybrid ZLD approach reduced the overall cost by $ 900,000, in addition, energy and operating costs by $ 680 per operating day was saved as well. Furthermore, EDR has been effectively employed to lower the hardness and thus reducing the scaling of RO [107].

Swift et al. [108] performed a comprehensive study to achieve zero discharge for brackish water desalination. In this pursuit, the authors used a hybrid system comprising of Salinity Gradient Solar Pond and Brine Concentrator Recovery System (SGSP-BCSR). The SGSP-BCRS system was thoroughly examined over a broad range of operating conditions for its approach and effectiveness for brackish water desalination/concentrate management, economic and technical feasibility. The study determined that coupling the BCRS with the SGSP technology and other desalination technologies can lead to a "zero discharge" desalination process. The results of the study revealed that such a system provides two major benefits: 1) reusing the brine concentrate, thus making it possible to achieve zero discharge; and 2) providing renewable and green energy for the desalination process. In addition, no fouling or scaling of membranes were observed for the duration of test.

Bond et al. [109] evaluated a ZLD process for the desalination of five different brackish water sources covering a broad range of TDS from 690 to 3,500 mg/L, and $CaCO_3$ hardness ranging from 68 to 1,720 mg/L, and silica from 9 to 57 mg/L as SiO_2. The proposed ZLD system comprised of five steps: 1) Primary RO, 2) concentrate treatment, 3) secondary RO, 4) brine concentrator (thermal desalination) and 5) evaporation pond. This ZLD scheme is different from traditional ZLD approach due to the addition of step 2 and 3, thus the goal of the study was to investigate the effectiveness of these two steps in order to minimize the cost and energy demands of the proposed ZLD system. The results of the study showed that the energy demand for the proposed ZLD system was 68–75% less than the energy demand for the traditional ZLD process (comprising of steps 1, 4 and 5). For all the five waters tested, concentrate treatment costs were 2–3 times lower for the proposed ZLD train when compared to traditional ZLD systems. The study concluded that the proposed ZLD consumed less energy due to less flow of brine that needs to be treated in the brine concentrator.

Heijman et al. [110] conducted two pilot-scale experiments for the treatment of two brackish water sources with the aim of approaching ZLD (99% recovery). The treatment scheme developed for the surface water consisted of fluidized ion exchange to remove positively charge multivalent ions, followed by UF, NF and granular activated carbon filtration. With this treatment setup, 97% water recovery was achieved. The authors suggested in order to achieving even higher recovery, it is essential to remove silica from the feed water since silica can limit the recovery. Another treatment concept tested for ground water consisted of: silica removal at high pH followed by sedimentation, weak acid cation exchange and NF. With this treatment scheme, an overall recovery of 99% was achieved. However, the authors warranted further studies for the techno-economic feasibility of the proposed concepts for achieving near-ZLD.

Ning et al. [45] employed tandem RO process for enhancing the product water recovery of inland municipal desalination facilities with the aim of developing a ZLD process. The authors described the importance of unique characteristics of site-specific water and foulant chemistry. In this context they performed autopsies, foulant analyses and cleaning studies of the fouled membranes from the three municipal RO plants investigated. The authors pointed out that if the intermediate precipitative treatment of limiting foulants become successful, water recovery of 97–99% can then be achieved using a secondary RO step, and the remaining 1–3% or the original water volume can be treated with the thermal/evaporative concentrators. Nonetheless, at such higher water recoveries, colloidal fouling was found to be the limiting factor for primary RO. The study concluded that the tandem RO process is highly promising process. However, the authors stressed that the detailed process conditions are dependent on site-specific water and foulant chemistry and need to be optimized accordingly.

Concentrate disposal to evaporation ponds (EPs) is a more common practice for inland desalination due to its simplicity; leaving brine in the ponds and allowing the water to evaporate by solar energy [111]. However, this approach is optimal only for dry and arid climates [112] that have high evaporation rate and low rain fall patterns. Furthermore, concentrate disposal to an EP requires large land areas, offers low productivity and the capital and O&M costs are subjected to acquisition of land and lining cost to prevent seepage [113]. The next section describes the major driving forces for the development of ZLD systems.

3.3. Volume reduction technologies (VRTs)

As pointed out in another report by U.S. Department of the Interior Bureau of Reclamation [114], VRTs (also known as high-recovery processing) are intended to reduce size and cost of the ultimate concentrate facilities. VRTs can reduce concentrate volumes by up to 90% depending upon water quality and technology used. VRTs that are commonly used today include: i) EDR, ii) vibratory shear-enhanced processing (VSEP), iii) precipitative softening and reverse osmosis, iv) enhanced membrane systems (EMS): e.g. high efficiency RO (HERO™), seeded/slurry precipitation and reverse osmosis (SPARRO™), and advanced reject recovery of water (ARROW™)), v) brine concentrator and vi) natural treatment systems. Other technologies that are still under development include: i) two pass nanofiltration, ii) forward osmosis, iii) membrane distillation, and iv) capacitive deionization (CDI). Detailed description of various volume reduction technologies including thermal, membrane and other techniques can be found elsewhere [32,94,114,115], however, the salient features of these technologies including advantages, disadvantages/short-comings, capital, and O&M costs are summarized in Table 4.

Mickley [94] has defined high-recovery technologies to be those capable of achieving recovery 92% or more. He further explained that concentrate volume reduction by any of these technologies is followed by an extra process required to entirely dispose of the concentrate. This is done either by discharging the liquid concentrate or solidifying the concentrate product. He also emphasized that the available final disposal options for brine or solid obtained from these technologies are limited and typically have an end step of disposing non-leachable salts or solid to a landfill.

3.4. Current and potential markets for ZLD systems

A large number of industrial processes use fresh water as a feed water and discharge contaminated water as an effluent. Depending on the nature of contaminants present in the effluent (or wastewater stream) and the detrimental effect of discharge of such effluents on the environment, disposal of these wastewater streams prior to appropriate treatment is strictly prohibited. The market for ZLD can be classified as follows:

1) Treatment and recycling of industrial waste effluents from the following industries
   - Petrochemicals, and fuels
   - Microelectronics

Table 4
Summary of various volume reduction technologies used in desalination industry [114]

Treatment process	Capital cost[a,b] (million dollars) Plant's capacity (1 mg d)	O&M[a,b] Cost/y (million dollars)	Advantages	Disadvantages/short- comings	Remarks
VSEP	$5.7 Feed TDS: 5000 ppm, SiO_2 concentration: 60 mg/L	$0.908	• Potentially high recovery rates. • Production of high-quality water (similar to conventional RO). • Minimal environmental issues associated with use. • Potentially no requirement for pretreatment chemicals (such as antiscalant and feed water pH adjustment).	• Through evaluation of the system at pilot scale is lacking. • Amorphous fouling with Al, Fe, and MnO_2 deposits is a potential problem. • Much higher fluxes (i.e., 40.8–51 LMH) compared to conventional RO (15.3–20.4 LMH) necessitate more frequent in-place cleaning. • Changing all membrane elements in a stack is required if one membrane plate needs replacement.	Higher capital and O&M costs than traditional RO. Proprietary technology from a single vendor in the USA. Sound attenuation technology typically required.
PS+RO	$13.0	$1.036	• Proven technology treatment train. • Applicable to concentrate with high silica content. • Regulatory issues similar to RO.	• Sludge and chemical treatment require additional space. • Certain feed water may require high consumption of chemicals. • High quantity of sludge produced needs to be disposed of. • Overall recovery limited by RO system osmotic pressure constraints.	Well-established technology but with large overall footprint, and might require additional chemical and sludge dewatering facilities.
HERO	$ 15.54	$ 0.927	• Suitable for feed water with high in silica content. • Small foot-print. • More product water is achieved than conventional RO due to prior removal of feed hardness. • Small aesthetic profile.	• Efficiency is limited to feed water TDS. • Both capital and O&M costs are higher. • Complex process requires skilled operators. • Simultaneous process control of RO systems, pH adjustment and the ion exchange make the control system complicated. • Huge quantity of precipitate is obtained.	HERO is a relatively newer type of membrane system and might require detailed pilot testing prior to implementation.

(*Continued*)

Table 4 (*Continued*)
Summary of various volume reduction technologies used in desalination industry [114]

Treatment process	Capital cost[a,b] (million dollars) Plant's capacity (1 mg d)	O&M[a,b] Cost/y (million dollars)	Advantages	Disadvantages/short- comings	Remarks
ED/EDR	$5.2 Feed TDS: 5000 ppm	$0.914	• Potential for higher recovery than other membranes. • Lower fouling potential as compared to RO. • Foulant may be removed by electric reversal.	• Inability to remove B, SiO_2 and uncharged micron particles. • Effective for TDS up to 8000 ppm. • Does not provide a barrier against turbidity and pathogens removal.	Multiple stages are required for treatment of high-TDS feed water that makes the process expensive.
MTE (vertical tube falling film type)	$17.698	$5.846	Advantages and disadvantages as mentioned in Table 3.		
Two-Pass NF	–	–	• Application to brine concentrate flows high in silica content with pH adjustment. • Small site footprint. • Lower energy cost.	• Lower product water recoveries than conventional RO. • Process is still under development and requires through testing both at pilot and full scale. • Complexity of process demands highly skilled operators.	Although two-pass NF was developed in late 2001, no full-scale application of this process exists.
FO	–	–	• Lower fouling potential than RO. • Lower energy demand than RO.	• High-performance (higher flux and salt rejection) membranes do not exist for FO process. • A draw solution that is easily separable has not been identified.	FO is promising, but the process is still under development stage.
MD	–	–	• High-quality water (distillate) is produced; however, distillate quality is dependent upon the extent of wetting of the membrane. • Suitable for concentrate streams that are high in silica content. • Both waste heat and low-grade energy can be used. • MD process require minimal or no pretreatment. • The process is rather simple compared to other thermal processes.	• The process is still under development; no-full-scale performance data are available. • MD has relatively low recoveries and fluxes. • Higher energy is needed with relatively low recovery and flux. • MD process is limited by high salinity of feed water. • The challenging task could be maintaining hydrophobic characteristics of membrane. • MD process requires membranes with specific set of characteristics which are not in the market.	MD technology is still under development. And the success of this of this technology will be dependent on the development of microporous membranes that have the desired porosity, hydrophobicity, low thermal conductivity, and a low potential for fouling.
SPARRO	–	–	• Low energy input compared to thermal processes.	• The process is not fully developed yet. • Capital cost, O&M cost and full-scale performance are missing.	Although the SPARRO process is not new, it is still under

(*Continued*)

Table 4 (*Continued*)
Summary of various volume reduction technologies used in desalination industry [114]

Treatment process	Capital cost[a,b] (million dollars) Plant's capacity (1 mg d)	O&M[a,b] Cost/y (million dollars)	Advantages	Disadvantages/short- comings	Remarks
			• Lesser pretreatment needed than other hybrid technologies.	• The SPARRO process results in lower salt rejection (80–85%) compared to RO processes (more than 95%). • Large footprint is necessary due to use of tubular membranes and large reaction tank required. • Relatively complex operation is required.	development as a brine concentrate management technology.
ARROW	–	–	• Higher quality of product water is achieved. • The process is particularly suitable for concentrate streams that are rich in silica content. • Concentrate generation and disposal cost is reduced due to higher water recovery (up to 95%). • The compactness of the unit helps in reducing both footprints and installation time. • The unit is suitable for applications of less than 0.25 mg d.	• The unit comes with higher chemical costs (needed for pretreatment and softening of feed water). • Skilled operators are required due to the complex nature of ARROW process. • The system still lacks pilot testing that is mandatory to determine key design criteria. • Sludge from precipitative softening might require separate disposal, which creates additional challenge and expense.	Process is still under development; no full-scale applications exist in municipal water or wastewater treatment.
CDI	–	–	• CDI has low consumption of energy. • No chemicals are used for regeneration of electrodes. • Silica does not limit the recovery.	• The process cannot remove all constituents (that is, boron, silica, and uncharged micro-pollutants). • CDI is not recognized as a water treatment technology for not being able to offer a barrier against pathogens. • Treatment of high-TDS feed water might necessitate multi-staging for brine-concentrate which increases capital and O&M costs. • CDI is limited by the lower recoveries of water when compared to conventional membrane processes.	CDI is still under development and lacks full-scale performance, capital, and O&M data.

[a] Class 5 cost estimation: association for the advancement of cost estimating defines order-of-magnitude costs as class 5 cost estimates without detailed engineering data.
[b] Total capital cost (including equipment, installation and building to house the equipment in millions of dollar for a plant capacity of 1 million gallon per day (mg d)) and O&M costs (including power, labor, parts and maintenance, chemicals and consumables).

- Textile [116–118]
- Mining of natural resources such as coal, metals, etc.
- Polymers and plastics processing

2) Tertiary treatment of municipal waste effluent [119]
3) Inland desalination [120].

Reject brine from brackish water sources cannot be dumped into seawater and their improper disposal into surrounding lands results in several complications that are not only related to environment but also to agriculture and desalination plants in the surroundings [121,122]. Desalination of brackish water by reverse osmosis may result in 3–10 times increase of salt concentrations resulting in scale formation on membrane [123]. Due to non-feasibility of current ZLD technologies or their combinations due to economics and sustainability, there is an urgent need of developing inexpensive methods that will maximize the product recovery.

Al Masri et al. [121] studied the feasibility of two-stage process for the efficient removal of calcium sulfate from the concentrate of a brackish water source. They were able to demonstrate that just by simple chemical methods it is possible to achieve significant reduction in the volume of the precipitated solid in the treatment system. Likewise, in another detailed study [124], employed a combination of pellet reactor for radium and hardness minimization, reverse osmosis with intermediate precipitation, and concentrated brine crystallization. They found that in spite of the transportation distance, the energy consumption for the overall brackish water desalination and concentration management was still lower than seawater desalination.

3.5. Basic elements of designing a ZLD system

A large number of industries use water in various processes and generate wastewater in some way. However, the waste stream produced by different industrial processes is widely varying. One of the major tasks while designing a ZLD system is clear and thorough description of the waste stream. As emphasized by Till berg [125], the essential factors to be determined prior to designing a ZLD system are the realistic estimate of composition and chemistry (including both organics, e.g., chemical oxygen demand, biochemical oxygen demand, total carbon and in organics (anions, cations and silica)) of feed/waste stream, feed flow rate and purity. It is important to point out the fact that due to the diversified nature of waste stream it is impossible to design a general ZLD system. So, each ZLD system is distinctive and has to be customized.

In order to have an optimally designed system a realistic description of waste stream is vital. The size and initial capital cost of the ZLD system is typically determined by the selection of the waste water flow rate. If the water flow rate is small, not many components are necessary. Till berg [125] provided general guidelines for designing a ZLD system, these are summarized as:

- Below 10 gallon per minute (g pm) of feed; combination of crystallizers and/or spray dyers may be employed.
- If feed volume is in the range of 10–50 g pm, only crystallizer should be utilized.
- If feed is unsaturated and its volume is in the range of 50–100 g pm, an RO/EDR/crystallizer combination is recommended.
- If feed is saturated with its volume ranging 50 –100 g pm, utilize an evaporator/crystallizer combination.
- If feed volume is in the range of 100–500 g pm, either an evaporator/crystallizer grouping or an RO/crystallizer may be the most cost-effective.
- If feed volume is ranging from 500–1000 g pm, all three should be utilized.

The detailed description of recent trends in ZLDs and future outlook of ZLD systems is given section 6.

4. Beneficial uses of concentrate/brine

One possible way of off-setting the cost of desalination and subsequent concentrate disposal is to extract valuable salts, minerals, chemicals, metals and other byproducts from concentrate/brine. However, this option strongly depends on the economic feasibility of the processes involved and recovery of marketable byproducts. Jordahl et al. [126] explored the feasibility of valuable and nontraditional utilization of concentrate. The author pointed out several important site-specific factors for useful utilization of concentrates such as costs, markets, climate, regulatory permits, and ecological hazards.

4.1. Recovery of salts and by products

Some of the chemical components such as salts, minerals and other by products can be extracted from concentrate by some chemical or physical processes for other applications. However, it is important to mention that the goal of these applications is to extract salts and minerals without any consideration to water recovery. In the past, several attempts have been made for the recovery of salts and minerals from concentrate, e.g. in Japan ED was employed at industrial scale for the production of NaCl from sweater, and it has been suggested that up to 20% more energy can be saved by using SWRO concentrate compared to seawater as a raw material [58].

Davis [127] treated the SWRO concentrate via ED to reduce the salinity of the reject prior to recycling SWRO. The valuable products such as NaCl, $Mg(OH)_2$ and bromide were extracted from the pre-concentrated SWRO brine. Ravizky et al. [128] produced high quality table salt from a blend of 20% BWRO and 80% SWRO concentrate. The salt was produced by feeding this blend to a series of evaporation ponds followed by further processing in a nearby salt factory.

SAL-PROC™ is a patented brine treatment process by Geo-Processors USA, Inc. The SAL-PROC™ is based on sequential extraction to recover valuable salts from inorganic saline water and is mainly suitable for brines with higher levels of dissolved salts.

Recently, Dae Hyun Kim [129] reviewed desalting processes and economic analysis of the recovery of salts from brines. The study concluded that the membranes based (RO and ion-exchange) techniques are cost-effective salt recovery process when compared to thermal (MSF-ED), NF-membrane crystallization Dow chemical process. In addition, the author advised that the membranes based methods should be further investigated for their technical developments in order to enhance their performance efficiency so that the cost associated with the desalting process may be further reduced.

4.2. Metal recovery and energy harvesting

Several research efforts have been devoted to harvest the potential (chemical) energy that exists between highly saline water (e.g. brackish and seawater concentrate) and lower salinity waters (e.g. municipal or river water). Rome et al. [130] stated that 0.5 k Wh energy was released by mixing equal volumes (1 m^3) of river water (~5 mM) and seawater (~0.5 M). In order to harvest the chemical potential energy various techniques have been investigated, e.g., Post et al. [131] evaluated retarded osmosis and reverse electro dialysis. Turek and Bandura [132], Dlugo1ecki et al. [133] and Veerman et al. [134,135] utilized reverse electro dialysis. Achilli et al. [136] investigated pressure retarded osmosis process. Recently, Swift et al. [108] used a hybrid system comprising of salinity gradient solar pond and brine concentrator recovery system (SGSP-BCSR). The SGSP-BCSR system was reported to providing renewable and green energy for the desalination process along with brine concentration and thus making it possible to achieve ZLD.

Some concentrate contains several precious and rare earth elements that may be of interest, and recovery of these valuable elements thus can offset the cost of desalination to some extent. Dirach et al. [6] designed a protocol to extract valuable metals including indium, gallium, rubidium, cesium, potassium, germanium etc. from brine. Petersková et al. [137] investigated several sorbents for extracting precious metals such as lithium, rubidium, cesium and uranium from RO concentrate. Although, recovery of valuable metals from brine shows some potential of offsetting the cost of desalination, these methods are not mature yet, and are not competitive with the traditional processes.

4.3. Eutectic freezing crystallization (EFC)

The eutectic freezing crystallization (EFC) process entails form the existence of the eutectic point. The eutectic point is a specific point in the phase diagram of salt-water mixture where both salt and ice coexist in equilibrium (the eutectic temperature) at a certain concentration (the eutectic concentration). In an EFC process effective separation between salt and ice from a saline water is carried on the basis of density difference at eutectic point [138]. As the heat of vaporization of water (2257 kJ/kg) is six times higher than the heat of fusion of ice (33 kJ/kg), so the EFC process requires considerably lesser energy to recover ice when compared to separating it by an evaporation process [139].

Stepakoff and co-workers [140] developed a bench scale EFC system based on direct cooling in a crystallizer followed by salt-ice separation. Another design comprising of a cooled disk column crystallizer that utilized EFC method was developed to recover $CuSO_4$ crystals from copper sulfate solution [141]. Randall et al. [142] employed an EFC process to convert liquid waste (brine) obtained from an RO plant. The study reported 97% recovery of pure water from the liquid waste along with high purity calcium sulphate and sodium sulphate (with purities 98.0 and 96.4% respectively). Moreover, Himawan successfully used EFC technique to separate $MgSO_4{\cdot}7H_2O$ from a magnesium sulfate industrial stream emitted from flue gas desulphurization [142].

EFC process offers several advantages over other conventional brine treatment processes some of which are listed below [142]:

1. The process is fairly simply as it does not require the addition of chemical compounds.
2. From the point of view of thermodynamics, EFC requires considerably lesser energy to carry out the separation of salt from brine when compared to an evaporative separation treatment of brine.
3. The nature of the process excludes the impurities from the ice structure during the crystallization.
4. At the eutectic point salt sinks to the bottom of crystallizer whereas ice floats thus separating the both on the basis of gravity.
5. The lower operating temperature of an EFC process minimizes the potential of corrosion.
6. Theoretically, a 100% separation of ice and salt is possible when operating at eutectic conditions.

Nevertheless, the applicability of EFC process to remove multiple salts from complex multi-component, hyper saline brines has not yet been reported.

5. Final disposal options

The concentrate/brine obtained from a brine concentrator needs to be finally disposed to a nearby water body or suitable underground location. Based on the quantity and hazardous nature, concentrate may also be disposed to a landfill. It is important to emphasize that depending on the volume and chemical nature of concentrate, its disposal can be very problematic from the engineering and economic point of view. In addition, Watson et al. [143] described that there are stringent environmental and regulatory legislative restrictions that prohibit desalting plants to discharging liquid wastes into underground or surface waters. However, as specified by Mickley [144] and Ladewig et al. [145], widely used methods of concentrate disposal include: 1) deep well injection, 2) disposal to sewer or wastewater treatment facility, 3) discharge to surface water, 4) landfill disposal option and 5) disposal to evaporation ponds. These final disposal options are briefly describe in the following sections.

5.1. Deep well injection (DWI)

As described by Xu et al. [146], DWI is a concentrate management technology that utilizes geologic formations that are suitable for permanently isolating stored liquid concentrate from shallower potable ground water sources, i.e. aquifers. The depth of the well generally depends on the existing geologic strata, the class of well used and the depth to groundwater aquifers1. Five classes of wells have been described by U.S. Department of the Interior Bureau of Reclamation. These five classes of wells are classified by the origin and characteristics of the liquid waste [98]. This disposal technique is suitable for inland desalination facilities. However, the method is limited due to several challenges and issues such as disposal cost (that is site-specific), availability of nearby appropriate geological formation. In addition, this method is not viable for regions of increased seismic activity or near geological faults. Moreover, the major environmental concern is greater potential of leakage to, and contamination of nearby water supply source (e.g., aquifer), and owing to this problem it is difficult to obtain discharge permitting [146]. Six different ways that may lead to potential leakage/migration of concentrate causing the contamination of aquifers have been reported by Shammas et al. [88], and United States Environmental Protection Agency [147,148]. Due to these limitations and specific conditions required by DWI technique, this method of concentrate disposal is not widely used.

5.2. Disposal via wastewater treatment facility

As an alternative final disposal option for the concentrate can be a nearby sewer system. This method of disposal involves direct disposal of the concentrate to sewer system of an existing wastewater treatment facility. However, this option depends upon the proximity of sewer system from the plant discharging the concentrate, and could be limited due to potential harmful/damaging effects on the ability of wastewater plants to fulfil regulatory discharge requirements. Mixing of the concentrate from a desalting facility with wastewater influent is a common practice and is carried out in order to reduce or eliminate treatment needs. As pointed out by U.S. Department of the Interior Bureau of Reclamation, capital cost for concentrate mixing is highly project-specific [98].

Xu et al. [146] mentioned that lower energy and costs are involved in this final disposal options; however, the method is usually used for wastewater facilities and brackish water desalination plants. Other limitations of this method include: hydraulic capacity of the sewer collection system and treatment capability of the wastewater treatment plant receiving the discharge. Furthermore, this method appears to be suitable only to small size facilities such as brackish water desalination plants and other small size inland desalination facilities.

5.3. Discharge to surface water

As described by Ladewig and Asquith [145], this is the most commonly used method of concentrate disposal that involves discharging concentrate directly to any surface water body, e.g., ocean, bays, river, creeks, estuary, lakes via a well-designed outfall system.

However as mentioned in reference [98], these disposal options also require regulatory disposal permits which most commonly require for toxicity, residual chlorine, total suspended solids (TSS), and biochemical oxygen demand (BOD) below a certain minimum level.

The benefits of using this disposal method include its suitability for facilities of all sizes and its cost effectiveness. However, Xu et al. [146] mentioned that major challenges faced by this disposal options are environmental which are caused by the salinity differences and major ion imbalance between surface waters and concentrate to be disposed of. This salinity difference has been pointed out to be the major adverse effect on aquatic life. Another major issue is to comply with strict discharge regulations.

As emphasized by Ladewig and Asquith [145], it is important to mention, however, that the harmful environmental effects of this disposal methods may be reduced by diluting the concentrate before discharging. Dilution of the concentrate may be carried out either through the design of the outfall structure and diffusers or by the pretreatment processes that may reduce the harmful effects on the environment that are likely to be caused by concentrate disposal [145].

5.4. Landfill disposal option

As mentioned in a report published by U.S. Department of the Interior Bureau of Reclamation [98], in this concentrate management technique, either concentrate-precipitated solid or slurry/liquid is finally disposed to a land fill. Reduction/disposal technique employed dictates the quantity of waste to be disposed of into a land fill. It is important to point out that classification of the concentrate is site-specific and is based on the waste characteristics. However, in the same report [98], it is described that any waste is considered a hazardous waste if it exhibits any one of the four characteristics, namely, corrosivity, toxicity, reactivity, or ignitability. Furthermore, concentrate is designated by the United States Environmental Protection Agency (USEPA) as an industrial waste, which is noteworthy because this designation confines disposal to a Class I landfill (the facilities as defined in the California Code of Regulations (23 CCR 2531, Municipal Solid Waste, Construction Debris, and Yard Waste)).

As described by Xu et al. [146], being cheaper, this disposal technique is rather easy to implement, and has been beneficially used for the land filling of parks, golf courses and irrigation of lawns or crops. However, this disposal method is limited to: small facilities, irrigation of salt tolerant tree and plants, regional climate, contamination of groundwater and soil.

5.5. Evaporation ponds (EPs)

According to Ladewig and Asquith [145], in this concentrate management method concentrate/brine is finally disposed of by pumping it into a large pond whereby water is slowly evaporated by solar heat. EPs offer a low technology solution for concentrate management and are widely used methods of concentrate management in the Australia and Middle East. However, their cost mainly depends on two factors, namely, acquisition of land and lining of ponds.

Xu et al. [146] specified that concentrate disposal into EPs benefit from simplicity of operation, lower maintenance cost and possibility of salt recovery. Although, EPs are an attractive concentrate disposal option for small desalination facilities (mainly due to their simplicity and lower operating costs) but, their implementation is limited to dry and arid areas with low rainfall patterns and higher evaporation rates.

However, Ladewig et al. [145] and Morillo et al. [96] have stated that EPs are not suitable for processing larger quantities of effluent since they require larger areas of land. In addition, there is a greater environmental threat posed by the potential leakage/seepage of brine and other chemicals through lining and thereby contamination of surrounding aquifers. As pointed out by Christen et al. [149], other problems associated to EPs include unpleasant odorous, aesthetic and potential salinization of surrounding land. Details of the above mentioned final concentrate disposal techniques can be seen here [22,145].

6. Conclusions, recent trends and future outlook of ZLDs

6.1. Recent trends and future outlook of ZLDs

6.1.1. Zero discharge desalination (ZDD)

Recently, another version of ZLD termed as zero discharge desalination (ZDD) was introduced by Davis [127]. ZDD is similar to a ZLD system but differs in that it specifically targets desalination and includes the separation of the salts into salable products at higher product water recovery (up to 97%). The ZDD technology makes use of the energy-saving feature of electro dialysis metathesis (EDM) to remove the monovalent salts from the RO reject and concentrate them about threefold before the evaporation step. It is claimed that if fully implemented, the ZDD process could produce high-purity NaCl, $Mg(OH)_2$, Br_2, and mixed dry salts with zero liquid discharge. Near ZDD designs have been implemented commercially for producing salt from seawater [72]. Moreover, ZDD system designs for seawater desalination that are economically feasible, have also been proposed [150].

6.1.2. Application of advanced components and systems

More recently, a US-based company (Oasys MBC™) [127], employed a membrane brine concentrator (MBC) system rather than using a conventional mechanical vapor compression evaporator for brine concentration. The plant utilized an MBC system incorporating forward osmosis process to further concentrate RO reject from total dissolved solids of 60,000 mg/L to approximately 280,000 mg/L. Another recent technological development by the New Logic Research [151] is the utilization of a VSEP system to pre-concentrating RO reject in water reuse and ZLD applications. The company installed a VSEP unit that was able to concentrate the HERO reject from 13,000 mg/L to nearly 50,000 mg/L to match the evaporator feed requirements. Following a successful economical assessment, UK-based and an Indian-based company will jointly develop and commercialize Modern Water's brine concentration technology, presumably employing forward osmosis. The two companies agreed to jointly fund and deploy a pilot test plant at an operational wastewater treatment site in India [152].

6.1.3. Inclination towards hybrid systems

In the past, ZLD systems were mainly used in power plants; however, their utilization in wastewater plants, municipal and desalination industries are relatively newer. Thermal-based ZLD systems comprise of evaporator/crystallizer units and are well-established technologies. However, they are energy-intensive and have high operational and capital costs due to high energy consumption (20–40 kWh/m^3 vs. 2–3 kWh/m^3 in desalination) [103], use of chemicals and expensive corrosion-resistant materials. Hybrids ZLD systems with high-recovery are and will be the dominant approach. So, there is a plenty of room for the research work needed for the development of hybrid and other cost-effective ZLD systems and designs to bring down costs of conventional ZLD systems.

The major advantage of hybridization is that one is able to overcome the deficiency or limitation of a particular technique (e.g. RO) by using it in combination with another approach. For example, Oren et al. employed a combination of reverse osmosis (RO) and electro dialysis reversal (EDR) for brackish water desalination and were successful in obtaining a recovery ratio as high as 97–98% [77]. In this manner they were able to extend the salinity limit of RO and at the same time reduce energy consumption relative to brine concentrators. Likewise, membrane distillation (MD), a thermal membrane-based process, has been used in conjunction with RO to achieve higher recoveries that are usually not possible with RO alone [153,154].

Over 200% yearly growth rate for recovery/reuse systems and processes is predicted by industry experts. It is expected that a major share of which could be accounted for by ZLD systems and components. Owing to flourishing economic and stringent regulatory situations ZLD or near-zero discharge will continue to flourish rapidly. From zero to hero – the rise of ZLD has been praised by global water intelligence [155] as, "If there was ever a Holy Grail of water recovery and reuse in an industrial plant, then it is undoubtedly zero liquid discharge or ZLD".

7. Conclusions

Based on the literature review performed in this study, the following conclusions can be drawn for managing the enormous volumes of concentrate generated by desalination and wastewater treatment industries worldwide.

- Sustainable concentrate management will become increasingly important as we strive to manage salinity and meet future water demands.
- In general, concentrate volume minimization by membranes-based processing prior to use of a brine concentrator is a recommended scheme. However, membrane processes need to be optimized by adopting the following measures: the use of proper pretreatment, the right choice of the membrane process and membrane, the appropriate choice of chemicals, and the operation at a high recovery. However, the volume of the concentrate has an optimal value because the concentrations in the concentrate increase as the volume decreases, and this leads to an increased energy consumption, which

Table 5
Summary of brine-concentrate technology applicability and evaluation criteria. Adapted from [98]

Technology	Applicability		Evaluation Criteria												
	Ground water	Recycled water	Performance	Amount of Water Recovered	Water Quality Produced	Design Flexibility and implementability	Technology Footprint	Amount of Waste Minimization	Hazardous Wastes/ Environmental Concerns	Chemical Usage/ Handling and Safety	Proven Technology	Regulatory Complexity	Maintenance and Labor Requirements	Aesthetics and Public Acceptance	Ease of Use
Volume reduction technologies															
Electrodialysis (ED) / Electrodialysis reversal	G	G	G	A	P	G	G	A	G	A	G	G	A	G	A
Vibratory shear-enhanced processing (VSEP)	G	A	G	A	A	A	G	A	A	A	P	A	P	A	A
Precipitative softening and reverse osmosis (PS/RO)	G	A	G	G	G	A	A	A	A	P	G	G	A	A	P
Enhanced membrane systems (EMS)	G	A	G	G	G	G	A	A	A	A	G	G	A	A	P
Two-Pass nanofiltration	G	A	A	A	A	A	G	A	A	A	P	G	A	G	P
Forward osmosis (FO)	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.	Uk.
Membrane distillation (MD)	G	A	A	A	A	A	A	A	A	A	P	G	A	G	P
Slurry precipitation and reverse osmosis (SPARRO)	G	A	A	G	A	A	A	A	A	A	P	A	A	G	P
Advanced reject recovery of water (ARROW)	G	A	G	G	G	A	A	A	A	P	P	A	A	A	P
Capacitive deionization (CDI)	G	A	A	A	P	A	A	G	G	A	A	A	A	G	A
ZERO LIQUID DISCHARGE															
Combination thermal process with ZLD	G	G	G	G	G	A	A	A	A	A	G	G	P	P	P
Enhanced membrane and thermal system ZLD	G	G	G	G	G	A	A	A	A	A	G	G	P	P	P
Evaporation ponds (EP)	G	G	G	P	P	A	P	A	A	G	G	G	G	P	G
Wind-Aided intensified	G	A	A	P	P	G	G	G	A	A	P	A	A	P	G
Dew vaporation	G	G	A	G	G	A	G	G	G	G	P	A	A	A	A
FINAL DISPOSAL OPTIONS															
Deep well injection (DWI)	G	G	G	NA	NA	A	G	G	G	G	G	A	G	G	G
WWTP effluent blending	G	G	NA	NA	NA	G	G	G	G	G	G	G	G	G	G
Ocean outfall	G	G	NA	NA	NA	P	A	P	P	G	G	P	G	P	G
Landfill	G	G	G	NA	NA	P	P	G	G	G	G	G	A	A	A

LEGENDS: G – good, A – average; P – poor; NA – not applicable; Uk. – Unknown.

is related to volume and concentration, thus increasing the operational costs.

- Best ZLD method may depend on water quality characteristics and treatment goals. Capital and O&M costs of both high-recovery and ZLD systems are significantly affected by salinity and composition of the feed water. In general, ZLD costs are lower for a low-salinity and low-hardness feed water. The performance and cost sensitivities of ZLD systems to salinity and composition of feed water advocate that careful and detailed analysis of salinity and composition of feed water is required for meaningful cost projections of complex processing steps involved in a ZLD system.
- Hybrid ZLD systems with high-recovery are expected to be the dominant approach. So, more focused research is needed for the development of hybrid and other cost-effective ZLD systems and designs to bring down cost of conventional ZLD systems.
- The final disposal challenge is what to do with sodium-dominated brine. The selection of final disposal option depends on factors such as total dissolved solids (TDS), volume of the brine and toxicity present in the concentrate to be disposed of. In general, environmental regulations are more stringent for disposal to a water body compared to a solid landfill or DWI option.
- Finally, all concentrate management technologies including VRTs, ZLDs and final disposal options are summarized and evaluated in terms of their applicability and performance criteria (refer to Table 5).

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