



Review

An overview of brine management: Emerging desalination technologies, life cycle assessment, and metal recovery methodologies

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ABSTRACT

This study examines which management methods are the most recent and advanced in managing rejected brine generated from desalination plants. It also provides up-to-date information regarding the most adequate technologies that generate a minimum quantity of rejected brine via the use of minimization techniques and analyzes the method of direct disposal that has lately received noticeable improvements. It further discusses the reuse of discarded brine to recover valuable goods and sequestration of carbon dioxide. Sustainability is an important parameter that needs consideration to achieve uninterrupted operation of the discarded brine management to achieve the least environmental, social, and economic aftermath. To properly deal with any environmental issues related to brine disposal, different methods are implemented so that, in the end, higher water recovery is achievable from the desalination processes, namely brine minimization and rejection technologies (pressure retarded osmosis, microbial desalination cell technology), membrane-based technologies (vibratory shear enhanced processing, forward osmosis, electrodialysis, electrodialysis reverse, and electrodialysis metathesis, pervaporation method, thermal-based technologies (wind-aided intensified evaporation, brine concentrators, ohmic evaporator, membrane distillation, multi-stage flash distillation). This review also critically examined the two conventional approaches commonly used in life cycle assessment (LCA), when evaluating the ecotoxic effect of discarded brine. It intends to discuss the currently available methods and propose an improved method for evaluating the toxicity potential of brine on the aquatic ecosystem originated from seawater desalination plants. The Group-by-Group method takes into consideration the demerits of the two methods of the traditional method of LCA or chemical-specific approach as it provides a more holistic coverage for complicated brine to be disposed of. Recently, attention has been focused on recovering valuable metals from the discharged concentrated brine waste. Certainly, attaining marketable products from the discharged concentrated brine would offer an economic benefit and reducing the whole desalination costs. Ion imprinting polymers have potential applications in metal recovery from brine. Finding selective, more efficient, and less expensive imprinted polymers for extraction/pre-concentration of valuable ions is a vital and challenging task. Lastly, the brine should be seen as a resource and not as a waste to attain sustainability in its management approaches. Hybrid processes would be highly recommended to get the absolute transformation of the discarded brine from desalination processes to more valuable constituents.

1. Introduction

The population increase across the globe has led to an increase in water demand in agriculture, industrial uses, drinking, etc. Consequently, the production of potable water has become a global issue. Many communities have estimated that a growing population and its

associated water demand are much greater than conventional (natural) water resources (Mustafa et al., 2020). It was reported that from 1990 up to 2010, approximately 2.3 billion people have access to upgraded drinkable water sources which include adequately secured wells and supplies through pipes (Connor, 2015). The scarcity of water for agriculture and drinking is a pressing issue, especially in the northern

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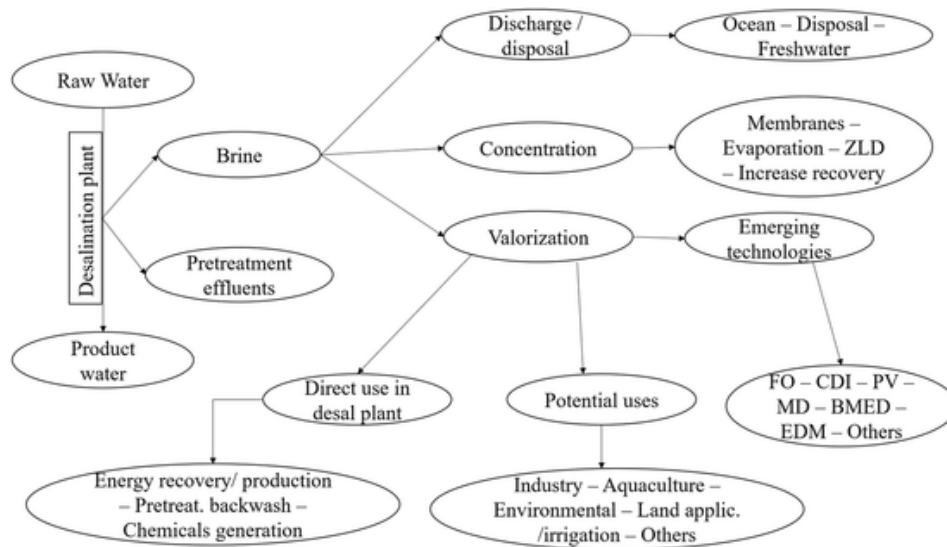


Fig. 1. Generalized brine management strategies/processes, modified from (Gude, 2018).

Table 1

Brines - chemical properties from different sources globally.

Country	Australia	USA	China	Italy	Tunisia	Spain	Om an	Qa tar	UAE
References	Gude (2018)	Martinetti et al. (2009)	Jiang et al. (2014)	Ji et al. (2010)	Hajbi et al. (2010)	Sadhvani et al. (2005)	Ahmed et al. (2001)	Dawoud (2012)	Dawoud (2012)
Plant Location	Abrera	California	Lab scale Hefei, Anhui	Calabri	Skhira	Canary Islands	Esheriah	Abu-fintas	Qidfa II Fujairah
Plant type	Electrodialysis reversal (EDR)	Eastern Municipal Water District (EMWD)	Reverse osmosis (RO)	BWRO	RO	SWRO	BWRO	NR	BWRO
Raw water source	River	Groundwater	Seawater	Seawater	Drilling water	Seawater	Groundwater	Seawater	Seawater
Temperature	NR	NR	NR	NR	NR	NR	NR	40	29.1
Potential of Hydrogen	NR	NR	NR	NR	NR	NR	NR	8.2	7.99
Calcium (mg/L)	960	1032	0.306	625	540	814	841	1350	631
Magnesium (mg/L)	344	318	6.193	2020	245	2751	1900	7600	2096
Sodium (mg/L)	1150	991	159.4	15,500	2084	20,657	14,800	NR	18,293
Potassium (mg/L)	422	NR	0.4830	NR	79	814	631	NR	NR
Strontium (mg/L)	103	NR	NR	NR	NR	NR	18.3	NR	NR
Barium	10.9	NR	NR	NR	NR	NR	NR	NR	NR
pH	6.9	7	NR	NR	4	NR	6.94	NR	NR
Bicarbonates (HCO ₃ ⁻) (mg/L)	885	576	NR	199	NR	452	221	3900	149.5
Carbonate, CO ₃ ²⁻ (mg/L)	909	1.6	NR	NR	NR	NR	NR	NR	NR
Chloride (mg/L)	3443	2823	NR	28,800	4068	37,639	24,062	29,000	31,905
Fluoride (mg/L)	NR	NR	NR	NR	NR	NR	NR	NR	NR
Sulfate (mg/L)	1344	1553	NR	3060	2160	5628	6139	3900	4800
Total phosphate, (mg/L)	NR	0.4	NR	NR	0.04	NR	NR	NR	NR
Nitrate, (mg/L)	104	NR	NR	NR	NR	NR	5.5	NR	NR
Free Chlorine Gas (Cl ₂), ppm	NR	NR	NR	NR	NR	NR	NR	Trace	NR
Silica SiO ₂ (mg/L)	4.9	116	NR	NR	56	NR	NR	NR	17.6
Electrical conductivity (µS/cm)	13,060	NR	1000	NR	13,500	NR	61,100	NR	79.6
Silicon (mg/L)	NR	NR	NR	NR	NR	9	NR	NR	NR

part of African countries, the Middle East, and a large number of other countries in the Southeastern part of Asia as well as Latin America (Ahuja, 2019; Hardoy et al., 2013; Manzoor et al., 2017). If adequate intervention is not taken, similar issues pertaining to water availability will be spread to several countries within Europe, particularly the member countries of the European Union (EU), as well as of the northern part of the Mediterranean by the year 2020; that will include Greece, Italy, Portugal, and Spain. Considering the Mediterranean alone, the

estimation of conservation activities has been greatly affected due to the scarcity of water to the tune of 10 million m³/day during the year 2020 (Ahmed et al., 2001; Le Dirach et al., 2005).

On the other hand, excessive pressure on freshwater resources leads to an alternative way of water supply; the one through desalination. The construction of desalination plants has been increasing globally, and on a daily basis, to reduce the scarcity of freshwater (Lattemann et al., 2008; Amma and Ashraf, 2020). The Gulf Cooperation Council

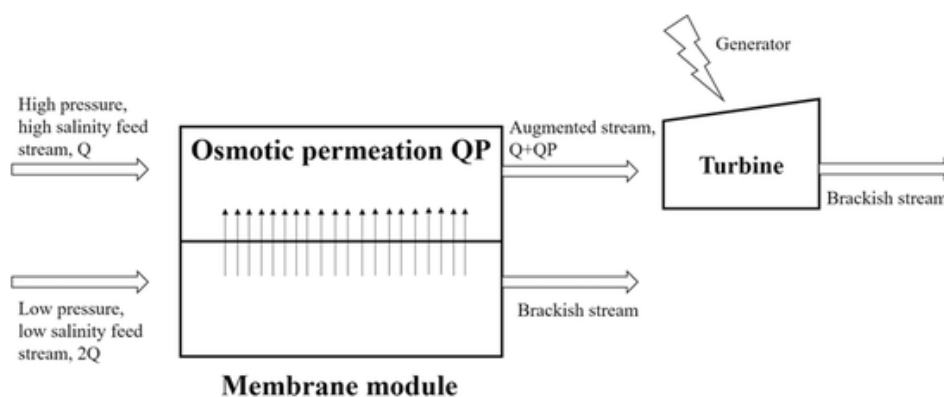


Fig. 2. Schematic drawing illustrating the pressure-retarded osmosis process. Water permeates through a selective membrane from a dilute stream (freshwater) into a pressurized concentrated stream (seawater) and is then expanded through a hydro-turbine (Ramon et al., 2011).

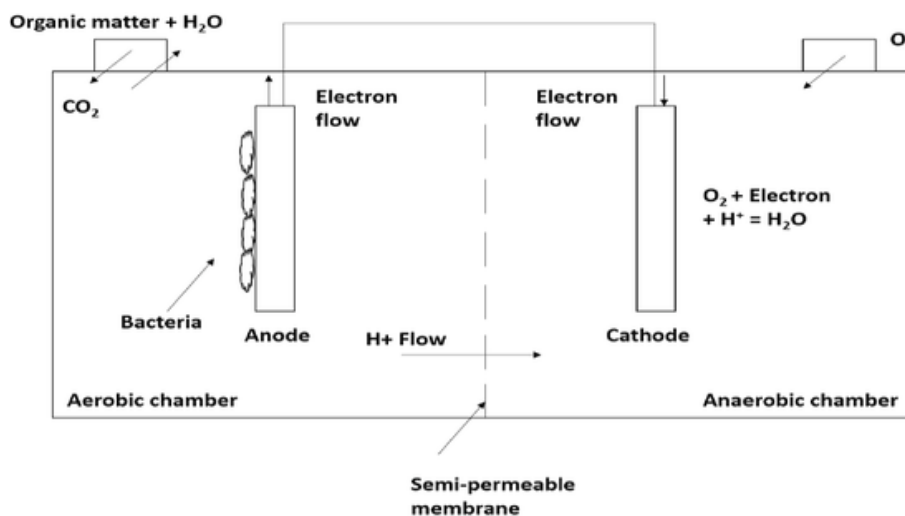


Fig. 3. General scheme of the microbial fuel cell, modified from (Mercer, 2015; Saeed et al., 2015).

(GCC) region is heavily dependent on the construction of desalination plants in large numbers around the Middle East (Fath et al., 2013). Desalination technology will keep growing within the GCC region because these countries are more stressed due to the prevalence of harsh climatic conditions in the region. Hence, agricultural production heavily depends on irrigation and most of the water comes from desalination plants. A good example is the United Arab Emirates (UAE), where the sources of potable water largely depend on desalination, by employing the most influential technology known as Multi-Stage Flash (MSF), while Reverse Osmosis (RO) is next in the hierarchy (Al-Othman et al., 2018). However, although desalination unarguably provides fresh clean water, the reject brine by-product has been known to be a very critical environmental contaminant (Afrasiabi et al., 2011; Al Bazed et al., 2014; Abdul-Wahab and Al-Weshahi, 2009); that is because there is a lot of residue from pretreated chemicals associated with the brine, also coupled with the high salinity and temperature levels. The reject brine contains several potentially toxic metals (copper, nickel, iron, chromium, zinc, and others), due to pipe corrosion, posing consequential environmental threats (Giwa et al., 2017; Wu et al., 2018).

The reject brine can inflict potential damages to the ecosystem, which may lead to pH fluctuation, eutrophication, proliferation associated with toxic metals deposited in the aquatic ecosystem, sterilizing qualities of disinfectants capable of causing various problems within the aquatic, as well as underground habitat (Petersen et al., 2018; Xevgenos et al., 2016). Thus, there is a need to apply a more appropriate method to manage brine that will be environmentally benign,

putting into account at the same time, all essential parameters involved, such as chemical components of concentrate, reject brine volume, associated cost (capital and operational), geographical region, as well as the disposal area (Giwa et al., 2017; Chung et al., 2017). The clear managerial system in relation to public allowance, storage capacity, and transportation, means of evacuating the reject brine to the final destination for treatment, are parameters that should be critically considered (Ahmed et al., 2001; Einav et al., 2003; Xevgenos et al., 2015).

The well-known different strategies adopted to reject brine management include, but are not limited to, brine minimization and direct disposal or reuse. The membrane and thermal-based technologies are associated with a minimization strategy, while direct disposal strategies are methods of disposing the brine directly into the inland offshore. In addition to the aforementioned strategies, managing rejected brine leads to the extraction of minerals and salts for various other purposes and applications (De Buren and Sharbat, 2015).

Based on our knowledge, no paper reviews brine management by taking into consideration the emerging desalination technologies, life cycle assessment (LCA) as well as methodologies for metal recovery. Therefore, the novelty and the main aims of this review article are to examine which management methods are the most recent and advanced in managing rejected brine generated from desalination plants. It provides up-to-date information regarding the most adequate technologies that generate a minimum quantity of rejected brine via the use of minimization techniques. It also analyzes the method of direct disposal that has lately received noticeable improvements. It further dis-

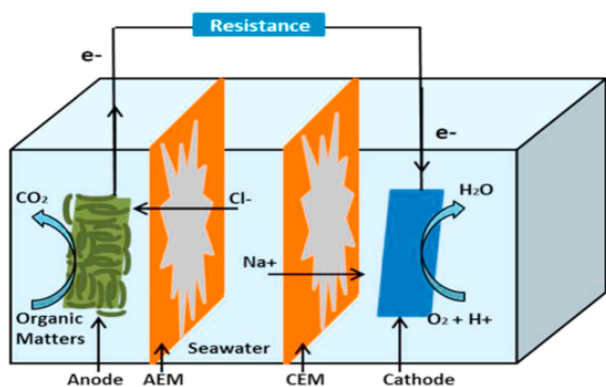


Fig. 4. A microbial desalination cell (Saeed et al., 2015).

discusses the reuse of discarded brine to recover valuable goods and sequestration of carbon dioxide. Sustainability is an important parameter that needs consideration to achieve uninterrupted operation of the discarded brine management to achieve the least environmental, social, and economic aftermath. Due to various environmental and cost problems associated with the disposal of brine, several recovery technologies have emerged. A good example is the generation of renewable energy, used within the evaporation ponds from where salt or industrial chemicals are produced (Ahmed et al., 2002). Finally, the review analyzes and evaluates recent and current management systems and minimizing strategies, with a specific focus on emerging technologies.

The paper is divided into the following sections: availability and supply, point source management and processing, exposure and usage, sustainability framework, and best practices by utility companies and users.

2. Availability and supply

Brine is the saline solution generated from desalination plants as a by-product with different chemical compositions and concentrations that are mostly determined/regulated by the source of water, quality, and plant recovery (Katal et al., 2020). Brine exhibits similar properties in different parts of the universe, however, it is totally different with regards to toxicity levels or content of potentially hazardous substances i.e. toxic metals (Hg, Co, and Ni), pesticides, and other pollutants that render the disposal of brine, making it a potential environmental threat.

Considering the schematic diagram showed in Fig. 1, the various existing brine management methods are itemized and linked, giving this review a more clarity and better understanding of raising concepts.

The brine characteristic or composition is greatly influenced by the quality of the raw water, as well as plant recovery. In the case of seawater reverse osmosis (SWRO) plants, the range of recovery has been often between 40% and 45%. In summary, brine salinity/salt levels will be almost twice when compared with seawater (Gude, 2018). However, the salt concentration in brine tends to be four folds the salinity of brackish water because the average recovery is as much as 75% (Li et al., 2013). Table 1 presents the chemical characteristics of brine that originated from various plants in different countries. However, some parameters and chemical constituents such as temperature, the potential of hydrogen, strontium, barium, carbonate, and bicarbonate are not reported (NR) in some of the literature used.

3. Point source management and processing

Virtually 100% water recovery is not achievable in nearly all desalination technologies. Hence, desalination plants generate sufficient amounts of brine waste, containing different substances (Rodríguez-DeLaNuez et al., 2012). To properly deal with any environmental issues

related to brine disposal, different methods are implemented so that, in the end, higher water recovery is achievable from the desalination processes.

The lately developed technologies and processes suggest and critically study the potential of higher water recovery in the course of a brine treatment (Cobban et al., 2011). These processes fall, mainly, into two categories, namely the thermal-based and the membrane-based (pressure and electrical potential driven). Some schemes such as zero-liquid discharge (ZLD) or near-to-ZLD are still under investigation to reduce the volume of rejected brine and equally get back sufficient water at the same time (Panagopoulos et al., 2019; Gorjian et al., 2019). In this case, a substantial amount of pure distillate attaining 95–99% recovery potential is obtainable from the well-planned waste brine streams. However, the generated residual waste can be sent to landfills, but it is not considered an optimal solution. To be able to recover water with high quality and purity, coupled with profitable and economic brine by-products, at a reasonable operational and energy consumption cost, will require a revolution in the desalination industry (Kazner et al., 2014; Martinetti et al., 2009; Burnett, 2011). Ferry et al. (2020) described the performance of commercial thermal evaporator powered combined with external compound parabolic concentrator (XCPC) as a solar energy collector that provides high operating temperatures. This combination provides an alternative to gas-fired evaporators as well as providing an environmentally friendly brine management solution with reduced costs. Results showed that 90 m² array of XCPC successfully powered a 10 gallon-per-hour commercial thermal evaporator, in which the 10 gallons were evaporated by a solar field of 30 kW at an outlet temperature of 150 °C with a total of 80% reduction in wastewater volume. Furthermore, Dindi et al. (2018) investigated a novel approach for brine treatment where mixed metal oxides derived from Mg–Al layered double hydroxide (LDH) were used. Results indicated the feasibility of this process for the treatment of reject brine where approximately 70% and 20% reduction of chloride and sodium concentration were obtained, respectively. This reduction ensures safe disposal of the brine as the concentrations are close to that of the seawater. Usually, the Solvay process focuses on the removal of sodium ions, but the proposed process can remove both sodium and chloride ions making it more advantageous over the other methods. Moreover, Desai et al. (2018) used a zinc/ferricyanide hybrid flow battery, which achieves extensive first-pass desalination with a simultaneous supply of 10 Wh/L electrical energy. Results showed that this technique was able to remove 86% (100 g/L NaCl) salt from hypersaline brine. The following subsections describe various brine minimization and rejection technologies.

3.1. Pressure retarded osmosis (PRO)

Pressure retarded osmosis (PRO) is one of the improved current techniques in use to separate a liquid from a concentrated solution subjected to high pressure so that salinity - gradient produces renewable and emission-free energy as a harvesting energy.

The cleanliness and reliability property of natural salinity gradients is responsible for its importance in harnessing the salinity gradient associated with moving river water characterized with “definite” quantity of seawater obtained (Cheng et al., 2018; Gong et al., 2017; Hoover et al., 2011; Ripin et al., 2019). In this system, the mixing of freshwater with brine was enhanced by employing the use of Gibbs free energy to generate power known as salinity - gradient energy or better called osmotic power. The operating system in PRO is relatively easy; facilitated by the chemical potential difference, diffusion of water occurs via a semipermeable membrane of low concentration (high chemical potential) into a high concentration (low chemical potential), excretes pressure in the stream; leading to its pressure and flow rate increase (Loeb et al., 1976; Norman, 1974; Ramon et al., 2011).

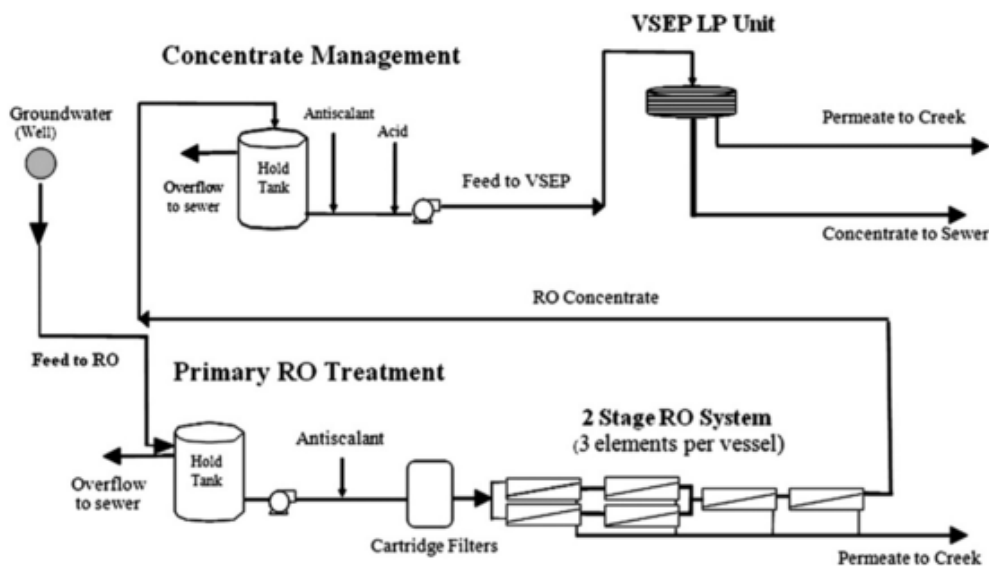


Fig. 5. Schematic illustration of the pilot-scale VSEP treatment system (Subramani et al., 2012).

The simple process is shown in Fig. 2 where the compounded pressurized streamflow via a hydroelectric turbine that responsible for power extraction. The water chemical potential is responsible for the osmosis across the membrane being driven by the driving force that occurs where the temperature of the system is constant (isothermal system), and it can be described as the differentiation between concentrated and dilute solutions in terms of their osmotic pressure. However, this driving force diminishes as a result of the hydraulic pressure applied, the resulted 'pressure-retarded' osmotic water flux is mathematically represented as:

$$J_w = A (\Delta\pi - \Delta P)$$

Where A stands for the membrane water permeability, ΔP the hydraulic pressure drop across the membrane, and $\Delta\pi$ the osmotic pressure differential across the membrane.

The PRO existence has been recorded since the 1970s, but gained more recognition lately, mainly via the development of a more reliable and effective membrane. The PRO membrane is characterized by its potential to resist the hydraulic pressure often associated with the inlet stream. The achievable maximum power generated is realized when the pressure applied is almost half the amount of osmotic pressure; this implies that the more the differences in concentration (the largest source of energy), the more the pressure applied to the maximized power output.

3.2. Microbial desalination cell (MDC) technology

There is a huge number of desalination technologies in operation nowa days with high efficiency in performance; however, the main limitation with virtually all is their high-energy demand for operation. The best option to overcome this challenge is the adoption of the microbial desalination cell (MDC) technology, with the ability to turn the stored energy in the wastewater to more beneficial and productive energy that could be utilized in desalination as the source of power (Al-Mamun et al., 2018; Li et al., 2017; Mavukkandy et al., 2019). The MDC is a derivative of the microbial fuel cell (MFC) technology. The component of MFC is made up of an anode (-ve ion), the cathode (+ve ion), the cation-selective membrane as well as wire externally placed as shown in Fig. 3. The anode and cathode are subjected to aerobic and anaerobic conditions and maintained throughout the process.

The operation of MDCs is often facilitated by utilizing the microorganisms that exist in the wastewater to transform the biochemical en-

ergy embedded in organic substances into electricity. The creation of a potential gradient across both anode and cathode terminals can make desalination occur. It shows a distinctive difference to the several types of water desalination methods that need as much as 6–68 kWh of energy to treat 1 m³ of seawater. While MDCs has the advantage of producing more energy to the tune of about 180–231% when compared with other technologies, in the H₂ form according to Wang and Ren 4 in the simple desalination the involves NaCl solution from 30 g/L to 5 g/L (Mavukkandy et al., 2019). A normal MDC component is made up of an anode and cathode compartment for the electron exchange or movements, coupled with the desalination chamber in the center built, in such a way that a cation-exchange membrane (CEM) and anion-exchange membrane (AEM) overlaps in the two sides of the unit as shown in Fig. 4.

The functions of the two compartments are different, while the anode compartment causes the breakdown of organic and generation of electricity; the central compartment facilitates the elimination of salt from seawater, and finally, the cathode compartment enhances the completion of the electrical loop within the system (Luo et al., 2012; Saeed et al., 2015). The oxidation of organic matter into carbon dioxide (CO₂) and releasing hydrogen ions (H⁺) into the analyte are enhanced by the bacteria present in the seawater. This chemical process further sees the movement of the electron towards the cathode terminal via an electric circuit external to the system and from this, the oxygen (O₂) is accepted in the external electron that later underwent reduction to produce water as one of the products. It has been established that this process is capable of salt removal to the tune of over 99% of salty water coupled with energy production ion excess more than the external required energy needed to power the system (Forrestal et al., 2012; Saeed et al., 2015).

3.3. Membrane-based technologies (low-salinity brine)

3.3.1. Vibratory shear enhanced processing (VSEP)

This is an emerging technology that enhances membrane base strategies compared to the conventional membrane-based system (Balasubramanian, 2013; Shi et al., 2011). The treatment of reverse osmosis (RO) takes place in a VSEP unit by utilizing configuration (Balasubramanian, 2013; Shi and Benjamin, 2011). The RO concentrate is used in feeding the system to improve total recovery from the brackish water origin. The principle or mechanism behind this operation is to establish vibratory shear to be able to make oscillation (50 Hz) within the surface of the membrane so that the shear is ten

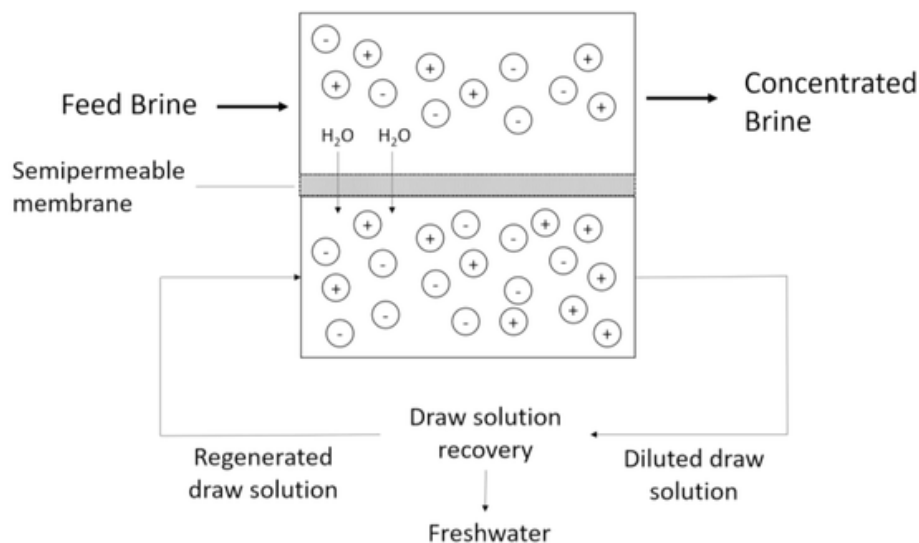


Fig. 6. Schematic illustration of the FO process, modified from (Panagopoulos et al., 2019).

times greater than the normal cross-flow system (Balasubramanian, 2013). Brine concentration reduction is often considered as the available residual. Unlike a normal RO process, VSEP distribution is not affected in any way by the availability of colloids, solid suspension, or salt solubility. Hence, better or higher filtration rate, membrane scaling resistance, and reduction in footprints are a few of the VSEP pros (Subramani et al., 2014). Using VSEP, adequate consideration is needed, in accordance with the energy requirement, to maintain vibration gear up through torsional spring. Higher fluxes (50–100 L/m²·h) and improved total recovery of water fed from 75% to 93% have been reported; plus, scaling potential was equally reduced (Subramani and Jacangelo, 2014). Furthermore, Subramani et al. (2012) used VSEP for the treatment of the generated concentrate from a spiral wound RO system during the desalination of brackish groundwater desalination. Results showed that the overall feed water recovery of the desalting process was enhanced, and high fluxes were achievable (50–100 L/m² H). Moreover, the deposition of colloidal silica was restricted to the surface of VSEP membrane. Fig. 5 illustrates the used VSEP treatment system used in this study.

3.3.2. Forward osmosis

The forward osmosis (FO) exhibits a major difference to RO due to the associated pressure present in both methods. RO uses applied force as its main force to achieve mass production via the membrane, whereas in the case of FO, the driving force is the osmotic pressure that enhances mass transportation (Chung et al., 2012a, 2012b). FO process is one of the most simple and reliable emerging technologies, that is characterized by low energy consumption and minimum pollution potential (Chung et al., 2012a, 2012b; McGinnis et al., 2008). The osmotic pressure needed is generated from a draw solution, known to be highly concentrated, to transport water from a feed stream with a low concentration of the draw solution that is highly concentrated (Neilly et al., 2009). Fig. 6 illustrates the typical FO process.

Martinetti et al. (2009) studied FO to maximize water recovery in the different water desalination processes. In this study, RO brine streams, which are two in number with an approximate total dissolved solids (TDS) concentration range between 7.5 g/L - 17.5 g/L, were subjected to additional desalination by FO with a draw solution of constant concentration (50 g/L NaCl). With FO, less than 80% of the water was recovered from the rejected brines, with salt precipitation around membranes. The energy requirements for FO are considerably low compared to several other methods of desalination emerging technologies. McGinnis et al. (2007) established that the proposed FO system by McCutcheon et al. (2006), was capable of saving energy to the

level of approximately 72% when compared to the RO and an MSF distillation of 85%. It has been equally established from recent studies that operations at a commercially acceptable rate of flow e.g., 15 L/m² to 20 L/m² created a threatening issue as regards fouling (Bell et al., 2017; Panagopoulos et al., 2019).

3.3.3. Electrodialysis (ED), electrodialysis reverse (EDR), and electrodialysis metathesis (EDM)

These processes are aggravated by electrical potential imbibed or used along membrane-based to reduce the volume of brine, as well as scaling ion removal from it. Electrical potential-driven technologies, in membrane-based methods of brine treatment, have generated many results (Korngold et al., 2009; Oren et al., 2010; Tran et al., 2012). These processes ED, EDR, and EDM are very similar in operation and are considered as the major ones for minimizing the brine volume (Giwa et al., 2017).

These processes permit the movement of anions and cations in the solution through membranes that are not permeable to water; thus, water is contained only in one part. The system is good to handle RO concentrate that is characterized as low salinity brine coupled with low cost. The removed calcium amounted to roughly 70–80%, at a pH of about 11. Meanwhile, at slightly increased pH (11.5), the removal efficiency of calcium reached 95%, while removal efficiency in magnesium was in the range of 5%–25% (Tran et al., 2012).

3.3.4. Pervaporation method

Applying the normal conventional method of the desalting membrane such as RO in brine treatment has been so challenging because of the high concentration level of TDS, as it needed high hydraulic pressures to summon the osmotic pressure associated with inlet solution. However, to solve this problem of high TDS, processes that are non-pressure driven in nature, such as pervaporation (PV) have been used (Drobek et al., 2012). Similar non-pressure-driven processes such as membrane distillation (MD) were developed to counter the challenges emanated from TDS in the feed water as reported (Mansour et al., 2017; Adham et al., 2013; Alkudhiri et al., 2013; Singh et al., 2012). PV as an evaporative process is very useful for desalting brines that are characterized by high salinity because it does not require to subdue the osmotic pressure (7 MPa) usually emanated from the inlet solution (Huth et al., 2014; Yacou et al., 2015). According to Lee et al. (2010), it was reported that processes, which are associated with non-pressure-driven factors, exhibit a high level of resistance to the formation of particular types of fouling when compared with pressure-driven processes.

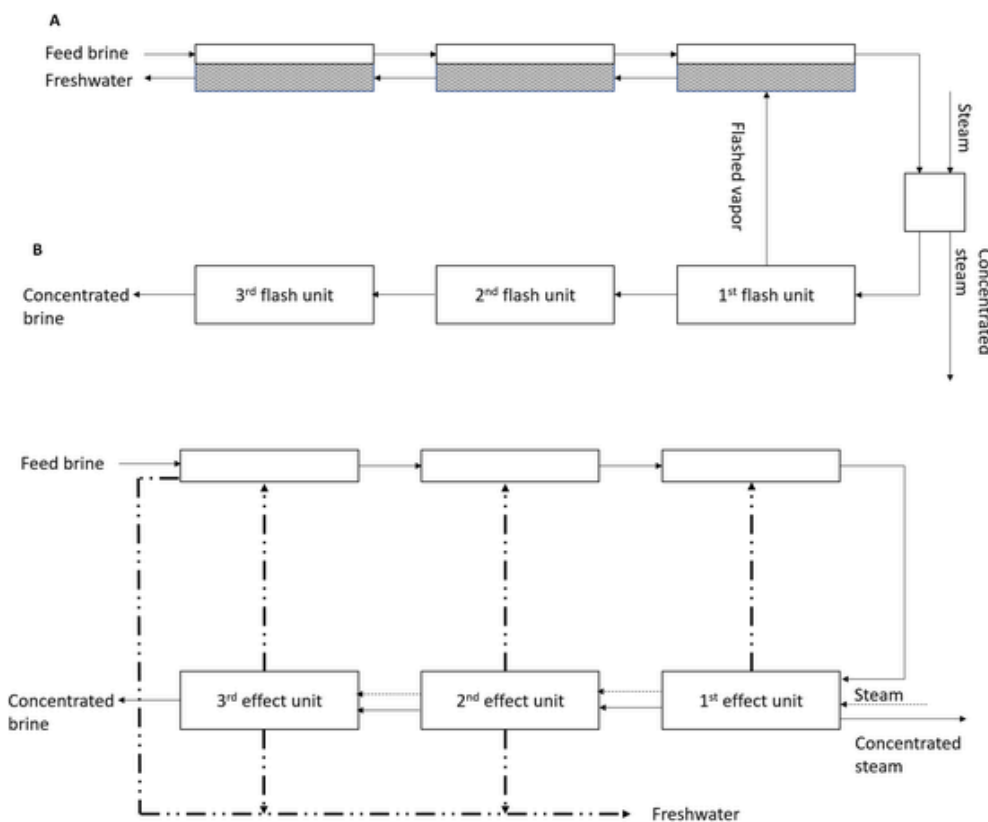


Fig. 7. Schematic representation of the typical: (A) MSF, (B) MED processes, modified from (Panagopoulos et al., 2019).

In the pervaporation desalination applications, it was reported that the efficiencies of salt rejection associated with different kinds of membranes were found to be less than or equal to 99%. It was established that irrespective of the characteristic of the membrane and the operating system, the penetrating ability of the solutes into the structure of the membrane is not preventable, especially if the material is hydrophobic in nature (Quiñones-Bolaños et al., 2005; Zwijnenberg et al., 2005). Besides, it has been established that the salts possess the ability to pass through nonporous forward osmosis membranes (McCutcheon and Elimelech, 2006). The benefit of this approach is that not much importance should be attached to the hydrophobicity of the membrane, in as much the diffusion of water vapor occurs at pore sizes relatively bigger than those found in the water molecule (Yacou et al., 2015).

3.4. Thermal-based technologies (high-salinity brine)

Evaporation is the basic method used in the desalination concentrate treatment, either induced or common natural approach (Giwa et al., 2016). This technique is commonly used in treating high salinity brines. Generally, evaporation ponds serve as a reservoir where the concentrate or reject brine is discharged and water evaporates as the sun heats the solution. This method is considered most suitable for arid regions due to land availability, high sunlight, and coupled with high salinity levels.

3.4.1. Wind-aided intensified evaporation (WAIV)

WAIV uses the thermal approach in other to achieve brine volume minimization (Gilron et al., 2003; Katzir et al., 2010; Macedonio et al., 2011; Oren et al., 2010). It uses wind power and allows the evaporation of wetted surfaces that are densely packed. WAIV is preferred to the traditional evaporation ponds, as it requires less land for the operation (Morillo et al., 2014). This technique employs the use of pressurized air, transported via a distribution pipe to the outside layer of the RO concentrate. The evaporation surface is made up of non-woven geotex-

tiles that enhance total wind energy efficiency. This system gives the evaporation ratio close to 90% compared to 78% of the conventional evaporation ponds. The concentration of TDS has been found to increase by as much as 23% (Morillo et al., 2014) with WAIV technology. Also, it has the capability of facilitating salt recovery, as a source of raw materials (Morillo et al., 2014). As found in a study, WAIV technology was employed in the RO - ED concentrates as a containment of EDR mode (Oren et al., 2010). For the treatment, it was found that TDS removal was around 70% and it exhibited a potential, as a method to get back mineral secondary products such as calcium and magnesium salts. Furthermore, RO systems with super concentrate brackish water were equally used. The TDS, in this case, using the WAIV system was greater than 30% (Gilron et al., 2019).

3.4.2. Brine concentrators (BC)

Another promising technology is the brine evaporative cooler concentrator (BECC), designed to minimize the amount of brine through the evaporative cooling technique principle (Cipollina et al., 2011). BECC is characterized by two functions: cooling down recirculating brine and subsequently concentrating it for adequate disposal. According to the study conducted by Cipollina et al., 2011, the stream of brine was, firstly, allowed to cool (via evaporation) as it was mixed with the supplying stream (seawater: chilly) and, secondly, was concentrated with the constituents of the atmosphere (air) when contacted. BECC system is made up of heat conductive surfaces that are kept apart into two streams, which permit cooling part of the system through the recovery of the generated heat, called latent heat, associated with evaporation. Results proved that a range of cooling between 5 °C and 100 °C is achievable when the relative humidity was found to be in the range of 40% and 70%, coupled with wind movement of slightly 2 m/s (Lozier et al., 2007). Additionally, some brine concentrators comprise a visual tube that functions as a pathway through, which the concentrate flow when fed (Cipollina et al., 2011). Evaporation of the concentrate took place inside the tube. Latent heat was generated from vapor-

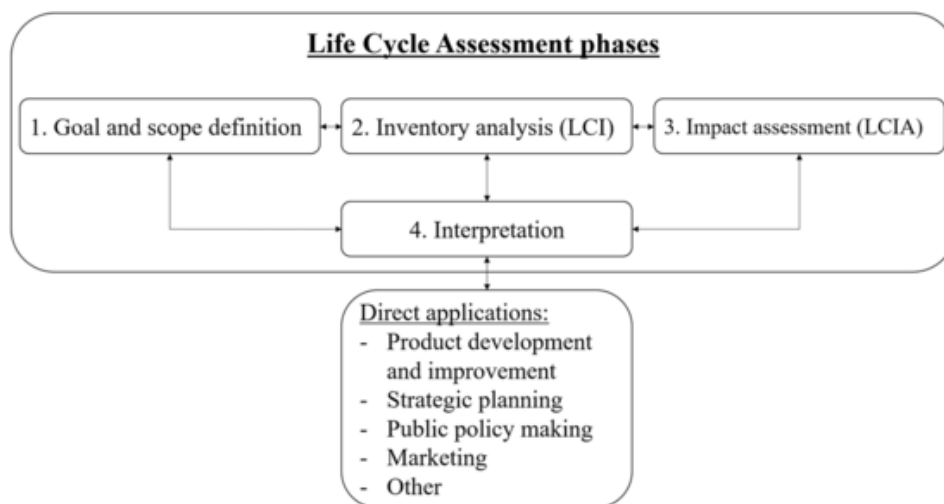


Fig. 8. Phases and applications of an LCA (Rebitzer et al., 2004).

ization when the vapor was condensed on the surface of the tube. Highly pure distilled water was produced from this process, which subsequently led to the reduction of the final brine volume. The associated limiting factors in this process include sulfate and chloride concentration, the brine elevated boiling point, and the sodium salt solubility (Lozier et al., 2007). Almost 95%–99% overall recovery is achievable by employing this system.

3.4.3. Ohmic evaporator (OE)

Similarly, already mentioned, thermal-related emerging technology is also used for brine volume minimization. This technique uses mainly an alternating electric current that operates roughly at 60 Hz frequency, with an electrical field capacity of 24 V/cm – 28 V/cm (Assiry, 2011). The technique can only be used to evaporate brine concentrate when its value is greater than 800,000 ppm. It has been established that an excellent recovery rate at a range of 81%–93.5% was recorded, at the efficiency performance level of OE within the electric field capacity of 56 V/cm (Assiry, 2011). This technique has not been scientifically investigated enough, taking also into account the high cost of establishing a respective brine treatment unit on a commercial scale (Assiry, 2011; Sakr et al., 2014).

3.4.4. Membrane distillation (MD)

The emerging technology approach employed in this case is the membrane distillation that combines the properties of both a membrane and thermal-based technology. Several studies have been conducted to examine the prospects of MD as a technique for treating concentrated brine. The MD combines the membrane, as well as the thermal advancement properties (Ashoor et al., 2016). It is a better substitute for dewatering or draining an aqueous solution of higher concentration. From a simple comparison between them, unlike membrane separation method where the hydraulic pressure differs, electrical potential slope or concentration slope generates the moving force; the moving force associated with MD is known to be the vapor pressure gradient (VPG), obtained from the difference in temperature across the entire membrane (Camacho et al., 2013; Kazner et al., 2014). By maintaining temperature differences of low range 10 °C–200 °C between the region of hot and cold stream, the permeate water is likely to be produced. The process of MD is influenced solely by vapor-liquid equilibrium that facilitates the diffusion of volatile constituents over a membrane with microporous and hydrophobicity properties. The existing various MD configurations include vacuum, air gap, sweeping gas, as well as direct contact MD. The direct contact membrane distillation (DCMD) technology is known for its reliability coupled with its easy configuration that can be employed in the process of desalination.

DCMD has one of the sides of the membrane permeable to the hot brine, as well as for the vapor to flow across the holes of the membrane with hydrophobic properties. Due to condensation, the vapor is recovered in a colder form, as distillate, within the second position on the membrane. The concentrated or residual stage was found to contain more of the dissolved salts, as well as other chemicals stuck to the side of the hydrophobic membrane. The benefits of the MD include but are not limited to its driving force, which vapor pressure does not possess under high concentrations of salt, the organic fouling and biofouling are low. Unrestricted potential to merge with various sources of heat, which include geothermal, solar thermal, or wasted heat from machines e.g. heat exchangers, diesel and electrical generators, low operational cost, and capital requirement. The main disadvantage of MD is that permeate flux obtained is low in virtually all cases (Adham et al., 2013; Dow et al., 2008).

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

The most prominent thermal-based technologies in use for brine treatment are multi-stage flash distillation (MSF) as well as multi-effect distillation (MED), which are shown in Fig. 7 (Panagopoulos et al., 2019). MSF is the most used technology considering all the available thermal desalination, it amounts to roughly 64% (Shatat et al., 2014). The emergence of these technologies traces back to the brackish and seawater desalination and they are very effective when the materials are upgraded before the actual treatment of the brine (Mabrouk et al., 2015). The simple mechanism in MSF requires the preheating of inlet brine by making use of condensing vapor, which is often generated from the flash units of the system until it attains the highest temperature (approx. 110 °C–120 °C) facilitated through an external source of energy. The heated inlet brine moves from the bottom vapor pressure of flash units that caused the parts of the inlet brine solution to evaporate and subsequently condensed in the heat exchangers. There is a difference between the two solutions while the condensed water vapor is known to be the freshwater the other liquid is the concentrated brine that emanates from the flash unit (Khoshrou et al., 2017). This technology shares some similarities, however, they differ in a number of ways, particularly in the heat generated and the highest temperature attained is between 70 and 80 °C (Elsayed et al., 2018). Despite the effectiveness of this technology, they still have their shortcomings in terms of the high cost of construction because of the special materials needed which are resistant to corrosion (Boillot et al., 2014). The energy requirement by these technologies is high, ranging from 12.5 kWh/m³ to 24 kWh/m³ for MSF and 7.7 kWh/m³ to 21 kWh/m³ for MED.

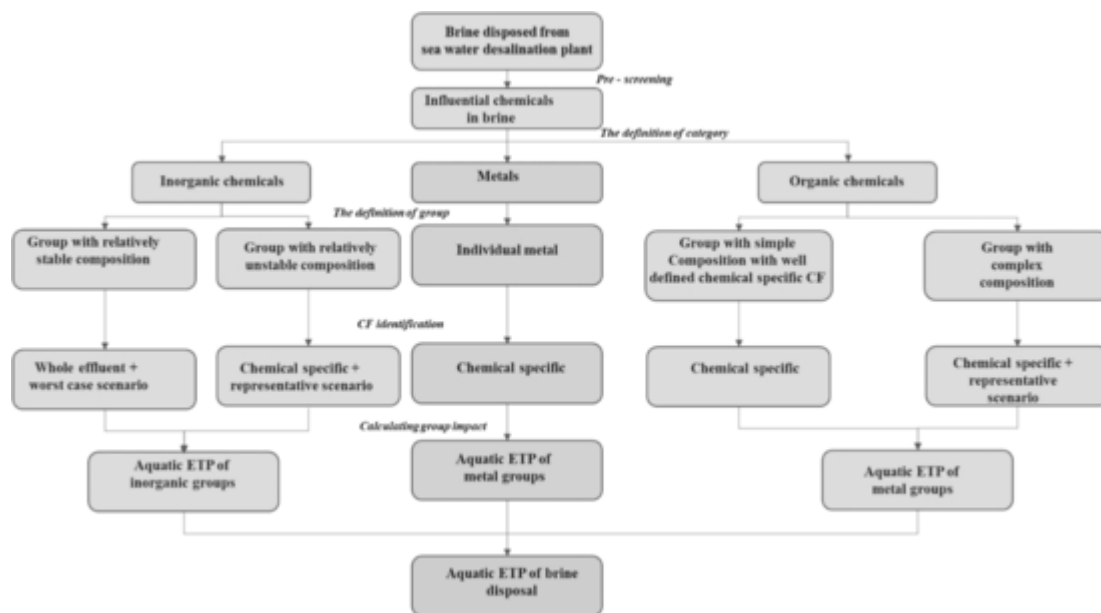


Fig. 9. The process flow of the group-by-group method, modified from (Zhou et al., 2013).

4. Sustainability framework

4.1. Life cycle assessment and life cycle impact assessment (LCIA)

According to Brancoli and Bolton (2019), LCA is a comprehensive technique that is normally used for the assessment of the associated environmental impacts with the product's life during all the stages including extraction, processing, manufacturing, distribution, and utilization of the materials. This analysis is commonly used to report the consumption of potential environmental loads and resources through the service supply chain of a certain product. The LCA is normally used for supporting the policies and decisions throughout the production supply chain for sustainable development. On the other hand, LCIA determines the potential impact of the obtained data from life cycle inventory by using the impact categories, category indicators, model characterization, equivalency factors, and weighing values. The primary procedure of LCIA consists of categorizing, classifying, characterizing, normalizing, grouping and integrating environmental impact (Kayo et al., 2014).

4.2. Phases and applications of an LCA

The LCA establishment serves as a valuable means of analyzing the impacts on the environment that results due to the freshwater generated from the desalination system because it takes into consideration all the potential environmental problems (Caro, 2019). The LCA comprises of four main phases, namely goal and scope definition, inventory analysis, impact assessment, and interpretation as shown in Fig. 8 (Kylili et al., 2018; Larsen, 2018). However, most of the applications of LCA in the desalination system are in relation to energy demand and water supply, additionally, to evaluate the potential effects of desalination system, and the contribution of concentrate disposal into the water ecosystem (Muñoz et al., 2010; Raluy et al., 2005; Zhou et al., 2013). This can lead to proffering solutions to alleviate the environmental challenges using various means, including effective pre-treatment of feed water (Beery et al., 2010) and using cleaner sources of energy such as natural gas (Zhou et al., 2011) and renewable energy sources that include wind and solar (Pehnt, 2006; Raluy et al., 2005).

Besides the energy demands of the desalination process, understanding the eco-toxic potential of brine disposed after desalination has been of great concern. It has been suggested that high salinity, which is

caused by the brine disposed, may lead to growth reduction or even death of the flora and fauna where brine is being disposed of. It was also discovered that brine from desalination plants has the ability to impair biological communities by causing toxic chemical accumulation in aquatic organisms such as mussels and algae (Elsaid et al., 2020).

A case study was conducted in Southern California, employing a hybrid LCA tool for comparison of three different types of water supply and the imported water case (Stokes et al., 2009). The outcome indicated that the environmental load of the current water importation case is 1.5–2.4 times less than that of alternative methods of desalination, which include brackish groundwater desalination and seawater desalination, coupled with recycling water case. Similarly, in other research conducted in Arizona, several factors like seawater desalination, reclamation of water, and water importation were compared, and seawater desalination was found to have the highest impact (Lyons et al., 2009). Also, LCA was employed to bring out the relationship that exists between environmental loads pertaining to groundwater treatment, RO, thermal desalination, nanofiltration, and ultrafiltration respectively (Vince et al., 2008). Additionally, another study was conducted in Amsterdam for future capacity increase, LCA was used to evaluate and analyze the comparison between two different alternative RO desalination cases (Mohapatra et al., 2002). However, the aquatic ecotoxic potential (ETP) in relation to brine production from desalination-based LCA researches/studies is scanty. An improved methodology to assess ETP was developed by Zhou et al. (2013).

Furthermore, LCA was mostly applied in analyzing the energy demand in the desalination process and only a few works were done by using LCA for measuring the toxicity potential of brine on the aquatic ecosystem. Meneses et al. (2010) studied the final disposal of brine alternatives using LCA. Nevertheless, they did not take into consideration the impact of salinity because the current method employed could not render the ionic salts into aquatic eco-toxic impact (Meneses et al., 2010). Another work (Vince et al., 2009) considered the potential of the liquid discharge, but this was specifically for a site with inadequate reference value compared to other research works. There are two main reasons that hinder the current LCA with respect to brine disposal. Firstly, much data is required, which is usually intensive, as it requires many efforts to do a comprehensive analysis and an on-site ecotoxicology test. This analysis is quite complex since there is usually a high variation of brine composition. Secondly, there is a misunderstanding of using the existing LCIA methods as a widely accepted standard procedure

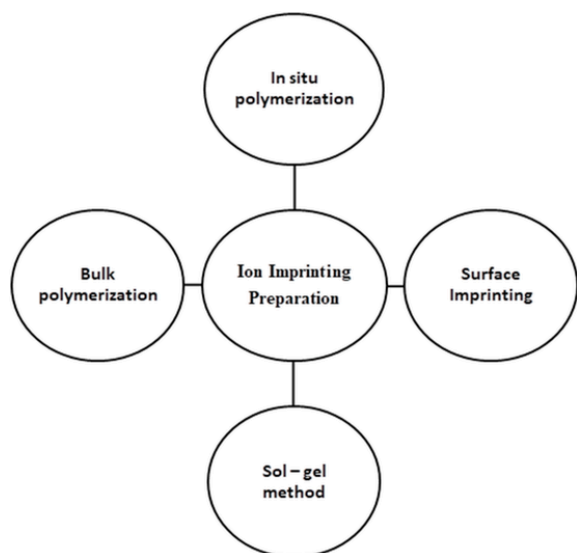


Fig. 10. Schematic diagram of the best method of preparation ion imprinting, modified from Boysen, 2018.

without bearing in mind the reliability and suitability of those methods (Zhou et al., 2013). This part intends to discuss the currently available methods and propose an improved method for evaluating the toxicity potential of brine on the aquatic ecosystem originated from seawater desalination plants.

4.3. Methods for life cycle assessment (LCA)

The standard equation considered when calculating the aquatic ETP of brine disposal is as follows:

$$\text{Aquatic ETP of brine disposal} = \sum_i m(i) \times CF^{\text{aquatic ETP}}(i) \quad (1)$$

The definition of the terms is as follows: $m(i)$ stands for the mass of 1 m^3 of a brine sample to be disposed of, and $CF^{\text{aquatic ETP}}(i)$ denotes the characterization factor (CF) of the aquatic ETP for i . The LCIA methods in question will depend on modifications of equation (1)

4.3.1. The traditional or chemical method

The traditional method of LCA is also known as the chemical-specific approach. This method calculates the average or mean effluent effects as the summation of the effects generated by the entire chemicals within the effluent based on the aquatic (ETP) of each elementary chemical (Vince et al., 2009). The USEtox (Henderson et al., 2011; Rahman et al., 2018) which was developed by the Society for Environmental Toxicology and Chemistry (SETAC) in conjunction with the United Nations Environment Program (UNEP) encompasses the chemical fate, exposure, and effect and is expressed according to equation (2)

$$CF^{\text{aquatic ETP}}(i) = FF_i \times XF_i \times EF_i \quad (2)$$

$CF^{\text{aquatic ETP}}(i)$ is the aquatic eco-toxic characterization factor which denotes the aquatic ecotoxicological influence of chemical individual i . Herein, the impact is enumerated as the potentially affected fraction (PAF) of species $[PAF \cdot \text{m}^3 \cdot \text{day}/\text{kg}]$. FF_i is the fate factor is calculated as the persistence time of the chemical i staying in the aqueous phase [day], XF_i the exposure factor, which shows the bioavailability of the chemical i to the aquatic organisms, and EF_i the effect factor, which denotes the ability of a chemical i to cause toxic effects to the exposed aquatic ecosystems $[PAF \cdot \text{m}^3/\text{kg}]$.

The chemical-specific approach is an analytical method appropriate for evaluating effluents comprising of contaminants, which themselves have well-defined ecotoxicological properties. Nevertheless, it has several drawbacks. Firstly, it is a method that involves many chemicals, including by-products, most of which are present at a low level of concentration. Secondly, it is not cost-effective with respect to time and other resources due to the analysis of the ecotoxicological properties of all the numerous compounds present. Finally, this method is limited by what is only available in the USEtox model.

4.3.2. The group-by-group method

This method takes into consideration the demerits of the two previous methods that are the traditional or chemical, and completely effluent methods discussed earlier. That is to adequately evaluate the complex mixture of effluents (i.e. effluents with unknown chemical mixtures) from brine disposal and take into consideration the instability of the composition of the brine. This method merges the advantages of both the chemical-specific (traditional) and the whole - effluent method. This is achieved by calculating the mean aquatic ETP impact as the summation of the impacts generated by the recognized groups of significant chemicals, hence its name group-by-group method. This method classifies the chemicals from the brine disposal (Zhou et al., 2013). A process flow is illustrated in Fig. 9 showing the stages from the brine disposal from desalinated plants down to the mean aquatic ETP calculated from the three main groups-metals, inorganic and organic chemicals. In this method, equation (1) can be modified as:

$$\text{Aquatic ETP of brine disposal} = \sum_j m(\text{group } j) \times CF^{\text{aquatic ETP}}(\text{group } j) \quad (3)$$

where $(\text{group } j)$ is the mass of the recognized group j , $CF^{\text{aquatic ETP}}(\text{group } j)$ denotes the characterization factor (CF) of the aquatic ETP for group j .

It is important to note that the pre-screening step that is to identify the recognized chemicals is based on two principles. Firstly, chemicals with higher concentrations that are greater than the regulated level (provided it is existing) or with higher concentrations than the other chemicals in the brine from the desalination plant to be disposed of if no regulation is available. Secondly, chemicals with characterization factors (CFs) much greater than other chemicals in the brine from the desalination plant. That is the first principle has to do with regulations while the latter has to do with CFs. However, the second principle is applied to evade the error due to truncation instigated by the postulations that would be made in the first principle. This implies that both chemicals, that is, those found in large quantities in brine disposal (e.g. copper) and those that may occur in small amounts (e.g. nickel) but characterized with high impact CF should be recognized simultaneously.

This method takes the merits of the traditional or chemical and completely effluent method, as discussed earlier. The advantages of the group-by-group method include the need for fewer data to guesstimate the related impact without compromising significantly on the dependability as compared to the specific chemical method. As depicted in Fig. 9, pre-screening is employed to classify and recognize the chemicals that serve as major contributors hinge on their concentration and CF into three groups (organic, inorganic, and metals). The aquatic ETP of each group may then be calculated using either the traditional, chemical-specific-method or the whole-effluent method depending on the group characteristics and CFs available. As for the chemicals that are quite difficult in groups, alternative chemicals that have similar activity to them can serve as their representatives and be employed during the pre-screening, as this will help reduce the data needed. The second advantage of this method is that it provides a more holistic coverage for complicated brine to be disposed of. This method considers the impact of inorganic chemicals, aside from organic and metals, which are quite challenging in the LCIA.

Table 2
Metal recovery from brine by different technologies.

Recovered metal	Technology	Efficiency	Economic feasibility & environmental impact	References
Rubidium (Rb ⁺)	Integrated MD-SWRO with an adsorbent of potassium copper hexacyanoferrate in MD feed tank	96.6% removal	The high cost of Rb ⁺ in the market can compensate for the process cost. Reduce environmental impacts by brine volume reduction.	Naidu et al. (2017)
Rubidium (Rb ⁺)	Cation exchange mechanism where ionic liquid C ₂ mi mNTF ₂ as a solvent to extract Rb ⁺ by bis(2-propyloxy)calix[4] crown-6	Around 100% at optimum conditions		Luo et al. (2019)
Uranium (U)	Adsorption by amidoxime adsorbents	3.95 mg/g were adsorbed.	High economic value. Understanding the economic feasibility requires more analysis.	Wiechert et al. (2018)
Lithium (Li ⁺)	Ion-exchange	> 95%	–	Arroyo et al. (2019)
Lithium (Li ⁺)	Electrodialysis with monovalent selective ion exchange membranes		Using brine to extract Li ⁺ is more environmentally friendly compared to the traditional recovery methods.	Guo et al. (2018)
Lithium (Li ⁺)	Electrochemical approach by using selective lithiation desalination battery (rGO/LiNi _{0.6} Mn _{0.2} O ₂)	93%	It consumes only 1.4 Wh/mol Li ⁺ indicating that it is a promising electrochemical lithium extraction approach	Zhao et al. (2020)
Cesium (Cs ⁺)	Adsorption with modified potassium cobalt hexacyanoferrate	97.33%	Capital and operational costs are less than other used processes. It is profitable only in the case of high-value minerals extraction.	Yang et al. (2018)
Magnesium oxide (MgO)	Calcination of Mg(OH) ₂ by NH ₄ OH and NaOH	–	Higher energy demand than producing MgO by dry-route methods. Further optimization is required.	Dong et al. (2018)
Nickel & vanadium (Ni & V)	Ion-exchange system	98%	–	Al-Jaser & Hamoda (2019)
Magnesium (Mg ²⁺)	Extraction with an organic system containing ionic liquid (by di-(2-ethylhexyl) phosphoric acid).	68.4%	–	Yu et al. (2020)
Cesium (Cs ⁺)	Solvent extraction with 4-tert-butyl-2 (α-methylbenzyl) phenol	99.8%	This extraction method is rapid and economically feasible.	Liu et al. (2015)
Rubidium (Rb ⁺)	Sorption by ferrocyanides	85%	–	Vol'khin et al. (2008)
Cesium (Cs ⁺)	Sorption by nickel potassium ferrocyanide based on hydrated TiO ₂ in the presence of Na ⁺ , K ⁺ , and NH ₄ ⁺	No effect of the single-charged cations on the adsorption of Cs ⁺	Capital and operational costs are less than other used processes. It is profitable only in the case of high-value minerals extraction.	Voronina and Semenishchev (2013)

4.3.3. The *in silico* ADMET/Model method

This method involves the use of applying computational techniques, such as artificial intelligence, particularly machine learning methods. *In silico* refers to “in silicon”, which is in connection to the silicon chips, present in all computer systems, hence the name. In recent times, the application of machine learning in the life sciences has grown particularly in the pharmaceutical industry (Klon et al., 2004; Lima et al., 2016). Machine learning methods help in predicting the toxicity and safety of compounds, both existing and modeled (computationally designed and not yet synthesized) compounds have helped in saving time, money and even reduce the exposure to danger all of which are absent when actually testing new and existing compounds experimentally. This method involves predicting the Absorption, Distribution, Excretion, and Toxicity (ADMET) properties of chemical compounds and hence is widely used in the drug (Chen et al., 2015; Smith, 2010). These ADMET properties predicted can be applied in LCIA by using the results from the categorized chemicals in the group-by-group method and predicting the eco-toxic effects on the models on which these machine-learning methods are based on provided they are aquatic organisms. Once the chemicals in the brine to be disposed of from desalination plants are known, they can be used to predict their eco-toxicity before being discharged into the sea. The predictions would help in the LCIA, also assess the risks involved, and hence recommend if the brine to be disposed of needs further treatment prior to being discharged back into the sea. In a very recent work performed by Suresh et al. (2018), where the Naive Bayes algorithm was used to design a machine learning-based software for risk assessment. The results from such work can be translated into LCIA by making models of aquatic organisms and then using machine-learning algorithms to predict them. However, one has to bear in mind that this method would complement the group-by-

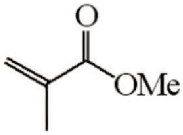
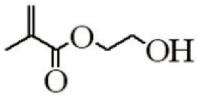
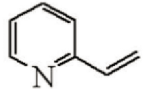
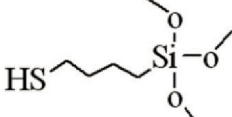
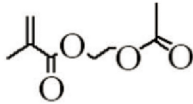
group method to make it a very effective tool in assessing the ETP of brine disposed from desalination plants.

4.3.4. Life cycle assessment case study on disposal or treatment of brine

In the case study conducted by Salih et al. (2017), three different case scenarios were assumed, namely Case 1: pretreatment of brine for the removal of TSS and disposed of by deep-well disposal (DWD), Case 2: treatment by a near-ZLD treatment and then disposing of both the salt and brine by-products and Case 3: treatment by a near-ZLD treatment with the assumption of a beneficial utilization of the treatment by-products. This comparative LCA study mainly found that higher overall environmental impacts (EI) are generated in Case 1 from pretreatment than the DWD because of the chemical usage, disposal of sludge, and infrastructure construction. The largest portion of the overall EI of the pretreatment process is due to the coagulation process. Furthermore, other treatment options were investigated, and results showed that the disposal of the pretreated brine by DWD has the smallest EI. This can be attributed to the high-energy demand for the desalination of the pretreated brine (cases 2 and 3) resulting in the highest EI which are global warming potential and resource-fossil fuels. Because of the shortage in the required inventory data and characterization factors, the injected brine effect on the receiving geological formation was not considered. This study analyzed the water depletion for the three cases and suggested that 0.6 m³–1.8 m³ fresh water for every 1.0 m³ of raw brine input can be used for the different disposal and treatment cases studied. For cases 2 and 3, no global new water gain was attained despite producing around 0.8 m³ of purified water for every 1.0 m³ of raw brine input. For case 3, when brine was desalinated and the by-products were used, 0.6 m³ was the overall freshwater consumption balance. Results from the sensitivity analysis showed that cases 2 and 3

Table 3

The chemical structure of chemical compounds commonly applied in IIPs (Chen et al., 2019).

Chemical compound	Chemical structure
Methyl methacrylate	
(2-) hydroxyethyl methacrylate	
2-vinylpyridine 2-VP	
3-mercaptopropyl trimethoxysilane	
Ethylene glycol dimethacrylate	

had the highest EI variability of 37% and 41%, respectively. This is due to the high impact of energy variation in which significant differences in the values of EI can be observed if the thermal energy source changed from natural gas to fuels to renewable energy resources which have significantly the lowest EI.

4.3.5. Effect of temperature and pH on brine management

Yan et al. (2017) investigated the applicability of RO brine treatment hydrophobic polyvinylidene difluoride (PVDF) membrane under various feed temperatures. A significant increase of the MD flux with increasing the temperature of the feed was observed. This can be attributed to the greater vapor gradient. However, higher feed temperature lead to aggravated membrane scaling causing an accelerated sharp decrease in the flux as well as lower water recovery rate. Furthermore, increasing the feed temperature increased the thermal efficiency of the membrane while the reversibility of the flux decreased with increasing the feed temperature due to the formation of more scaling compact layers at higher temperatures. Elcik et al. (2020) used MED brine as a feed source for the MD system and investigated the influence of temperature on the scaling process. Since there is an exponential relationship between temperature and vapor pressure, results showed that increasing the feed temperature gradually from 50 °C to 80 °C leads to an increase in the permeate flux from 12.5 kg/m²h to 58 kg/m²h. Furthermore, inorganic salts solubility is affected by the feed temperature as increasing the temperature reduces the salt solubility and the crystallization of salts will be more intensified at higher feed temperature. Chen et al. (2020), used t-BAMBP extractant for the recovery of Rb and Cs from brine and the results illustrated the importance of reaction temperature on the extraction process. Results showed that the extraction percentage had a drastic decrease when the temperature increased from 35 °C to 45°C which can be due to the exothermic reaction of the extraction process as well as the decrease of distribution ratio as a result of the high temperature. Qu et al. (2020) studied brine droplets evaporation with various mass concentrations under different temperatures. Results showed that decreasing the temperature caused a decrease in the evaporation rate. Furthermore, the performed preliminary sensitivity analysis indicated that the evaporation rate was more sensitive to temperature. El-Naas et al. (2017) used

a modified Solvay process without the use of ammonia for CO₂ capturing as well as reducing the salinity of brine in the presence of calcium hydroxide. Results illustrated that increasing the reaction temperature lead to a decrease in sodium removal. Increasing the temperature from 10 °C to 50 °C caused a decline in sodium removal efficiency from 45.2% to less than 5%.

Furthermore, Huo et al. (2020) demonstrated the use of a hybrid catalytic hydrogenation/membrane distillation process, which enables the ion exchange of waste brine reuse as well as captures nitrogen as a fertilizer product. In this work, a low-cost commercial Ru/C catalyst was utilized to reduce nitrate to ammonia present in brine. Results revealed that rates of ammonia mass transfer through the gas-permeable membrane increased with increasing the feed solution pH. Furthermore, the treated brine pH is usually increased by the catalytic nitrate hydrogenation reaction, thus facilitating the recovery of ammonia in the subsequent membrane distillation step. Chancellor et al., 2016, evaluated the effect of superabsorbent polymer (SAB) when introduced to the brine solution that contains calcium ions at different pH values. Results showed that polymer precipitation with calcium ions could be significantly inhibited by a very low pH value. Furthermore, Zoppas et al. (2018) applied catalytic reduction for the treatment of brine with high nitrate concentration by the employment of low noble metal loading in the catalyst (Pd 1%, in 25%) supported on alumina. Results indicated the viability of the catalytic reduction technique for the treatment of nitrate brine. It was proved that controlling the pH of the process is crucial due to the direct influence on the catalytic activities as well as the selectivity to ammonium that is an undesirable product.

5. Exposure and usage

Furthermore, RO has been used as a potential and effective technology for providing clean water and it has become the most used alternative process especially in the regions that are suffering from a shortage of water supplies (Petersková et al., 2012; Stacklin, 2012). It converts seawater into potable clean water through a desalination process that would generate a concentrated brine effluent as a waste. The brine waste is normally discharged back into the sea and becoming diluted with seawater (Jeppesen et al., 2009). However, the potential environmental challenges of the RO desalination plants have grown in addition to the thermal distillation plants. RO desalination plants consume huge volumes of water and dispose of a heavy brine concentrate back into the environment. However, the RO destination plants' brine waste with a high salt concentration, minerals, and other pollutants is usually disposed into the sea via specific channels as hypersaline brine. RO concentrate is usually disposed of in various ways; surface water disposal is one of these ways. Additional methods would be through deep well injection, ponds, and land application (Ly et al., 2013; Breunig et al., 2013). The ZLD systems are considered one of the new advances and desirable systems that are aimed to advance process the RO concentrate to avoid discharge it into surface waters, effective re-use of water, and to produce dry salts. However, scale formation, owing to the precipitation of alkaline earth metals, in highly concentrated brines is still a challenging technical problem (Davenport et al., 2018). Qatar Petroleum and its partner Shell are currently working to achieve a model capability that would have zero liquid discharge.

The effect of the brine disposal on the sea environment is still principally unidentified; however, it is normally assumed that the brine waste shall eventually be diluted into the sea and can be harmful to marine life and on the composition and distribution of biota. Other potential environmental impacts are the stratification problem as a result of increasing salinity and density, eutrophication problem because of phosphate supplementation, discoloration owing to high iron(III) concentration with high suspended solids and turbidity. Nonetheless, the desalination plants have always been taken special care to regulate the brine waste outlets.

Table 4
Application of IIPs to extract the different type of potentially toxic metals.

Technology	Toxic Metal	Functional monomer	Cross-linking agent	Initiator	Application(s)	References
Pb-IP	Lead II [Pb (II)]	4-vinyl pyridine (VP)	Ethylene glycol dimethacrylate (EGDMA)	2,2'-azobisisobutyronitrile (AIBN)	Recognizing lead/pre-concentration and removal from water samples.	Khajeh et al. (2011)
Cu-IP	Copper (Cu)	Methacrylic acid (MAA)	Ethylene glycol dimethacrylate (EGDMA)	2,2'-azobisisobutyronitrile (AIBN)	In wastewater, treatment to adsorb particular heavy metal contaminant and concurrently determines pH sensitivity traits.	Yuan et al. (2015)
Ni-IP	Nickel (Ni)	Methacrylic acid (MAA)	Ethylene glycol dimethacrylate (EGDMA)	2,2'-azobisisobutyronitrile (AIBN)	In the adsorption of Ni ²⁺ ions from the water environment.	Kumar et al. (2019)
Cd-IP	Cadmium (Cd)	Methacrylic acid (MAA)	Ethylene glycol dimethacrylate (EGDMA)	2,2'-azobisisobutyronitrile (AIBN)	Employing the novel cadmium ion-imprinted polymers to remove cadmium (II) from wastewater	Xi et al. (2015)
Cr-IP	Chromium (Cr (VI))	2-vinylpyridine	Ethylene glycol dimethacrylate (EGDMA)	1,1'-azobis(cyclohexanecarbonitrile)	In the removal/adsorption of chromium (VI) from negative metals (anions) and sulfate in aqueous environments	Pakade et al. (2011)
Hg-IP	Mercury [Hg (II)]	Methacrylic acid (MAA)	Ethylene glycol dimethacrylate (EGDMA)	2,2'-azobisisobutyronitrile (AIBN)	To determine the concentration level of mercury (II) in natural water (river, lagoon, and mineral water) and subsequently using it as an adsorbent for the removal.	Lins et al. (2019)
As-IP	Arsenic [As (III)], [As (IV)]	Methacrylic acid (MAA)	Ethylene glycol dimethacrylate (EGDMA 98)	2,2'-azobisisobutyronitrile (AIBN)	In the selective removal of arsenic from some chosen water, rice, and vegetables	Jalilian et al. (2019)

Recently, attention has been focused on recovering valuable metals from the discharged concentrated brine waste. Certainly, attaining marketable products from the discharged concentrated brine would offer an economic benefit and reducing the whole desalination costs.

Owing to the environmental problems and challenges that might be caused by brine disposal, various methodological techniques have been investigated for metal recovery gaining the benefit of their reasonably high concentrations in brine. However, the assessment criteria for the metal extraction would be economic, concentration, and other physicochemical criteria, and technical and extraction procedures criteria.

Recovery of valuable and rare metals from their novel and abundant sources around the globe can increase its profitability by decreasing the water production cost as well as limiting the environmental issues associated with brine disposal (Katal et al., 2020; Loganathan et al., 2017). However, technologies used for metal recovery are still undeveloped and require more investigation to enhance achievement in extraction steps and obtain a suitable level of improvement to be used at the industrial scale. Extraction methodologies of alkali and alkaline metals such as sodium, magnesium, potassium, and bromide are well documented. These include precipitation, ion exchange, adsorption, membrane separation, and others. However, trace metal recovery from concentrated brine may face difficulties concerning low metal concentration, limited selectivity, and the complexity of the brine system. Many investigators have attempted to overcome the above-mentioned difficulties, but quantitatively trace metal recovery remains a challenging task (Guerra et al., 2011; Le Dirach et al., 2005; Morillo et al., 2014).

The literature showed that concentrated brine contains important concentrations of various valuable metals such as lithium (Li⁺), cesium (Cs⁺), and rubidium (Rb⁺) (Le Dirach et al., 2005; Chen et al., 2020; Li et al., 2017; Naidu et al., 2018). Our preliminary investigation has shown that the concentrations of Rb⁺ and Cs⁺ are 0.194 and 0.0008 mg/L, respectively. This represents the potential usage of developing recovery methodology for the significant amount of Rb⁺ and Cs⁺ present at the concentrated brine. It is, therefore, necessary to develop an appropriate methodology to recover Rb⁺ and Cs⁺ from the concentrated brine, with an emphasis on the associated efficiency, costs, and environmental impacts. Various natural and synthetic materials have been investigated for metal recovery from waste such as zeolites and synthetic ion-exchangers. However, these materials seem to be not economically valuable as they are associated with low efficiency

and high operational cost. The employment of biological materials in recovering valuable metals from brine systems would have a potential substitute for conventional methodologies with high efficiency (Gurung et al., 2013; Rodriguez-Rojas et al., 2020).

Moreover, Rb⁺ and Cs⁺ have unique chemical and physical characteristics. It is acknowledged that the resources of Rb⁺ and Cs⁺ are globally rare. They have been used in various key industries such as fiber optics, lamps, night vision devices, for Rb⁺; aeronautics, high-pressure oil, and gas wells for Cs⁺ (Loganathan et al., 2017). Therefore, further scientific research on Rb⁺ and Cs⁺ is a dire need. Brine is considered as one of the noteworthy resources of Rb⁺ and Cs⁺ (Li et al., 2017; Shahmansouri et al., 2015; Mavukkandy et al., 2019). The richness of Rb⁺ and Cs⁺ in the concentrated brine depends on its nature. However, as the physical and chemical properties of Na⁺, K⁺, Rb⁺, and Cs⁺ are similar, the separation of Rb⁺ and Cs⁺ from the brine system would be difficult (Ye et al., 2009). Consequently, the development of a simple, selective, and practical method for the separation of Rb⁺ and Cs⁺ from concentrated brine is of importance.

5.1. Metals recovery methods

Few investigations have been implemented to develop recovery methodologies for Rb⁺ and Cs⁺ from brine systems such as membrane, adsorption, ion exchange, chemical precipitation, and coagulation methodologies (Chen et al., 2017; Gurung et al., 2013; Ye et al., 2009). However, these methodologies have their advantages and boundaries in the application. For example, chemical precipitation is inadequate when the metal concentration is low. This involves a great number of chemicals and generating huge amounts of sludge that will necessitate further treatment. The efficiency of the other methodologies in metal recovery such as ion exchange and membrane technologies would be high with low chemical consumption and high metal selectivity. However, the operation costs are expensive (Bao et al., 2017). Table 2 illustrates various metal recovery methods from brine.

5.1.1. Adsorption

Metal adsorption on an adsorbent has the benefit of liquid-liquid extraction. The latter requires mixing and settling. Metals in brine are 2.5 times higher than their concentration in seawater, which results in making their crystallization prior to or after the adsorption process more favorable for further concentration (Loganathan et al., 2017).

Table 5
Comparison of the advantages, limitations, as well as cost and energy requirements of brine treatment technologies.

Technology	Technologies' maturity level	Technical shortcomings	Economic scalability prospects	Treatable range of brine salinity	References
VSEP	Distribution is not affected by colloids, solid suspension, availability, or salt solubility - Ability to reduce the occurrence of fouling and scaling that is common with conventional RO system.	Maintenance of oscillatory vibration of a tensional spring requires energy that must be considered.	Costs are determined by considering the feed water factors (BOD, boron, chloride, fluoride, TDS, TSS, sulfate, TN, TOC as well as associated energy consumption.		Petala et al. (2006); Zouboulis et al. (2019); Lozier et al. (2007)
ED, EDR, and EDM	The membrane fouling is often controlled by the polarity reversal. It allows performance at higher feed water recovery with small-scale control chemicals. Contrary to the other membrane process utilized in drinkable water and reuse, water does not pass through the EDR, but the ions do.	The removal of poorly ionized solute, as well as particulates, is not eliminated and the removal of pathogens from the process is not credited.	Cost of energy increases with the TDS of feed brine	High salinity limit (> 100,000 mg/L)	Giwa et al. (2017); Morillo et al. (2014); Lozier et al. (2007); Pram anik et al. (2017)
FO	Applied pressure is not essential for the osmotically driven process. Good for high salinity desalination. The energy consumption is less when used together with RO. The waste heat source is useful for the regeneration of the drawn solution. The feed water recovery is high. The fouling potential is low because applied pressure is lacking.	Full-scale installations are limited. The selection of optimal osmotic agents (draw solution) is very challenging. The rates of flux are less than RO causing higher membrane area requirement. FO applications require membrane specific.	In general, this technology is less energy-intensive compared to other technologies. The costs are influenced by the type of technology in use. In wholly FO applications that involve gaseous mixtures as draw solution, the main cost needed for recovery of the draw solution will be the thermal energy. In FO/RO hybridization utilizing reuse water to feed RO and FO for seawater desalination, the desalinating water cost will be lesser because less electrical energy will be needed in the RO stage because of the dilution of feed seawater.	High salinity limit (> 200,000 mg/L)	Morillo et al. (2014); Martinetti et al. (2009); Chung et al., 2012a, 2012b; Tow and McGovern (2015)
WAIV	The evaporation rate increases ten times and land requirements are relatively reduced when compared to the conventional evaporation ponds method.	Groundwater pollution is not avoidable	The cost of operating WAIV is low because its main driving force is air dryness and allows this technology to be suitable for areas associated with high costs of energy and air dryness.		Morillo et al. (2014); Macedonio et al. (2011)
Brine crystallizers	The technology is used almost everywhere because it uses fossil fuels and get rid of climate requirements compared to solar energy	The multiple equipment modules are required because of large systems that negatively affect the economy of scale using Evaporative Crystallization (EC)	The high cost of consumed energy is predominant, with the approximated final cost of 0.095 euro per kilogram of evaporated brine. It is considered an energy-intensive technology.		Morillo et al. (2014); Ji et al. (2010); Pram anik et al. (2017)
Brine concentrator	It is peculiar with the production of distilled water of great quality that subsequently leads to a reduction in the volume of the final brine. The management of reject brine is easier because of the cooling and concentration systems	Characterized by serious challenges in the setting up and management of both intake and outfall structures. The solubility of Na ⁺ salts, the relative concentration of SO ₄ ²⁻ , Cl ⁻ , and the boiling point elevation of the brine.	Energy-intensive technology		Morillo et al. (2014); Cipollina et al. (2011); Pram anik et al. (2017)
MED	Operating temperature is very high reaching up to 172 °C with the possibility of producing low compression work, heat transfer with a small area, and compressor size reduction as rewards	Pretreatment stages were essential to minimize the concentration of silica and stop the formation of scale on the surfaces of the heat exchanger, which makes the process complicated.	Costs are determined based on the thermo-compressor and the efficiency of technology within the stages. Can be considered as energy-intensive technology, but less than BC and BCr.		Giwa et al. (2017); Macedonio et al. (2011)
MD	Applied pressure is absent. Rejection capacity with nonvolatile removal is high. When the vacuum is used, the operating temperature is at the lowest. It allows the use of plastic materials to prevent corrosion. It permits the use of various energy sources (e.g. solar energy, heat energy, and wind energy)	Only studies on the bench – scale or pilot – scale were conducted. Specifically, membranes and modules designed for MD are lacking. When the membrane is wetted, it causes fouling of hydrophobic membranes, which is a critical issue. Feedwater pretreatment is required from the source.	Yet to be known. Technology still in piloting/demonstration or bench scale. Waste heat source availability to heat feed water stream will determine the costs. Higher energy consumption relative to energy use of RO, but less than traditional evaporation and crystallization systems. Furthermore, it could be coupled with a solar collector system, which reduces energy consumption.	High salinity limits (> 200,000 mg/L)	Martinetti et al. (2009); Subramani et al. (2015); Ji et al. (2010); Pram anik et al. (2017)

Table 6
Compilation of brine treatment technologies in various studies.

Technology	Productivity	Operating Conditions	References
Forward Osmosis	After 18 h, maximum water recovery attains 76%; and salt rejection stood at 99.7%	FO is set up on a laboratory scale; Cellulose acetate asymmetric (CA) and Polyamide composite (PA) membranes; Sodium Chloride, Deionized water; Diluted fructose; Feed solution	Tang et al. (2008)
Reverse Osmosis and Forward Osmosis	The water recovery for brine A is approximately 86% and 60% for brine B	RO – FO hybrid system; TDS in brine A is 7500 mg/L and 17,500 mg/L in brine B; NaCl in draw solution is 50 ± 2 g/L; Cellulose triacetate (CTA); operating temperature is 23 ± 2 °C	Martinetti et al. (2009)
Forward Osmosis	The water fluxes from PA and CTA membranes are $0.0315 \text{ L(m}^2\text{)}^{-1}\text{.m}$ to $0.56 \text{ L(m}^2\text{)}^{-1}\text{.m}$ and $0.0315 \text{ L(m}^2\text{)}^{-1}\text{.m}$ to $0.56 \text{ L(m}^2\text{)}^{-1}\text{.m}$ respectively.	FO system; membrane – PA & CTA; 35 g/L – 200 g/L TDS in draw solution; 5 g/L – 15 g/L in feed solution	Martinetti et al. (2009)
VSEP	80% recovery of concentrate	VSEP system	Delgado (2009)
DT	Concentrate recovery is 50–80%	DT filtrations; conditions of flux differ: $30 \text{ L(m}^2\text{)}^{-1}\text{.h}$ – $34 \text{ L(m}^2\text{)}^{-1}\text{.h}$	(Subramani et al., 2011),
EDM	Water recovery attains 99.9%	EDM system; TDS in the samples of concentrate ranges between 3000 and 16,000 mg/L	
VSEP	Final water recovery is 75–93%	VSEP system; cross-flow operation is continuous; $50\text{--}100 \text{ flux L(m}^2\text{)}^{-1}\text{.h}$	Subramani et al. (2012)
ED	COD, total nitrogen (N), and total phosphorus (P) removal stands at 20%, 32%, and 32% respectively	Combined ED and Willow field	Ghyselbrecht et al. (2012)
ED	Removal of Calcium approximately 70–80%.	ED system, pH is approximately 11, pellet reactor treatment.	Tran et al. (2012)
	Removal of Calcium and Magnesium: 95% and 5–25%, respectively	ED system, pH is approximately 11.5, pellet reactor treatment	
Brine Concentrator	Final water recovery 99%	The Aquasel's system – A non-thermal brine concentrator (NTBC)	Peng et al. (2012)
EDR	Final water recovery 97%	EDR system	Xu et al. (2013)
EDR	Final water recovery 98.9%	Combine EDR and Ion exchange pretreatment	(He et al., 2013),

Table 6 (continued)

Technology	Productivity	Operating Conditions	References
Forward Osmosis and Reverse Osmosis	Energy consumption by FO drop by 3% in FO – RO (Nicoli's model); the thermally operated FO plot reduced energy consumption by 21%	FO pilot method coupled with RO regeneration (FO/RO); thermal source regenerated FO; 7% of NaCl draw; fall in hydraulic pressure in feed as well as draw streams to just 2 bar	Tow & McGovern (2015)
MSF	The discharge density is 1022.9 kg/m^3 , < ambient with thermal energy discharge of 101.52 GWh/d. The seawater intake to the product ratio (Mc/D) is 9.64 [Mc = $11.352 \text{ Mm}^3\text{/d}$] while the reject stream (Mc - D) is $10.152 \text{ Mm}^3\text{/d}$	MSF	Darwish et al. (2013)
Pervaporation	The salt rejection is approximately 99%	Setup of pervaporation water desalination; up to 75 °C of temperature; salt concentration of brine stands at 7.5 wt% and 10 wt%.	(Yaou et al., 2015),

The chelating adsorption appears to be the appropriate and efficient methodology for the Rb⁺ and Cs⁺ recovery from the concentrated brine. Since adsorption may be triggered due to the competition between metals in the brine, it has been suggested that chemically modified materials with specific inorganic compounds would selectively recover specific ion(s) of concern. The material could be ion-exchange resin, activated carbon, and cellulose (Diallo et al., 2015; Loganathan et al., 2017; Mavukkandy et al., 2019). These results in the development of novel materials to improve the adsorption characteristics of the modified material that can enhance their mechanical properties. Solid adsorbents with high selectivity and removal capacity toward specific metals are essential to various fields such as separation, purification, and treatment. Adsorbent selectivity could be succeeded by physical and/or chemical modification of its surface.

Our previous researches have been focusing on the development of using natural biological origin resources as a substitute to common adsorbents for metal elimination and recovery (Al-Ghouti et al., 2010, 2013). It was concluded that the modified date pits by various modification methodologies were active in removing various metals from water. Gurung et al. (2013) showed in their studies that polyphenolic resins could selectively recover Cs⁺ from the brine system. The phenolic OH groups acted as a metal eliminator at low pH to recover metals for water. The possible effectiveness of date pits as a low-cost adsorbent for various metals and organic compounds was proven earlier (Al-Ghouti et al., 2013). The metal ion would form a stable complex with the OH-phenolic groups available in date pits. The date pits comprise of three main groups, specifically cellulose, hemicellulose, and lignin. The main functional groups of cellulose and hemicellulose are hydroxyl, ether, and carbonyl. Lignin acts as a strengthening matrix between cellulose and hemicellulose (Al-Ghouti et al., 2010).

A modification of date pits for the recovery of Rb⁺ and Cs⁺ from the concentrated brine seems to be a highly encouraging approach. However, to the best of our knowledge, no studies have investigated the adsorption and recovery behavior of date pits towards Rb⁺ and Cs⁺. Na⁺ is the most available interfering ion with Rb⁺ and Cs⁺ from

concentrated brine. Vol'khin et al. (2008) reported that the adsorption techniques would be advisable to recover the Rb^+ brine system. Ferrocyanides [hexacyanoferrates(II)] of (Cu, Ni, and Zn) can selectively adsorb various ions such as Rb^+ , Cs^+ , and Tl^+ from brine system with high separation coefficient (K_d) for Rb^+ and K^+ , Rb^+ and Na^+ , and Cs^+ and K^+ (Vol'khin et al., 2008). Milyutin et al. (2009) studied the removal of micro-amounts of Cs^+ from brine solutions using ferrocyanide materials. They noticed that the distribution coefficient (K_d) of ^{137}Cs was dependent on solution pH and the type of sorbent used. The results also showed that the Cs^+ adsorption significantly decreased at $\text{pH} > 11$ owing to the dissolution of the ferrocyanide component. Voronina and Semenishchev (2013) studied the effect of K^+ , Na^+ , and NH_4^+ concentrations on the Cs^+ uptake onto ferrocyanide-modified titanium dioxide. They noticed that the prepared adsorbents were greatly specific to Cs^+ in the presence of K^+ , Na^+ , and NH_4^+ . Most of the published articles in the literature studied the Rb^+ and Cs^+ adsorption from solutions comprising Na^+ ions. However, information on selective adsorption using ferrocyanides in the existence of other cations such as K^+ and NH_4^+ ions is almost deficient. The NH_4^+ affinity is highest for ferrocyanides (Voronina and Semenishchev, 2013).

It was also reported that Rb^+ and Cs^+ removal and recovery from the brine system was carried out using transition metal ferrocyanide adsorbents on a solid support such as ion-exchange resins, chitosan, zeolites, and silica gel (Egorin et al., 2014). Ni-K ferrocyanide supported on zirconium hydroxide is one of the best adsorbents that exhibited a high performance toward Rb^+ and Cs^+ removal. The stability of the solid support material is of importance to have potential adsorption-selective characteristics of the prepared adsorbent in the brine system (Egorin et al., 2014). However, silicic material used as supporting material is chemically unstable in alkali solutions, which could limit its use in metal removal and recovery. Our previous investigations of the adsorption characteristics of date pits will lead to develop modified material (s) for Rb^+ and Cs^+ adsorption, which would be used later for analytical purposes for removing Rb^+ and Cs^+ from the brine system. Date pits are stable in alkaline solutions, can be recommended as a support for a ferrocyanide sorbent. Metal fixation on adsorbent depends on various factors; namely its relative affinity (its speciation) and concentration. Petersková et al. (2012) studied the speciation of various metals such as Li^+ , Rb^+ , and Cs^+ . The speciation diagrams showed that these metals are mainly presented in brine as M^+ cations, and displayed a low affinity to form complexes with the anions.

5.1.2. Imprinting polymers

Recently, studies on the development of selective materials have been focused on imprinted polymers. Imprinting polymer (IPs) is a processed polymer using an imprinting methodology that creates selective recognition sites in the prepared polymer. It involves initiating the polymerization of monomers in the existence of the specific analyte (Haupt, 2001). They can function under harsh environmental conditions (Kala et al., 2004). IPs have been effectively investigated for selective metals extraction (Rao et al., 2004), organic molecules (Caro et al., 2003), chiral separation, and pre-concentration methodologies (Caro et al., 2006). Two pathways are identified for IP preparation; namely covalent and noncovalent (Haupt, 2001; Mosbach et al., 1996). The latter would be a more practical methodology for imitating the interactions present in nature (Shea, 1994). Various key factors are needed for a successful IPs preparation, which are the monomer's type, the crosslinkers, and the experimental conditions needed for a specific analyte (Abu-Surrah et al., 2009, 2010). The polymerization of polar acrylates-based IPs is typically accomplished via radical initiators. Recently, transition metal complex-based polymerization has also been developed (Abu-Surrah et al., 2007; Ibrahim et al., 2004; Matyjaszewski et al., 2001; Yliheikkilä et al., 2006). They can function with low metal-complex concentrations and under mild polymerization conditions (Abu-Surrah and Qaroush, 2007). In general, finding selec-

tive, more efficient, and less expensive imprinted polymers for extraction/preconcentration of valuable ions is a vital and challenging task.

The rapid industrialization and technology revolution has greatly contributed to water pollution with toxic metals, such as cadmium, nickel, lead, mercury, etc. This fact poses serious negative impacts on the human habitat and aquatic organisms due to eco-toxicity effects (El-Taher et al., 2018; Jafari et al., 2018; Kobielska et al., 2018; Ting et al., 2017; Yi et al., 2017). Thus, there is the need to reduce toxic metal pollution, which often necessitates the adoption of common traditional methods of treatments, such as ion exchange (Martins et al., 2017), membrane separation (Rajewski et al., 2016), biological flocculation (Zhang et al., 2009), oxidation-reduction (Nguyen et al., 2017), chemical precipitation (Striebig, 2005) and adsorption (Yang et al., 2017). Out of them all, adsorption is the widely accepted and applied method because of some merits it has over others. These merits are simple to operate, cost-effective, and noticeable effect; but there are few demerits about this system too: regeneration of absorbability is poor, noticeable influence on the condition, and competing ions.

Most of the reviews on the ion imprinting technology (IIT) focus more on the ion imprinting polymer (IIP) and molecular imprinting technology (MIT) despite the fact that there is a scarcity of information on these two methods. Recently compiled literature from the year 2000 to early 2019 clearly showed that 6.3% of the results favored IIPs, while 10.3% of the searched results favored the MITs without any doubt more research or studies should focus on IIP compared to MIT (Chen et al., 2019).

IIT is the type of technology that establishes multiple actions within the site structure within a polymer matrix i.e. ion-imprinted polymer by the process of copolymerization functional monomer, as well as a crosslinker in the presence of target ion.

The target ion acts in the position of template molecules with an emphasis on coordination or electrostatic interactions. The template ion is disconnected from an acidic reagent. Thereafter, the template ions are formation occurred as a cross-linked polymer matrix. Ion imprinting technology is an integral part of MIT, frequently used in the detection, separation, and adsorption removal of toxic metals.

The application of IIPs technology is growing in removing many metal ions as they help to improve the recycling efficiency of these metals. Some of the applications of IIPs in metal removal are explained below. The comparison with other conventional metal recovery processes such as ion exchange and membrane separation is in vogue because of its advantages.

Copper (Cu) is a potentially toxic metal and it usually makes up high concentrations of brine disposal from desalination plants. However, copper is also a vital mineral resource, hence the great need for its removal, as this would come with a plethora of financial and economic benefits. In a recent study (Yuan et al., 2015), a new kind of surface IIP was made using methacrylic acid (MAA), attapulgite, ethylene glycol dimethacrylate (EGDMA), 2-2, azobisisobutyronitrile (AIBN) as a functional monomer, support material, and initiator respectively to prepare Cu(II)-IIP microgels. The outcome proved that the microgels had a high affinity for copper ions over magnesium and calcium ions. Another very recent study (Ren et al., 2018) made use of Cu(II) ion as the template and the adsorption capacity of Cu (II) was 39.82 (mg/g). Compared with conventional methods, which used solvent extraction wherein calcium ions competed in the selectivity (Fillipi et al., 1998).

Nickel (Ni) is also another major component of disposable brine and, thus, its removal is important. Moreover, just like copper, it has other industrial uses. Ni-IIP was prepared using a polyvinyl alcohol by combination of CTS, PVA, Ni(II) Fe_3O_4 to form beads. The nickel ions were imprinted on the beads and were gotten by the elution of Nickel from the CTS/PVA (Zhang et al., 2015). The adsorption capacity of the Ni (II) ions was 500.0 (mg/g) which is quite high compared to an earlier study that used the conventional method of electrocoagulation (Akbal et al., 2011).

Table 7
Quantitative indicators of various brine treatment techniques.

Technology	Quantitative Drivers	Quantitative Barriers	References
RO	Energy-efficient, for seawater it uses 2 kWh _e /m ³ - 6 kWh _e /m ³ product water; for brackish water: 1.5 kWh _e /m ³ - 2.5 kWh _e /m ³ product water	Limited salinity range as upper concentration is around 75,000 mg/L, the unit cost is estimated to be \$0.75/m ³ of freshwater produced; water recovery up to 50% for feed brine with <70,000 mg/L TDS and up to 10% for feed brine with 85,000 mg/L TDS	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
FO	Salinity limit > 200,000 mg/L; water recovery up to 98%	0.8 kWh _e /m ³ - 21 kWh _e /m ³ of feedwater having salinity of 73,000 mg/L; costs \$0.63/m ³ of freshwater produced	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
ED/EDR	Water recovery 86%-99%, salinity limit > 100,000 mg/L	Energy use is 7 kWh _e /m ³ - 15 kWh _e /m ³ of concentrated brine from RO; effluent with high salinity > 10,000 mg/L; costs \$0.85/m ³ of freshwater produced	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
MD	TDS limit up to 350,000 mg/L and water recovery up to 90%	Requires 22 kWh _e /m ³ - 67 kWh _e /m ³ of product water; costs \$1.17/m ³ of freshwater produced	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
Brine concentrator	Salinity limit > 250,000 mg/L; water recovery up to 98-99%; high quality product water with TDS <10 mg/L	Energy requirement of 15 kWh _e /m ³ - 70 kWh _e /m ³ of feedwater; costs \$1.11-\$1.22/m ³ of freshwater produced	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
MSF	Produce freshwater with <10 mg/L TDS; water recovery up to 85%-90%	Energy consumption is 12.5 kWh _e /m ³ - 24 kWh _e /m ³ , cost is \$1.40/m ³	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
MED	Produce freshwater with <10 mg/L TDS; water recovery up to 85%-90%	Energy required is 7.7 kWh _e /m ³ - 21 kWh _e /m ³ , cost is \$1.10/m ³	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)
WAIV	produce final brine with TDS > 100,000 mg/L used to recover mineral by-products such as magnesium salts; lowest energy consumption of 0.3 kWh _e /m ³ - 1 kWh _e /m ³	Cost is around \$1.37/m ³ of freshwater evaporated, no water recovery	Panagopoulos et al. (2019); Tong and Elimelech (2016); Morillo et al. (2014)

The advantages of IIPs are quite promising as they have an edge over conventional methods including biological flocculation, membrane separation, adsorption, and chemical precipitation. The main advantages of IIPs include: a) easy use, b) regenerative ability that enables their multiple uses in removing metal ions, and c) high selectivity, which means they have good specific recognition; hence other metal

ions, which are not intended to be removed, would compete for their active sites and good stability.

Despite the promising nature of IIPs, there still exist challenges with this technology. These include the method of preparation, which appears not to be fully developed. For instance, using a bulk polymerization method to prepare IIPs would damage the imprinted hole. The template cover is deeply embedded so it is not easily washed off. In sol-gel, method preparation the use of organic raw materials is toxic and quite expensive and in the use of in situ polymerization method, there is the use of the high-pressure column, which often, leads to poor binding ability and selectivity due to its slow flow rate. All these leads to low production of IIPs (J. Yang et al., 2018). Another challenge with IIPs is the absence of anionic polymers; hence, most of the IIPs are metal cations. This hinders IIPs from being used in removing anionic pollutants such as chlorides. Besides, there are only a few monomers used as the starting material, which are the alkenyl pyridines and imidazole. Employing the use of functional monomers needs to be developed to enable its wide usage.

6. Best practices by utility companies and users

Table 5 represents the techno-economics evaluation of desalination brine treatment technologies and future prospects and an overview of the treatment technologies as it evaluates the technologies' ability to treat brine as well as their economic evaluation. Furthermore, Table 6 compares the production and operation conditions of different brine treatment technologies. Besides, as shown in Table 7 the main barrier for most of the used techniques are the energy requirements, which in turn increases the cost of the treatment method. Therefore, future research should focus on enhancing the disadvantages of the treatment techniques in which novel, low-cost and cost-effective materials could be used for the enhancement and sustainability of the ZLD system. Moreover, simulations of the process, techno-economic analysis as well as lifecycle assessments are required for the evaluation of the treatment technologies viability in various ZLD systems.

7. Conclusion

Pure potable water with high quality should certainly be produced to guarantee good human health when consumed. However, an adverse negative impact on the environment arises from the poor handling, management, and reject brine disposal. Management of brine is mandatory in order to preserve and conserve the environment, as well as protect the entire ecosystem in the long run. From this study, it was concluded that brine is best managed when reducing its volume to the bare and accepted levels, using an appropriate technology that supports ZLD. While the generated salts could be poured on land or water, taking into consideration that the environmental impacts are greatly reduced. From all the reported studies in this paper, it can be concluded that all the emerging technologies are suitable for minimizing the brine volume. Various types of salts and metals are of economic value that can potentially generate profit when sold. The best brine management techniques are those that have the potential to combine several processes so that water is also recovered in addition to the substances. Lastly, the brine should be a resource and not a waste to attain sustainability in its management approaches. Hybrid processes would be highly recommended to get the absolute transformation of the discarded brine from desalination processes to more valuable constituents. Advanced technologies in resource recovery and treatment of brine would need to utilize renewable energy from wind, solar radiation, or geothermal as power sources so that environmental degradation can drastically be reduced. Moreover, many researchers tend to underestimate the ecotoxic effects of brine disposal when conducting LCA analysis on desalination, simply because of the shortcomings associated with the current LCIA. This review article critically examined the two con-

ventional approaches commonly used in LCA, when evaluating the ecotoxic effect of discarded brine. These approaches have been simply identified as chemical-specific approaches, characterized by the inability to carry out complex composition analysis on complicated desalination effluents. The whole effluent is the completely effluent approach, though not required, to characterize the effluent, but only work with temporal estimation.

However, an improved approach called the “group-by-group” approach is able to evaluate the impact of more complex and variable seawater desalination concentrate. This approach takes collectively the advantages of the chemicals and the whole effluent, as earlier mentioned. It also rectifies their shortcomings and that is why it is considered the most suitable approach while conducting the analysis. Firstly, the “group-by-group” approach operates with less data to forecast the possible impact without compromising the reliability outcome significantly. It is able to cover the entire complex brine by providing comprehensive coverage. This approach not only focuses on the impacts of organic chemical and toxic or non-toxic metals but, also, equally considers the roles of inorganic chemicals that are known to be problematic when conducting impact assessment as a result of the unavailability of associated characterization factors. Presently, despite the facts that IIP possesses a very good reward, as far as its application in the metals recovery from brine is concerned, a lot of problems are still needed to be tackled simply because preparation mechanisms are yet to be fully matured, namely, metal ion-imprinted polymer is mainly settled within the cations and little research on metal anions (anionic polymers), in terms of productivity, the real production of the ion-imprinted is minimal, and the polymer selectivity should be high enough and strengthened, functional monomers should not only be limited to alkenyl pyridine and alkenyl imidazole. Additional monomers that are characterized by anionic coordination effects need to be developed to fulfill practical uses or needs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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