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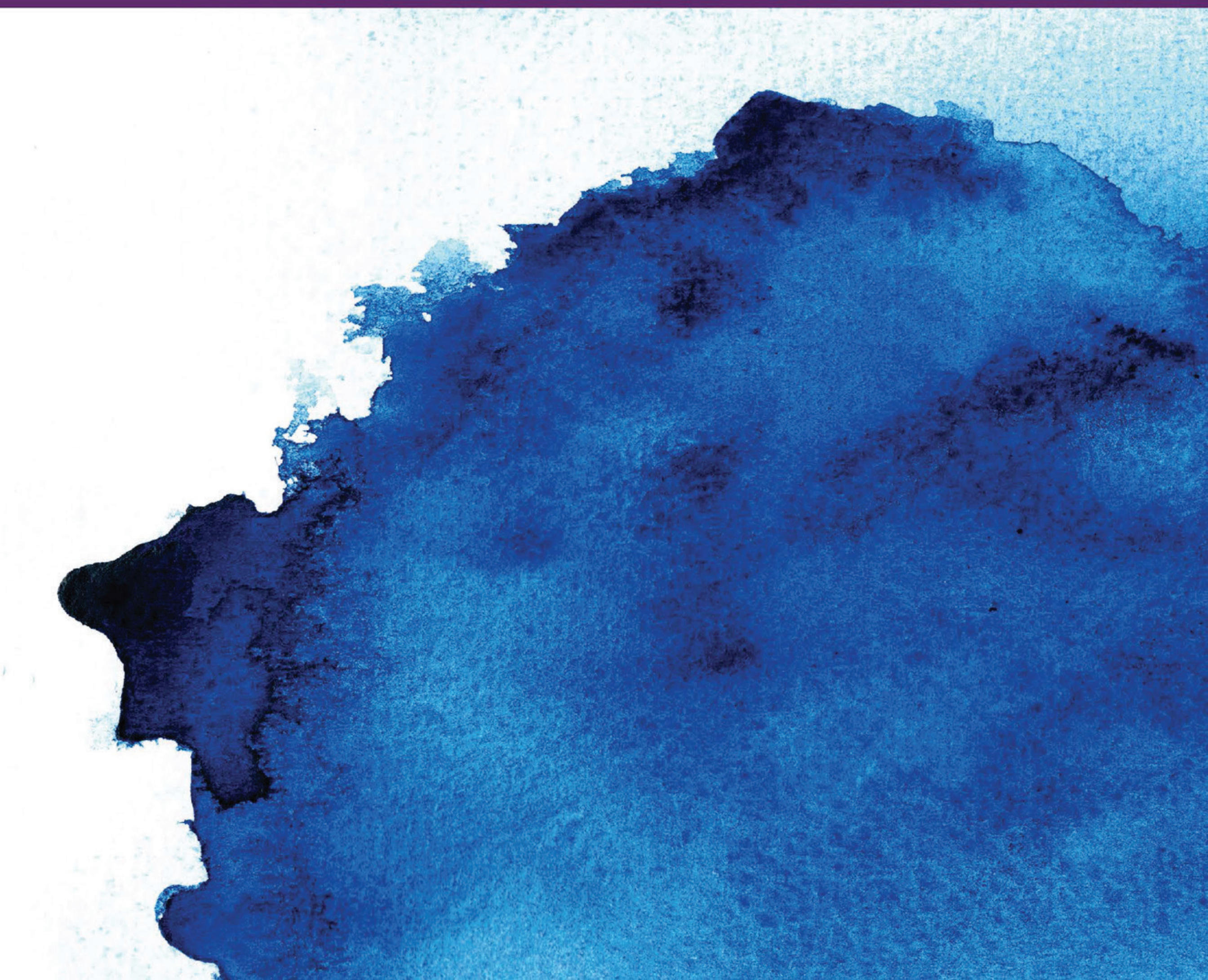
WATER TREATMENT

Resource Recovery and Sustainability

Edited by NIDAL HILAL
and DANIEL J. JOHNSON



Water Treatment

Water Treatment: Resource Recovery and Sustainability provides a comprehensive overview of the latest research in increasing the sustainability of water treatment processes. The use of nontraditional water sources, such as desalination of seawater and reuse of treated wastewater, is increasingly important given the paucity of freshwater resources globally. Only a very small fraction of the Earth's water is fresh surface water easily available for use, while 40% of the global population are classed as living in high water stress areas. As such, increasing effort is being made to tap into nontraditional water sources, such as desalination of seawater and reuse of treated wastewater, to make up this shortfall.

This book presents the latest research into methods for limiting the environmental and economic costs of the processes involved in using nontraditional sources of water. To increase the efficiency of treatment processes, research has focused on recovery of resources from their associated waste streams; generation of heat, pressure, and electricity from salinity gradients; recovery of nutrients such as nitrogen and phosphates; recovery of valuable minerals such as metals concentrated in desalination brine; and optimization of water reuse from wastewater. This comprehensive book is aimed at graduate students, researchers, and academics working or teaching in this subject area and will be of interest to water industry professionals.

Water Treatment

Resource Recovery and Sustainability

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Nidal Hilal is a UK Chartered Engineer (CEng), a registered European Engineer (Eur Ing), an elected Fellow of the Institution of Chemical Engineers (FIChemE), the Learned Society of Wales (FLSW), and the Royal Society of Chemistry (FRSC). He received his bachelor's degree in chemical engineering in 1981 followed by a master's degree in advanced chemical engineering from Swansea University (United Kingdom) in 1985, where he also obtained his PhD degree in 1988. In 2005, he was awarded a Senior Doctorate, Doctor of Science degree (DSc), from the University of Wales in recognition of an outstanding research contribution to the field of Water Processing, including Desalination and Membrane Science and Technology. He was also awarded in 2005 the prestigious Kuwait Prize (Kuwait Medal) of Applied Science by the Emir of Kuwait and in 2020 was awarded the Menelaus Medal by the Learned Society of Wales, for excellence in engineering and technology. In 2024, he was awarded the GPID – Global Prize for Innovation in Desalination Award – in the category of Advanced Water Production Technologies. He was also included in the Highly Cited Researchers 2022 and 2024 lists by Clarivate.

He has supervised 46 students through their PhDs and more than 70 postdoctoral research fellows and authored over 600 publications including several patents and books. His research interests lie broadly in the identification of innovative and cost-effective solutions in the fields of nano-water, membrane technology, and water treatment including desalination, and colloid engineering. His internationally recognized research has led to the use of atomic force microscopy (AFM) in the development of new membranes with optimized properties for difficult separations. His research has produced several breakthrough innovations: the smallest AFM colloid probe reported in the literature, the first AFM coated colloid probe technique, the first AFM cell probe technique, the first direct measurements of the interaction of single live cells with membrane surfaces, the first direct measurement of the force of adhesion of single particles with membrane surfaces, the first to show pores on nanofiltration membranes, the first use of the AFM in mesoscale cavitation studies, the first development of composite imprinted membranes, and the first development of self-cleaning membrane for sustainable desalination and tapping into salty water for agriculture. He is ranked by Google Scholar in the top ten desalination leaders (currently number 7) around the world. He is the most cited author (lifetime) in the *Desalination* journal and is also the most cited author in the *Journal of Water Process Engineering.*

Nidal sits on the editorial boards of a number of international journals, is an advisory board member of several multinational organizations, and has served on/consulted for industry, government departments, research councils, and universities on an international basis.

Daniel J. Johnson received a BSc in Biochemistry from the University of Sheffield, before pursuing a PhD in investigating dissociation of peptide structures using atomic force microscopy at the University of Nottingham. Since then, his main research interests have been in the fields of membrane separation, advanced water treatment, membrane surface characterization, and colloid and interface science, all primarily within the context of improving wastewater treatment technology and processes.

He has made significant contributions to the characterization of process equipment surfaces, the development of novel membranes with improved fouling resistance, and the assessment of fouling of polymer filtration membranes and other surfaces of relevance to water purification processes. Recent activity has been in the fields of organic and biological fouling of membranes; the development of polymer membranes for removal of heavy metals from contaminated sources; mitigating of scaling in membrane distillation systems for seawater desalination, the development of novel biofouling resistant membranes, and the treatment of industrial wastewater using forward osmosis. These activities have largely been aimed at improving water sustainability through enhanced membrane processes.

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Preface

In an age of ever-increasing demands on finite naturally occurring resources, much effort is being directed into increasing the sustainability of our exploitation of these resources and making our economic and industrial development sustainable. As such, sustainability is the degree to which a process or endeavor can be continued without the depletion of the resources upon which it depends, while sustainable development is often described as any development that meets current needs without impairing our collective ability to meet our future needs. This goes beyond our use of natural resources, it rather also includes economic sustainability, as the economic viability of an activity often determines whether it will be continued, and maintenance of the quality of our natural environment including air and water quality.

It is the sustainable use of our water resources that this book is concerned with, in terms of maintaining environmental water quality, improving the efficiency of our use of water resources and subsequent waste streams, and improving economic sustainability by maintaining and recovering nutrients from those waste streams.

Despite approximately 71% of the Earth's surface being covered by water, only a very tiny fraction of this is suitable for use in its current state, with 0.0075% of this water existing as fresh surface water. Already 40% of the global population are classed as living in high water stress areas where more than 40% of available freshwater resources are abstracted every year. Combining this paucity of freshwater resources with increasing global population, increasing industrial and agricultural requirements, and increasing aridity of many areas due to shifts in climate, we expect demand on our limited freshwater resources to only increase.

As such, increasing effort is being made to tap into nontraditional water sources, such as the desalination of seawater and reuse of treated wastewater, to make up for this shortfall. These nontraditional sources generally require more resources, in terms of energy, time, materials, chemical treatments, and waste disposal along with the myriad environmental impacts that they bring. To limit the environmental and economic costs of these processes, much research interest has focused on the recovery of resources from their associated waste streams. This includes the recovery of energy and materials, including the generation of heat, pressure, and electricity from salinity gradients; recovery of nutrients such as nitrogen and phosphates; recovery of valuable minerals, including metals concentrated in desalination brine, and optimization of water recovery and reuse from wastewater sources.

This publication will concentrate on the state of the art in increasing sustainability of water treatment processes, through recovery of these valuable resources, increasing the efficiency of treatment processes, and optimizing water recovery and reuse. It is aimed at graduate students, researchers, and academics working or teaching in this subject area and we hope it will be of interest to water industry professionals looking for a comprehensive overview of the current state of research in this area.

Nidal Hilal and Daniel J. Johnson
January 2025

Part I

Resource Recovery from Desalination and Wastewater Streams

1 Metals Recovery from RO Brine

Muayad Al-Shaeli, Raed A. Al-Juboori, Basheer Hashem Hlihl, Ahmed Faiq Al-Alawy, Bradley Ladewig, and Nidal Hilal

1.1 INTRODUCTION

In the pursuit of sustainable resource management and environmental protection, the treatment and disposal of industrial effluents have become focal points of concern. Among these, the recovery of valuable metal resources from reverse osmosis (RO) brine shows a remarkable opportunity to address simultaneously both environmental and economic challenges [1]. As industries increasingly adopt RO technology for desalination and water purification, the generation of concentrated brine streams containing trace metals has emerged as a significant problem that is demanding innovative solutions.

RO, a commonly utilized membrane-based process, has revolutionized water treatment by efficiently removing all contaminant categories employing polymeric membranes with sub-nanoscale pores [2]. However, this purification process concentrates minerals and salts into a brine stream, which, if left untreated appropriately, poses environmental consequences due to its high salinity and potential toxicity to aquatic ecosystems [3]. Furthermore, the brine contains valuable minerals such as magnesium (Mg^{+2}) and calcium (Ca^{+2}), as well as alkali, rare earth, and transition metals, including lithium (Li) and palladium (Pd), which are important for a diverse range of industrial domains: energy storage, electronics, and manufacturing [4]. If these metals are recovered, it can offset the environmental impact of brine disposal while simultaneously meeting the global demand for such materials in diverse industrial sectors.

The recovery of valuable resources from RO brine represents a multifaceted problem that requires a convergence of principles from different disciplines such as engineering, material science, chemistry, economy, and environmental sciences. Traditional approaches to brine management, such as dilution and ocean disposal, are increasingly identified as unsustainable due to their adverse environmental consequences and the loss of valuable resources [5, 6]. As a result, there is a growing interest in developing environmentally efficient technologies for mineral recovery from RO brine, thereby transferring waste into a valuable commodity.

Different processes have been explored and proposed for the recovery of metals from RO brine, each with their costs and benefits. These include adsorption, ion exchange, chemical precipitation, membrane filtration, solvent extraction, electrochemical processes, and biological methods. The selection of a suitable metal recovery method depends on different factors, including the concentration and speciation of metals present, the composition of the brine, economic viability, and environmental considerations. Moreover, consideration must be given to the integration of metal recovery processes with the existing desalination plants ensuring a smooth paradigm shift from resource consumption to resource generation.

Interests in converting the brine (which is regarded as a waste) to valuable resources were first suggested in the early 1980s, but the research work progressed slowly until 2010, which marks the year at which the number of research studies has drastically increased, as shown in Figure 1.1.

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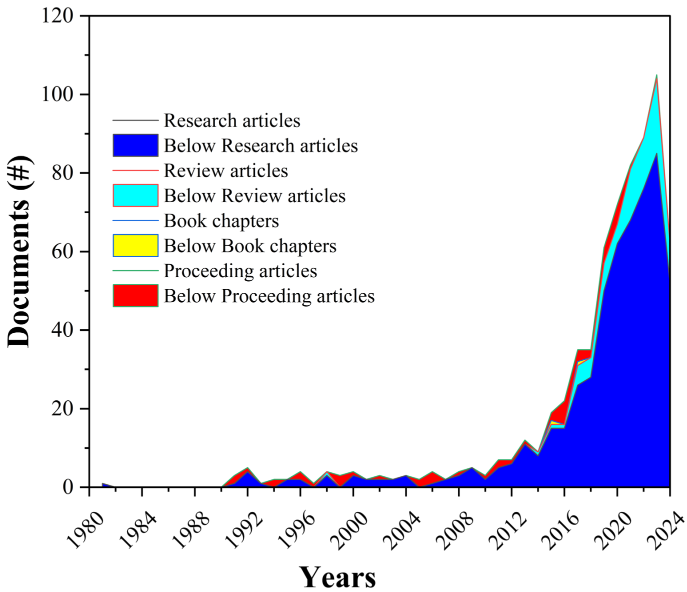

FIGURE 1.1 Literature analysis of metal recovery from brine based on data extracted from Web of Science (WoS). Keywords used were *metal recovery* and *brine*.

Interestingly, there was a very limited number of chapters that addressed this topic. This chapter aims to provide a critical analysis of the recovery technologies from brine with a focus on the RO reject stream.

1.2 ADSORPTION

Adsorption is a selective, cost-effective, and efficient separation technique that can be utilized for recovering resources from RO brine solution [7]. It is specifically useful for recovering valuable resources at low concentrations [8]. The low concentration of some minerals in brine makes their recovery with common techniques such as precipitation or crystallization challenging due to the solubility constraints. This gives the competitive edge for adsorption over the aforementioned techniques, especially in these scenarios [9]. The high adsorption capacity and selectivity are two critical factors that are required in adsorbents. Achieving complete mineral recovery from brine requires both design and operational flexibility.

The adsorption process involves the utilization of adsorbent materials that anchor metal ions on the active sites of their surfaces. Generally, the adsorbate adheres to the adsorbent surface through either physical or chemical bonding. The mechanism of chemical bonding occurs when covalent bonds dominate the interaction between the surfaces, while physical bonding takes place when physical forces such as van der Waals and electrostatic are involved. Weak van der Waals forces facilitate the desorption enabling the regeneration of the solid material through desorption, as demonstrated in Figure 1.2. Regenerating the adsorbent allows for repeated use, improving its environmental footprint and viability, while also enabling the recovery of high-quality products [10].

The adsorbents used for mineral recovery can be in different forms such as inorganic or organic structures, resins, or nanomaterials [11]. Different adsorbent materials have been used including zeolites, activated carbon, alumina, silica gels, and chitosan. Titanium- and manganese-based adsorbents have been used to recover Li from seawater or brine. Manganese-based adsorbents have the limitation of low chemical stability, which restricts their application with desalination brine [12]. In contrast, titanium adsorbents are characterized by their strong structure and tolerance to the

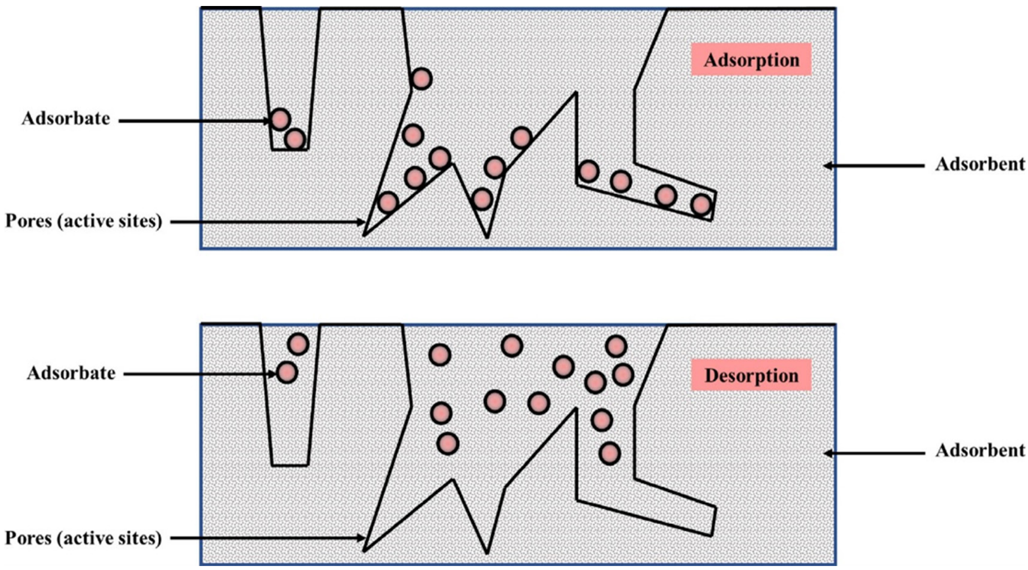

FIGURE 1.2 An illustration of the adsorption/desorption process in active sites of porous adsorbents. Adapted from Ref. [7], with permission from Elsevier.

chemically harsh environment [11]. However, the high cost and environmental concerns of titanium restrict their application as adsorbents.

Researchers typically choose the optimal adsorbent for specific applications based on different factors such as cost-efficiency, selectivity, stability, adsorption capacity, availability, regeneration capacity, large active surface area, and user-friendliness [13]. Despite the notable efficiencies of emerging adsorbents, they often lack many desired properties, such as simplicity, cost-effectiveness, and environmentally friendly production processes. The synthesis of new efficient adsorbents frequently involves chemical modification, leading to the generation of harmful waste. These chemicals require cautious disposal measures, further increasing the overall costs of the process [14]. Consequently, there is a growing interest among academics in exploring the potential of using agricultural and food industry wastes for preparing efficient adsorbents for removing minerals from waste streams [15]. Some research studies have been conducted and the results were promising. For example, Al-Absi et al. prepared copper ferrocyanide composite with roasted date bits and achieved a high adsorption capacity of ~100 mg/g for 100 mg/L Li solution [16]. Recyclable biowaste can also be an attractive alternative to costly and hazardous chemicals due to their availability in the market. Other materials such as acrylonitrile were used for crafting a modified adsorbent (amidoxime) for uranium (U) recovery from RO brine [17]. Interestingly, this study showed that U adsorption in brine was lower than that with seawater likely due to the high level of competition from other ions. This highlights an important point that metals recovery does not necessarily require a pre-concentration step and can directly be done from the desalination feedwater. Other studies have combined mineral recovery with other environmental remediation applications such as carbon capture which is the case with the study of Dindi et al. [18]. This study proposed a novel way to utilize desalination brine and CO_2 stream to produce sodium bicarbonate and brine with less Na^+ and Cl^- that can be processed further for recovery of other minerals. The process can also produce Cl products (e.g., HCl) after the calcination process of metal oxide, as shown in Figure 1.3. The produced materials such as $NaHCO_3$ and the cost of CO_2 removal can improve the viability of the process. In addition to these examples, other studies that examined the potency of adsorption for mineral recovery from brine have been summarized in Table 1.1. The studies listed in Table 1.1 were all conducted at a laboratory scale and none of these studies has considered the

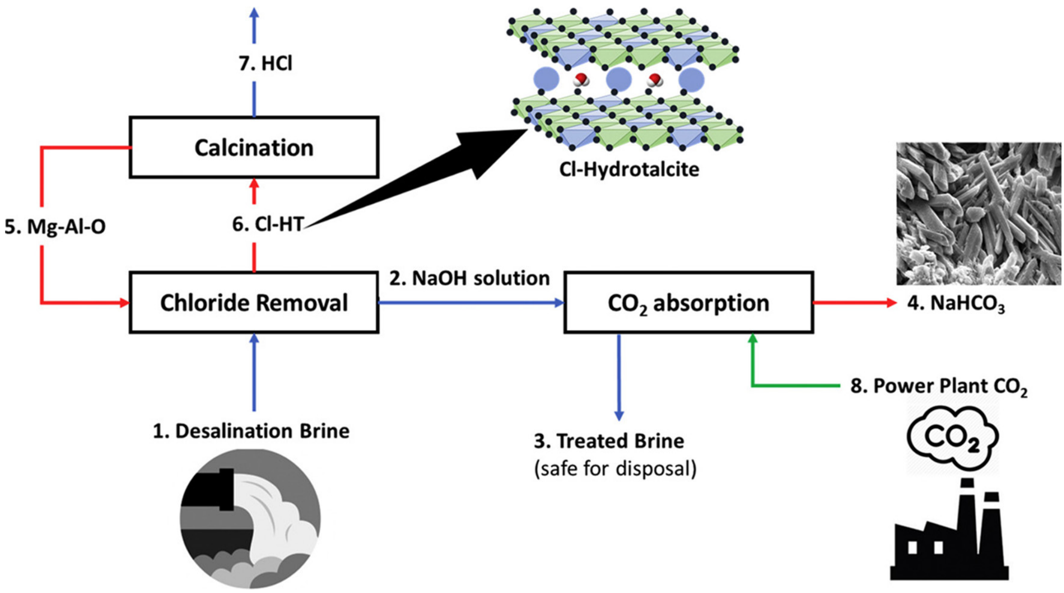

FIGURE 1.3 Schematic illustration of $NaHCO_3$ and Cl products recovery from combining RO brine and CO_2 waste stream. Adapted from Ref. [18], with permission from Elsevier.

commercialization of the adsorption process for large-scale applications. One praiseworthy aspect that could be noticed in these studies is the use of real brine. The recent research trends focus on developing complex novel adsorbents. Despite their high efficiency, these adsorbents are unlikely to be scalable, and their synthesis processes may have significant environmental impacts, undermining the goal of mineral recovery. Hence, researchers should always consult the previously outlined criteria that make a successful adsorbent.

1.3 ION EXCHANGE

Ion exchange is a mature technology that can be utilized for mineral recovery from RO brines. It is a reversible and simple process that enables the efficient removal of small amounts of impurities from solutions [26]. This technology benefits from the selective exchange of ions between the liquid phase, represented by the brine solution, and the solid phase, the ion exchange resin [27]. The first step includes selecting an appropriate ion exchange resin that targets specific minerals present in the RO brine. The resin should have a high affinity for the target minerals while demonstrating minimal interference with other components in the brine. The common configuration of this process encompasses RO brine percolation through a packed column with ion exchange resin. As the brine flows through the resin bed, the target minerals in the RO brine are selectively bound to the resin's exchange sites. Simultaneously, counterions (e.g., sodium ions Na^+) from the resins are released into the brine solution. Once the ion exchange resin becomes saturated with the target minerals, the resin bed needs regeneration to restore its ion exchange capacity. This is typically achieved by rinsing the resin with a regenerant solution, which displaces the captured minerals from the resin and replaces them with the counterions. The regenerant solution may vary depending on the specific minerals being targeted.

Ion exchange technology exhibits attractive traits, including straightforward operation, cost-efficiency, and the ability to achieve high recovery rates with low levels of dissolved solids in the feed solution, resulting in high-purity recovered materials [28]. However, ion exchange may perform poorly with concentrated feeds such as desalination brine. The optimal use of ion exchange lies in

TABLE 1.1
A Summary of Adsorption Studies for Metal Recovery from Brine

Process	Target Ions Concentration	Brine Source	Operation Conditions	Remarks	References
Adsorption of $Mg(OH)_2$ using magnetite microparticles	Mg conc. = 2600 mg/L	First-stage seawater desalination brine	Batch experiments at pH = 4–6, mixing at 200 rpm for 30 min	$MgCl_2$, $MgSO_4$, and $Mg(HCO_3)_2$ solutions with 97% purity	[19]
Boron recovery with composite microbeads of chitosan and iron (III)	B conc. in seawater = 4.2 mg/L	Seawater collected from the Mediterranean Sea	Column setting with a flow rate of 0.3 mL/min at pH 8.3	A maximum adsorption capacity of 0.13 mg/g was attained. The adsorbent maintained similar performance over five cycles	[20]
Extraction of lanthanides and other minerals from seawater using amidoxime/carboxylic fiber adsorbents	Lanthanides conc. range of ~0.1–1.2 ng/L	Seawater collected from Sequim Bay in Washington and filtered through 0.45 µm	Flume channel with braided adsorbents at 20ºC for 56 days contact time	Lanthanides along with palladium, iridium, cobalt, and titanium had the highest distribution coefficient (K_D) of 10^7–10^8, while Li had the lowest (10), and the K_D of the remaining elements fell in between	[21]
Li recovery from seawater with manganese oxide adsorbent	Li conc. = 0.17 mg/L	Seawater likely to be collected from Shikoku shores	Batch experiments (a 2 L stirred at 25°C reaching equilibrium in seven days), and column experiments percolated for 20 h at 25°C and flow rate of 10 mL/min	Li uptake was higher with dispersion experiments (4.4 mg/g) than with column experiments (2.0 mg/L). The adsorbent exhibited a consistent performance for five cycles	[22]
Recovery of Li using Fe(III)-tannate adsorbent derived from natural tannic acid	Li conc. = 250 mg/L	Synthetic brine with Li to alkali and alkaline cations (Na^+, K^+, Ca^+, and Mg^+) ratios of 1:1, 1:2, and 1:5	Pack columns with 10 g of adsorbent were soaked in Li solution for 24 h	Achieved Li adsorption efficiency of 88% and reduced Mg/Li and Ca/Li by four- and tenfold, respectively	[23]

(Continued)

TABLE 1.1 (CONTINUED)
A Summary of Adsorption Studies for Metal Recovery from Brine

Process	Target Ions Concentration	Brine Source	Operation Conditions	Remarks	References
Recovery of boron, cobalt, germanium, and gallium, from seawater using three commercial *N*-methylglucamine adsorbents (Diaion CRB03, Purolite S108, and Diaion CRB05)	Conc. (mg/L) is as follows: B = 121, Co = 0.282, Ga = 0.278, and Ge = 322	Synthetic bittern	Kinetic study for 24 h with adsorbent dosage of 30 g/L, and column study with bed mass of 2.8 g at a flow rate of 7.46 ml/min	The adsorption capacity followed the following order: Ga > Ge > Co > B for S108 and CRB03. The order is different for CRB05 where Ge had the highest capacity followed by Co, Ga, and then B. Based on the breakthrough curves, the S108 and CRB03 columns were first saturated by B, then Co, but did not reach saturation with Ga and Ge within the operation of 60 pore volume (~37 h). The saturation order for CRB05 is Ga, Co, and then B, but did not get saturated with Ge for the 37 h of operation	[24]
Recovery of Li from Salt Lake brine by using Li ion-imprinted polymers (Li(I)-IIP)	Li conc. = 50 mg/L	Synthetic solution	Batch experiment at pH = 10 and Li(I)-IIP dosage of 200 mg/L	The maximum adsorption capacity achieved was 22.82 mg/g. The selectivity coefficients for Li^+/Rb^+, Li^+/Na^+, and Li^+/K^+ were 1.427, 2.476, and 1.582, respectively. Adsorption capacity decreased by 12.5% after ten cycles	[25]

CF: concentration factor.

integrating it into a hybrid system that combines precipitation and membrane technology. In such an approach, ion exchange can efficiently be used to capture target elements, especially those that are present in low concentrations. A recent example of this process arrangement is the system developed by Mona Gulied et al. [29] who combined direct contact membrane distillation (DCMD) with electrically switched ion exchange (ESIX) for Li recovery from RO brine. The DCMD operated with a composite membrane of polyvinylidene fluoride (PVDF) and reduced graphene oxide (rGO) could concentrate Li by 2.4-fold and recover 12% of freshwater. The concentrated brine was further treated with ESIX where 91.8% of Li was recovered.

1.4 PRECIPITATION

Precipitation is the oldest method for mineral recovery from brines. It is widely favored for its exceptional properties, including simplicity, cost-effectiveness, scalability, ease of implementation, and suitability for large-scale applications [30, 31]. Precipitation can be combined with other techniques such as membranes (e.g., nanofiltration [NF]) and evaporation for improved recovery. The main limitation of precipitation is the poor selectivity that significantly impacts the quality of the recovered products, especially in the presence of harmful elements such as heavy metals and micropollutants [32]. Precipitation reactions are frequently temperature- and pH-dependent, requiring careful control and tuning of these parameters.

The precipitation process harnesses the supersaturation degree to selectively separate target metals from the brine. This can be achieved through chemical precipitation wherein the soluble metals in the solution undergo a reaction with a suitable precipitating agent, converting it to insoluble precipitates. Within chemical precipitation, carbonation is highlighted in the literature as a valuable technique for the recovery of minerals from brine resulting in the formation of carbonates and bicarbonates [30, 33].

The precipitation recovery process involves different steps such as pH adjustment, sedimentation, flocculation, reagent addition, and solids separation. Membranes could be used to replace the sedimentation, flocculation, and separation steps [34]. One common example of the precipitation process is the recovery of metal hydroxides from aqueous solutions. For example, in the recovery of Mg from brine solution, sodium hydroxide (NaOH) as an alkaline source is used as a precipitating agent. The reaction between magnesium ions (Mg^{2+}) and hydroxide ions (OH^-) results in the formation of insoluble magnesium hydroxide ($Mg(OH)_2$) precipitate[35]:

$$NaOH(aq) \rightarrow Na^+ + OH^- \quad (1.1)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\,(s) \quad (1.2)$$

Dong et al. [35] comprehensively studied the recovery of magnesium oxide (MgO) from RO brine using NaOH as a precipitation agent. The reaction yields reactive $Mg(OH)_2$ along with a trace of $CaCO_3$. The $Mg(OH)_2$ can be calcinated producing MgO, which can be applied in different applications [36]. The results of Dong et al.'s study showed that increasing the duration and calcination temperature reduces the reactivity and MgO-specific surface area (SSA). At 500°C calcination temperature and a duration of 120 min, the most reactive MgO with an SSA of 51.4 m^2/g is produced. The production cost of MgO in the market stands at $617/ton, while producing MgO from RO brine using NaOH incurs a cost of $1526/ton, demonstrating the need for further improvement of the recovery process. Notably, the synthesized MgO shows higher reactivity and purity compared to commercially available MgO. Mohammad et al. [37] studied the Mg recovery from brine through precipitation with ammonium hydroxide (NH_4OH). The recovered $Mg(OH)_2$ can be used in the post-treatment of desalinated water for remineralization, thereby reducing transportation and production costs. Their results showed that at 15ºC, a maximum recovery of 99% from a brine with a salinity of 85 g/L and NH_3/Mg molar ratio of 4.4:1 was observed. Given the direct correlation of $Mg(OH)_2$ solubility with temperature, low temperature is highly recommended for the complete recovery of magnesium. In a later study, Na and Kim [38] developed a three-step process for recovering Mg from brine. In this work, magnesium was precipitated using paper sludge ash, dissolved in 1.0 M sulfuric acid (H_2SO_4), and then magnesium sulfate ($MgSO_4$) was precipitated using ethanol (EtOH) at a 1:1 solution to ethanol ratio. The results demonstrated reaction efficiencies of 98%, 70.8%, and 88% for each respective step, with an overall efficiency of 61.1%. The common inorganic salts present in brine have lower solubility in organic solvents. This phenomenon can be exploited for expediting salt precipitation resulting in more efficient recovery [39].

1.5 SOLVENT EXTRACTION

Solvent extraction is one of the most efficient and widely applied methods for recovering valuable minerals [40, 41]. It is mainly based on the differing solubility of the target material in two separate immiscible liquids. Solvent extraction is a well-regarded method for extracting minerals from RO brine due to its simplicity and high selectivity rate. However, it generates secondary toxic waste [42].

This method has been used to recover Li from different sources [43]. There are many examples in the literature of the application of his recovery method. For instance, a 40% tributyl phosphate (TBP)/methyl isobutyl ketone (MIBK) was utilized to recover up to 98.9% of the Li in Salt Lake brine [44]. In another study, two binary extractants were employed to extract Li^+ from Mg-rich brine [45]. This binary extractant was used to reduce the excessive consumption of acid and base during the removal of magnesium from the brine. Following a four-stage stripping process, 97% of Mg was extracted along with about 13% of Li^+.

Boron (B) recovery has been effectively obtained by combining solvent extraction technology with a stripping method. A continuous three-stage countercurrent process was used to extract the B from Salt Lake brine [46]. First, the extractants and brine were passed through a 150 ml separating funnel and mixed for 5 min, then set aside to allow phase separation. Thereafter, B was stripped into the organic phase. The extractants were then recycled back into the feed for an additional extraction process. Approximately 99.5% of the B was extracted with a purity of 95.5%. Following a two-stage washing process, the extraction rate of other minerals such as Li, Mg, Fe, and Cl was 100%, 99.8%, 100%, and 93.4% respectively. Although the purity of B increased from 95.5% to 99.5%, about half of the concentration was lost during the washing process [46]. Therefore, this method needs to be optimized to achieve a higher extraction rate and increased purity.

Solvent extraction has also been applied for recovering rare alkali metals such as rubidium (Rb) and cesium (Cs) [47]. Common extraction agents used for metal recovery include phenolic alcohols, sodium triphenylcyanoboron (STPB), crown ethers, substituted phenols, and ionic liquids [40, 48–50]. Phenolic alcohols, such as 4-*tert*-butyl-2-(α-methylbenzyl) phenol (*t*-BAMBP) and its acidic derivatives, are the most common extractants used to extract Rb from brine due to their higher selectivity, low water solubility, high stability, non-volatility, ease of stripping, low cost, and other advantages [47, 49, 51]. *t*-BAMBP has shown the highest efficiency for extracting rubidium and cesium, achieving extraction rates of 95% and 99.8%, respectively [52], and yielding purities above 98% for rubidium carbonate and cesium carbonate [47]. The use of *t*-BAMBP provides excellent stability and selectivity, rapid reaction, and high efficiency compared to other extraction agents. Even though solvent extraction is easy to implement and solvents can be recycled, most of the conventional organic solvents are toxic and may have serious environmental impacts [32]. This trait makes handling solvents and dealing with their traces a challenging and expensive practice. The emerging green solvents can be utilized as an alternative to conventional toxic solvents for metal recovery [53]. However, these solvents are costly and have only been trialled on a lab scale. Future research should focus on improving the viability of the synthesis and applications of these solvents.

1.6 MEMBRANE PROCESSES

1.6.1 Microfiltration (MF) and Ultrafiltration (UF)

MF and UF are frequently used as pre-treatment for other advanced separation processes such as nanofiltration (NF) in the metal recovery processes train. MF and UF membranes possess pore sizes larger than the diameter of all ions. Still, they can efficiently remove larger particles, colloids, and macromolecules reducing fouling and blocking problems in the downstream processes. These pre-treatments could also extend the lifetime of the recovery processes and improve overall efficiency. There are minimal reports on the direct use of MF for metal recovery without the aid of more advanced filtration technologies, for example, NF. One study explored the utilization of flotation with MF for copper (Cu^{2+}) and chromium (Cr^{6+}) recovery [54]. This study could reach a recovery of 98.3% for Cu^{2+} and 95% of Cr^{6+} using sodium dodecyl sulfate as a flotation collector and goethite as a bonding agent for Cr^{6+}. MF was used to separate the precipitated salts and produce clean water. MF was also applied in a recent study to recover salt precipitates from the electrolysis process for mineral recovery from RO brine [55].

There have been more literature reports concerning UF application for metal recovery compared to MF. UF has been applied in tandem with coagulation for treating RO brine for further metal recovery [56]. This study found that the best coagulant used was ferric chloride which achieved 55% and 99% organic carbon and phosphorous removal, respectively. In another study, UF was combined with single-cation electrolysis (SCE) for $CaCO_3$ and $Mg(OH)_2$ recovery from NF concentrate (Figure 1.4) [57]. The achieved recovery rates were 95% and 64% for $CaCO_3$ and $Mg(OH)_2$, respectively. The purity of the obtained salts could be improved but at the expense of their yield. There is another path for employing UF for metal recovery. This path involves synthesizing UF membranes functionalized with supramolecular hosts for target ions [58].

1.6.2 Nanofiltration

In pressure-driven membranes, NF membranes have shown great promise for metal recovery from brine due to their capacity for separating ions based on charge and size and their lower operating pressure compared to RO [59]. However, monovalent, and non-charged species can easily pass through the membrane's active layer. The primary retention mechanisms in the NF process are size exclusion, dielectric exclusion, and the Donnan potential [59]. NF membranes typically have a pore

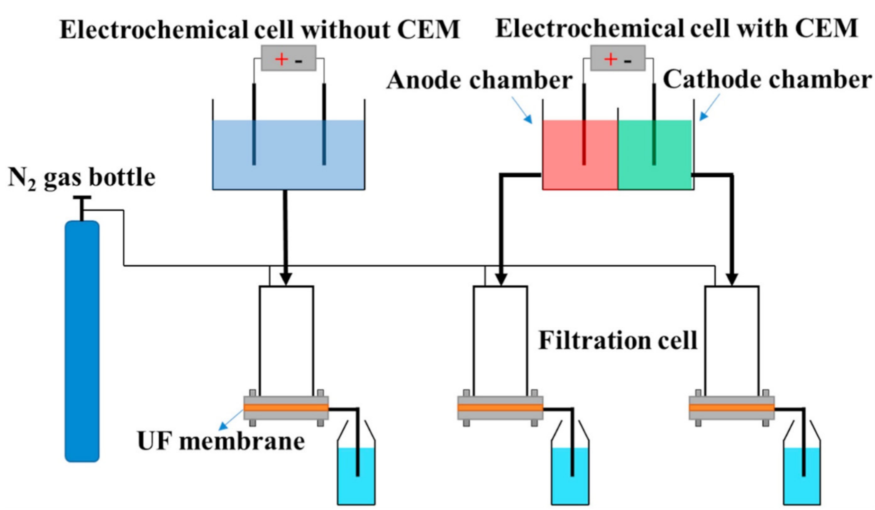

FIGURE 1.4 SCE-UF system for minerals recovery. Adapted from Ref. [57], with permission from Elsevier.

size of around 1 nm, which corresponds to a molecular weight cutoff (MWCO) range of 100–5,000 Da [60]. This pore size allows the passage of 20–80% of monovalent ions while rejecting up to 95% of multivalent ions [61].

In the literature, Li^+ is the main research focus of specific ion recovery using NF membranes. NF membranes can effectively recover Li^+ from concentrated brine, especially when there is a high Mg^{2+}/Li^+ ion ratio [61]. Polyamide spiral-wound membranes and polyacrylonitrile (PAN) hollow-fiber membranes are widely used for Li^+ recovery from the brine [62–65]. NF membranes have also been used as a pre-treatment for RO and other techniques for metal and water recovery from brine. Many projects and research studies have utilized NF in their works as a pre-treatment for the final stages of metal recovery [66]. Ali [67] proposed using NF as a pre-treatment for desalination brine in a zero-liquid discharge (ZLD) setup, preceding a series of RO stages. The rejections achieved were 98% for Mg(II), 91% for Ca(II), 54% for Cl^-, and 46% for Na^+. In another study, Du et al. [68] developed a train of processes for NaOH recovery from brine. The train starts with NF pre-treatment and ends with a membrane electrolyzer. They estimated that their system could produce about 35,000 tons of NaOH from 10,000 kilotons of brine, which would suffice the seawater treatment plant requirement of this chemical with some surpassed amount that could be sold in the market. Ihsanullah et al. [8] envisaged the application of NF for ions separation in two scenarios (Figure 1.5), underscoring the significant role of this technology as a pre-treatment for metal recovery.

Table 1.2 presents a summary of the results from various studies on metal recovery from brine using NF technology. Most of the research studies presented are lab-scale, However, there are few research studies where NF has been implemented on a pilot scale for the recovery of metals, which is a positive sign for the technology progression. Some of the studies listed in Table 1.2 reported that increasing the pressure may increase monovalent ions (e.g., Li^+) convective flow, leading to better separation, but this can exacerbate fouling and increase energy consumption. Generally, NF performs well for rejecting multivalent ions, but poorly for monovalent ions. Chemical modification of the NF membrane surface can improve its permselectivity; however, this practice can increase the process cost and the environmental footprint.

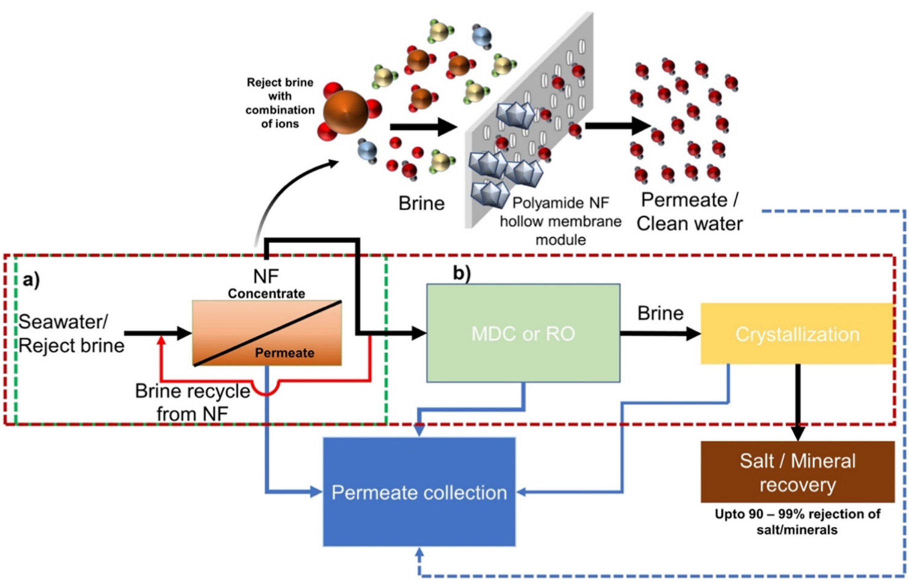

FIGURE 1.5 Possible scenarios for NF application in metal recovery scheme from RO brine. (a) In a recirculation mode for concentrating brine. (b) A pre-treatment for RO or membrane distillation crystallization. Adapted from Ref. [8], with permission from Elsevier.

TABLE 1.2

Example Studies of NF Application for Mineral Recovery from Brine

Membrane Configuration	Target Ions Concentration	Brine Source	Operating Conditions	Remarks	References
Spiral-wound NF membrane (commercial DK polyamide, PA)	Li^+ conc. = 204 mg/L	Synthetic lake salt brine	Pressure = 3.5 MPa Temperature= 25°C, pH = 4	➢ Li^+ yield = 99% at Mg^{2+}/Li^+= 4.0 ➢ Water flux ~ 13 $L/m^2.h$ (LMH) ➢ Monovalent ions compete with Li^+	[63]
Spiral-wound NF membrane	Li^+ conc. = 10.9–21.7 mg/L	Synthetic brine	Pressure = 0.5 MPa Temperature = 20°C	➢ Li^+ recovery = 85% ➢ Mg^{2+}/Li^+ decreased from 40 to 0.9 ➢ Separation factor (SF) = 42	[64]
Planar module NF membrane (NF90, PA)	Li^+ conc. = 59.9 mg/L	Ten times diluted natural Salt Lake brine	Pressure = <15 bars Temperature = 21 °C	➢ Mg^{2+} rejection = 100%, Li^+ rejection = 15% ➢ Poor separation with Na^+ (<15%)	[65]
Hollow-fiber composite NF membrane, PA	Li^+ conc. = 164 mg/L	Synthetic brine	Pressure = 0.3 MPa Temperature = 25°C	➢ Li^+ rejection = 21.8% ➢ Rejection order Mg (Cl and SO_4 salts) > NaCl > LiCl, but the flux followed a reverse order	[62]
Flat sheet positively charged NF membrane, PA modified with EDTA	Li^+ conc. = 100 mg/L	Synthetic brine	Pressure = 1 MPa Temperature = 25°C	➢ Li^+ rejection = 68.1% ➢ SF = 9.2 for Mg^{2+}/Li^+ of 24 ➢ Rejection of Mg salts was the highest followed by Na salts and then Li salts	[69]

(*Continued*)

TABLE 1.2 (CONTINUED)
Example Studies of NF Application for Mineral Recovery from Brine

Membrane Configuration	Target Ions Concentration	Brine Source	Operating Conditions	Remarks	References
Flat sheet commercial NF membranes (Filmtec NF270, Fortilife XC-N, DuPont, and PRO-XS2)	Major elements conc. (mg/L): Na^+ = 21,700, S^{6+}= 1,900, K^+ = 800, Cl^- = 39,650, Mg^{2+}= 2,800, Ca^{2+} = 860 Minor elements (Li^+, In^{3+}, Rb^+, V^{5+}, Ga^{3+}, Sc^{3+}, Mo^{6+}) conc. = 0.5 mg/L except for B^{3+}= 8.45 mg/L	Synthetic seawater RO (SWRO) brine	Pressure = 30 bar, pH = 7.5	➢ PRO-XS2 had the highest SF compared to the other membranes ➢ Multivalent ions had higher rejection than monovalent ions in both major and minor ion groups ➢ S^{6+}, Sc^{3+}, Mo^{6+}, In^{3+} reached the highest rejection of almost 100% ➢ The dielectric exclusion was the dominant rejection mechanism	[70]
Flat sheet commercial NF membranes (NF90 DOW Filmtec, NFS, and NFX from Synder, VNF Vontron, and DK Veolia)	Major elements conc. (mg/L): Na^+ = 22,727, SO_4^{2-} = 6,200, K^+ = 818, Cl^- = 40, 181, Mg^{2+} = 2,636, Ca^{2+} = 818, Br^- = 118, HCO_3^- = 291, CO_3^{2-} =143 Minor elements (mg/L): Li^+ = 0.9, B = 7.6, Rb^+ = 0.9, Sr^{2+}= 15.0	Synthetic (SWRO) brine	pH = 6.5, Temperature = 25°C, Pressure = 20 bar	➢ DK membrane was the best membrane in terms of permeability and selectivity ➢ Multivalent ion rejection was dictated by the dielectric and the Donnan exclusion mechanisms ➢ All membranes exhibited good separation of multivalent ions from monovalent ions ➢ Mg^{2+}, Ca^{2+}, Sr^{2+}, and SO_4^{2-} had the highest rejection (85–100%)	[71]

1.6.3 Membrane Distillation

Thermal-driven techniques are popular for metal recovery from brine due to their efficacy in handling such high-salinity solutions. The most common thermal-driven techniques that can be utilized for metals recovery include membrane distillation (MD) and its extension; membrane crystallization (MCr), also known as MD crystallization (MDC); multi-effect distillation (MED); multi-stage flash (MSF) distillation; and adsorption desalination (AD) [72]. Among them, MD and MCr have recently garnered considerable interest due to their ability to process salt mixtures exceeding the saturation point with minimal drop in permeate flow [73] and could also produce fine salt crystals with high purity [74]. In these processes, the water vapor passes through a microporous hydrophobic membrane, usually made of polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP) polymers, under a vapor pressure gradient and condenses on the permeate side forming a supersaturated feed solution that facilitates crystal formation. These crystals are finally collected in an external crystallizer, as shown in Figure 1.6. MD system configuration varies depending on the vapor harvesting technique on the permeate side. When a condensation plate is used, it is known as direct contact membrane distillation (DCMD). The heat losses in DCMD can be improved by incorporating an airgap producing the configuration known as airgap membrane distillation (AGMD). When vapor collection is aided by a carrier gas or vacuum pressure, the systems are termed sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD), respectively [75].

Despite its high-salinity tolerance compared to other membrane technologies, MD faces several limitations that hinder its progress toward large-scale applications. These include (i) the wetting problem that develops after membrane aging and fouling, (ii) the commonly experienced fouling challenges that are experienced in all membrane technologies, (iii) thermal and concentration polarizations, which are typical heat and mass transfer problems and impede flows across porous media, and (iv) the inherent poor energy conversion and recovery [75]. The first three problems can be assuaged by modifying membrane surface chemistry and MD design by applying localized heat and vibration to improve the transfer phenomena and water-repelling properties [76–78]. The intrinsic

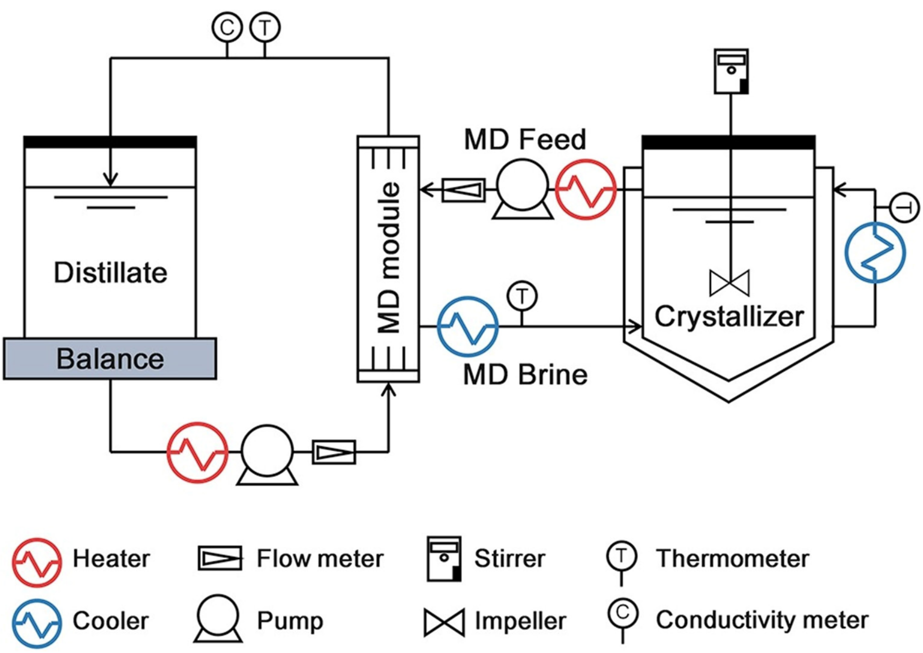

FIGURE 1.6 Schematic illustration of MDC setup. Adapted from Ref. [86], with permission from Elsevier.

high-energy demands of MD can be mitigated by low-grade thermal, solar, or other renewable energy sources [61].

Pilot trials were carried out in Australia for testing DCMD for power plant wastewater treatment utilizing waste heat extracted from the boiler circulation pump (~40°C) [79]. A water recovery of 92.85% was achieved with almost complete removal of dissolved solids (99.9%). The fouling started impacting the membrane performance pronouncedly at the end of the three-month trial. Reflecting on this example, a similar arrangement can be implemented, but fouling events are expected to occur more frequently. The high-energy demands of MD present an interesting and complex problem that continues to inspire creative and novel solutions. For instance, Lu et al. proposed combining freeze desalination with MD and crystallization harnessing solar energy for heating and liquefied natural gas (LNG) regasification for cooling [80]. Although their investigation heavily relied on theoretical modeling, the results they achieved were promising. Their optimized bench-scale system could produce 69.48 L of water and 2.52 kg of salt completely sourcing cooling energy from LNG regasification and 50% of the heating energy from solar.

Several studies were devoted to testing MD as a stand-alone technology or combined with other technologies for metal recovery from brine. Quist-Jensen et al. [81] applied MDC for metal recovery from NF retentate and RO brine. Their results showed that multivalent cations such as Mg^{2+}, Sr^{2+}, and Ba^{2+} could reasonably be recovered from NF retentate with a recovery of 66.2%, 87.5%, and 86.1%, respectively. However, monovalent ions such as K^+, Na^+, and Ni^+ could only be recovered from the sequential NF/RO system. When comparing conventional evaporation ponds with MD for concentrating Salt Lake brine, it was found that the latter could concentrate the brine to twice its initial contraction 17 times faster than the ponds [82]. The MD footprint was also 168 times smaller, underscoring MD superiority in dealing with hypersaline streams compared to the conventional approaches. MD has also been successfully combined with adsorption using potassium copper hexacyanoferrate (KCuFC) as an effective adsorbent for selective recovery of rubidium (Rb^+) from RO brine [83, 84]. The adsorption of this cation is endothermic, which makes the MD feed channel a suitable environment for the recovery. KCuFC can be regenerated using KCl salt in a separate desorption chamber and then selectively separated using resins (e.g., resorcinol formaldehyde [83]). These studies reported 80–90% Rb^+ recovery from brine. The main concerns with the MD-adsorption approach are the competition of other ions and the scaling that could negatively impact membrane water productivity and the adsorption capacity of adsorbents. MD system was also combined with solvent extraction for H_2SO_4 recovery from mining waste reaching nearly 99% recovery after three successive extraction stages [85]. Solvent extraction efficiency increases with increasing the target species concentration which can be achieved with MD.

1.6.4 Forward Osmosis (FO)

Forward osmosis (FO) is gaining immense attention for its ability to recover metals from RO brines. FO is an innovative technology that uses a semipermeable membrane to separate high-salinity brine (feed solution) from a low-salinity solution (draw solution [DS]). This process uses osmotic pressure difference to drive the water that naturally flows from the brine into the draw solution [87]. This movement concentrates the brine and dilutes the draw solution. The concentrated brine can later be processed for metal recovery.

The technical terminology of the process changes depending on the membrane orientation. When the membrane's active layer is on the feed side, the process is termed FO, and when it is facing the draw solution, it is called pressure-related osmosis (PRO) [88]. Due to the active involvement of the two membrane sides in the separation process, their structural properties are important. There are two designs of FO membranes: symmetric and asymmetric. FO technology shares the same challenges of fouling and concentration polarization with other membrane technologies. However, FO has additional barriers, such as internal concentration polarization where the ions from the brine side get entrapped in the membrane pores or permeate flow dilutes draw solution within the support layer, depending on whether the dense selective layer is draw-facing or feed-facing, respectively, and reverse salt flux (RSF) when the ions from the draw solution migrate to the feed side. Both of these problems weaken the osmotic pressure difference across the membranes leading to water flux drop and cross-contamination of recovered products [89]. These challenges can be mitigated by manipulating the water flow conditions in the membrane vicinity and designing a membrane with low structural parameters [90, 91].

The main attractive attributes of FO technology are the low energy required for water passage across the membrane and fouling reversibility stemming from low operating pressure [89]. However, the expensive draw solution regeneration is probably a hindrance to the scalability path of the technology. Hence, the selection of a draw solution is a key parameter in FO operation. Some studies developed a list of characteristics that define the ideal draw solution. These characteristics are related to its cost, availability, ability to regenerate, ease of handling and pumping, osmotic pressure, and environmental impact [92]. Although conventional inorganic salts meet most of these criteria, they fall short in their ability to regenerate cost-effectively and their tendency to cause concentration polarization and reverse flux problems. Hence, many research studies attempted to develop efficient draw solutions that circumvent these challenges such as the use of gases, hydrogel, functionalized nanomaterials, and organic compounds [93].

The practical development of the FO process for metals recovery is restricted by the lack of a suitable draw solution with high osmotic pressure exceeding that of the brine. For this reason, brine has always been thought of as a suitable draw solution for wastewater treatment, with more interest in utilizing FO for nutrient recovery than mineral recovery [94]. There are several studies reported in the literature that have examined the use of FO for metal recovery, particularly for the extraction of lithium (Li+) from brine. For example, Pham et al. [95] used the FO process for the concentration of Li from Salt Lake brine, using sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) as draw solutions under different operational conditions. Cellulose triacetate (CTA) and thin-film composite (TFC) PA membranes and their orientations were compared. Their findings showed that Li^+ rejection and water flux were higher for TFC compared to CTA. Li^+ rejection was also better with FO orientation than with PRO orientation. Similar observations were reported by Li et al. [96], except the latter found that CTA had a slightly better Li^+ rejection than TFC. This could be attributed to the intricate differences in the chemical structures of the membranes used in the investigations. The enrichment of Li^+ using FO technology was mostly carried out in short-term studies of a few hours. However, Wagh et al. [97] were successful in fabricating a robust Kynar PVDF membrane that maintained a high Li^+ rejection for 550 h, concentrating it nearly five times from 36 mg/L to 175 mg/L. Although their results are promising, their tests were conducted at 85°C which is 60°C higher than other studies. This corresponds to an added thermal energy of about 251 kJ/kg of water treated. Recently, Amani and Kolliopoulos [98] employed deep eutectic solvents (DESs), namely, choline chloride:2 ethylene glycol and choline chloride:2 levulinic acid as draw solutions for concentrating Li^+ in synthetic brine. They found that DESs had a slightly better water flux than the conventional inorganic Mg, Ca, and Na chlorides. This was likely due to the reduced RSF with DES compared to the inorganic salts. Choline chloride:2 ethylene glycol had the highest water flux accompanied by a Li^+ concentration increase of 3.6.

Osmotically assisted reverse osmosis (OARO) is another filtration technology that can be utilized to enrich the brine. This technology combines the principles of RO with FO systems and was proposed for treating high-salinity brine streams [99]. However, the motivation behind developing this technology was water recovery more than metal concentration, and using it for these purposes may require tuning and optimization.

1.6.5 Electrochemical Membranes

Electrochemical processes have emerged as effective approaches for the recovery of metals from RO brines [8]. These methods use the electrical field to induce chemical reactions that allow the

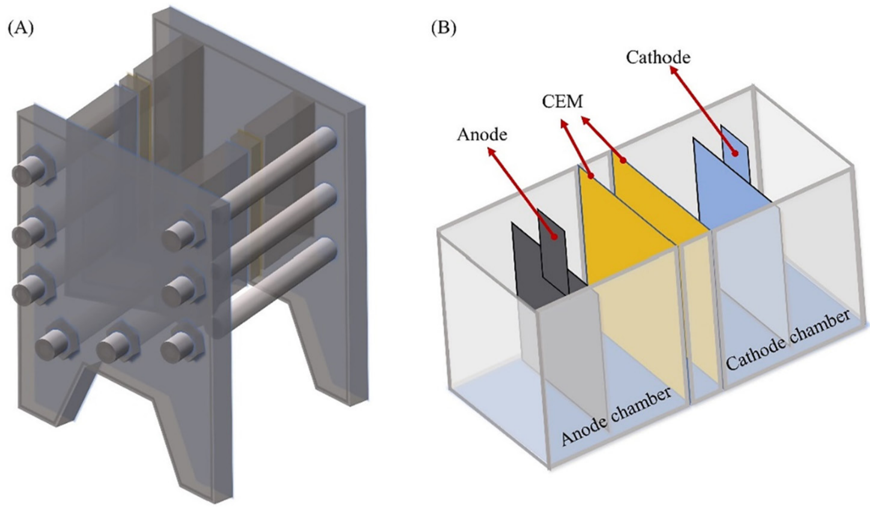

FIGURE 1.7 An illustration of a typical ED cell. (a) Cell assembly. (b) Detailed features of the cell chambers. Reproduced from Ref. [102], with permission from Elsevier.

selective extraction and recovery of valuable metals. The main electrochemical processes used for metal recovery from RO brines include electrodialysis (ED), capacitive deionization (CDI), and electrodeposition [100]. This chapter will focus on ED due to its high selectivity and potential for recovering high-purity metals.

Typically, the ED system is composed of a series of ion (IEM) and cation exchange (CEM) membranes that are stacked together forming anode and cathode chambers, as illustrated in Figure 1.7 [101, 102]. Under the effect of the electric field, oxidation reactions at the anode and reduction reactions at the cathode are initiated. To maintain neutrality, anions and cations migrate to the anode and cathode chambers passing through ion exchange membranes [103]. In general, the ionic transport rate in ED relies on the material properties of the membranes (i.e., ionic site density and overall density), electrode compositions, and the concentration of the ionic species [104, 105]. Membrane and electrode fouling are the main challenges in mineral recovery with ED. Due to their low solubility, Ca^{+2} and Mg^{+2} carbonates and hydroxides can readily precipitate on membranes and other surfaces. Nevertheless, fouling can be somewhat managed by either chemical cleaning or reverse electrodialysis. In reverse electrodialysis, the electrical polarity is reversed at certain intervals causing the removal of deposited materials.

ED offers a high recovery rate, making it invaluable for treating high-salinity water. However, the efficiency of metal recovery with ED is affected by many factors such as applied energy, temperature, flow rate, pH, feed concentration, and membrane characteristics [106]. The higher the applied voltage in ED, the stronger the driving force, and consequently a high separation is achieved. Nonetheless, high voltage can cause several problems such as exacerbation of concentration polarization, possible membrane damage, and excessive generation of protons and hydroxyl ions that alter the pH in the separation chambers [106]. The increase in the temperature improves ions' mobility and reduces membrane resistance, but at the same time increases energy demands and may deteriorate electrodes and membrane materials after prolonged exposure [107, 108]. The flow rate is a pivotal factor in the optimization of mineral recovery with ED. The low flow rates allow enough time for ions to transfer across the membrane; however, such conditions can increase the overall system resistance [106]. The pH of the brine impacts the separation in the ED process through different routes. It affects the charge and speciation of ions, affecting their selectivity. The alkaline pH range induces metal precipitation, and the acidic range generates H^+ that disturbs the transport of ions [109, 110]. Ion concentration plays an important role in determining the efficiency of ED as it serves as a conductant for the applied voltage. The energy requirement increases with the salt concentration in the feed [111]. Operating the ED below the water-splitting voltage is crucial to maintaining a high overall efficiency [112]; however, this does not apply to bipolar membrane electrodialysis (BMED) which in principle relies on water-splitting for creating an acidic and alkaline environment. Membranes are the core of the electrodialysis (ED) process, acting as barriers that selectively separate ions in mixtures. Membrane chemical characteristics such as charge and functional groups are responsible for ions' transfer efficiency and selectivity [113, 114]. The membrane porosity, pore size, and roughness also impact the separation with the ED process.

ED processes have shown promising results in laboratory- and pilot-scale studies for metal recovery from RO brines. Nie et al. [115] used ED with monovalent selective ion exchange membranes to recover Li^+ from a synthetic mixture. The results showed that ED cells recovered about 95.3% of Li^+ and contracted the Mg/Li ratio from 150 for the feed to 8 for the product. In another study, Liu et al. [102] developed a two-chamber ED process (Figure 1.7) for Li^+ extraction from brine with a high Mg^{2+}/Li^+ ratio. A liquid membrane made of tributyl phosphate and ionic liquids loaded with Li^+ was used as the separation barrier between the two CEMs. The liquid membrane achieved an impressive reduction of Mg^{2+}/Li^+ from 53:1 to 0.26:1 after 12 h consuming a specific energy consumption (SEC) of only 16 Wh/g Li^+. The liquid membrane could also prevent the permeation of other monovalent ions such as K^+ and Na^+ almost completely. The application of liquid membranes could be a potential solution for the low-selectivity problem of ED for ions with the same valence. Selective electrodialysis (SED) that employs a series of monovalent anion and cation exchange membranes is another way to improve the selectivity of target monovalent ions. For instance, Guo et al. [116] adopted SED using 11 monovalent selective CEMs and 10 monovalent IEMs and could achieve Li^+ recovery of 76.45% with SEC of ~0.05 kW/g Li^+. While a large portion of the literature concerning ED application for mineral recovery deals with Li^+, ED was successfully used for separating a wide range of elements with removal efficiency varying between 16% for cadmium and >99% for iron, zinc, manganese, arsenic, silver, and lead [106].

Despite the attractive qualities of the ED system, there are still many challenges that warrant further research work to address them. Such challenges include high investment costs for building large-scale systems, the high-energy demands emanating from the cell components' resistances, and operational problems such as scaling, precipitation, and membrane fouling [106]. Future research and development in this technology should focus on creating efficient membrane and electrode materials with multifunctional capabilities. Additionally, exploring coupling technologies that can simultaneously generate multiple products will enhance the economic viability of the combined system.

1.7 CONCLUSIONS

As the global population grows, competition for resources and increasing waste generation are expected to intensify. Therefore, mimicking nature's cyclic approach to managing waste as a resource is the only effective and safe way to sustain our planet. RO brine exemplifies this principle, as millions of cubic meters are produced annually worldwide. It contains an abundance of elements that are hazardous to dispose of but valuable if extracted and utilized in various industries. This chapter discusses the commonly used technologies available for achieving this goal. Generally, the technologies can be categorized as follows: mature technologies like chemical precipitation, ion exchange, adsorption, solvent extraction, and pressure-driven membranes; developing technologies such as ED; and proof-of-concept stage technologies like FO and MD. The economic viability of mature technologies is already established. However, the main shortcomings of these technologies are poor selectivity, a lengthy recovery process, and the generation of hazardous waste. Considering these shortcomings, a combined system would be the best arrangement for these technologies. NF appears to be the most promising pressure-driven technology due to its separation capability and low operating pressure, making it an ideal core component for such a combined system. Green solvents can be utilized to replace conventional hazardous solvents for the extraction and regeneration of adsorptive media. ED can be coupled with precipitation to produce mineral salts along with acids and bases. MDC can be employed if high-purity mineral salts with defined crystal sizes are required.

All the above-mentioned recovery system scenarios require robust separation media to cope with the harsh nature of RO brine. This necessitates ongoing efforts to develop new membranes, electrodes, resins, and adsorbents with robust chemical and physical structures, along with active sites for the reversible anchoring of target elements. The economic feasibility of metal recovery from brine should not solely rely on market value. Instead, a business model should be developed that incorporates the savings from brine treatment to secure the buy-in of the desalination industry.

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