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Review

Challenges and opportunities of recovering lithium from seawater, produced water, geothermal brines, and salt lakes using conventional and emerging technologies

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ABSTRACT

Energy storage plays a crucial role in the modern energy landscape, with its applications spanning from renewable energy integration to the electrification of transportation and microgrids. Lithium is a key component of lithium-ion batteries at the core of energy storage technologies. Increasing demand for lithium has challenged supply chains and required a rethinking of how we source it. This comprehensive review presents a critical and holistic assessment of the opportunities and challenges of sourcing lithium from diverse feedstocks, such as seawater, geothermal, produced water (oilfield), and salt lake brines. We assess various lithium extraction technologies (precipitation, extraction, electrochemical techniques, and membrane processes) considering these three feedstocks. A quantitative comparative analysis is conducted across all technologies, considering factors such as cost, commercial maturity, operation duration, and other relevant parameters to determine the most promising technologies for each feedstock while identifying remaining research and technological gaps. Our analysis reveals that Direct Lithium Extraction (DLE) technologies, characterized by higher selectivity and lower environmental impact, demonstrate significant promise for enhancing lithium yields from geothermal brines. In contrast, membrane processes are identified as more suited for seawater and salt lake brines, offering cost-effective scalability despite challenges with selectivity and membrane fouling. Ultimately, the efficient integration of these technologies is illustrated for harvesting lithium from each unconventional resource. The analysis shows that adsorption and chemical precipitation are the commercial technologies for lithium recovery from geothermal, salt lake, and oilfield brine.

1. Introduction

Global energy demand is expected to at least double within the next two decades. The finite availability of nonrenewable fossil fuels, as well as their uses and impact on climate, poses substantial challenges to meeting this demand sustainably [1]. The future of the energy industry and the global energy mix is expected to heavily rely on renewable sources such as solar, wind, and wave energy to address this dual challenge. The intermittent nature of these sources, however, necessitates the use of energy storage for transportation and load-level grid balancing. Lithium-ion batteries (LiBs) have emerged as the technology of choice for these applications due to the highest energy density of any rechargeable device [2–4]. Lithium is particularly interesting from an electrochemical standpoint because of its low electrode potential (-3.04 V) and high specific capacity (3.86 Ah g^{-1}). Apart from its primary application in LiBs, there is a substantial demand for lithium compounds in diverse commercial sectors, including light aircraft alloys, glass, catalysts, cosmetics, and pharmaceuticals [5–9] (Fig. 1). Nonetheless, the rising demand for smaller LiBs in portable electronics and larger LiBs in electric vehicles (EVs) and stationary power storage will be the main driving force behind the future growth of the lithium market [10–14]. Meeting this demand hinges on the capability to expand

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production, preferably without endangering the environment.

At the moment, geothermal brines, salt lake brines, clays and ores are typical land sources for lithium, with an estimated amount of 55–86 million tons (Mt) and a recent United States Geological Survey (USGS) report even shows that the available sources are approximately 98 Mt [15] and over half of the lithium production is sourced from various brines [15] (Fig. 1). In 2015, the global production of lithium amounted to approximately 168,000 metric tons (mt) of lithium carbonate equivalent (LCE), as reported by the USGS in 2017 [16]. However, this figure has since increased by 5.5-fold, reaching an estimated 915,000 mt LCE in 2023 [17–19]. Projections suggest that by 2030, the demand for lithium will reach 2 million mt LCE, and by 2050, the demand is expected to increase by 40-fold with the implementation of new and more sustainable mining policies, according to various sources (Fig. 2) [5,20–22]. This projected surge in lithium demand necessitates identifying alternative sources of lithium and corresponding recovery methods that are cost-effective and sustainable.

Previous estimates have highlighted concerns about the inadequacy of the current lithium supply to meet growing demand, attributed to limitations in existing mining infrastructure that can only accommodate lower production levels, resulting in a significant bottleneck in meeting future demand [23–28]. However, in response to the spike in lithium prices in 2021 and 2022, and increasing demand, new lithium projects have been initiated and existing facilities have been scaling up production worldwide.

More recent projections indicate that the global demand for lithium is expected to be met through the increased output from Australia (via the Mt. Holland and Kathleen Valley projects), Chile (via expansions by SQM and Albemarle brine operations), and Argentina (via new and expanded brine operations by Allkem, Livent, and Minera Exar). Lithium production in Australia has increased from 335,000 mt LCE in 2021 to 399,000 mt LCE in 2022, with a forecasted production of 470,000 mt LCE in 2023, according to the Australian government [29]. Combined lithium production in Chile and Argentina increased from 182,700 mt LCE in 2021 to 241,000 mt LCE in 2022 [15]. Moreover, at least 15 new projects worldwide (Fig. 3) are anticipated to come online by the end of 2024, adding an estimated 570,000 mt LCE in production capacity, which would be an increase of 62 % from 2023 levels [30]. Furthermore, in the United States, where lithium production capacity has been negligible, two new conventional lithium mines, Thacker Pass and Rhyolite Ridge, are expected to be operational by 2026 with production capacities of 80,000 mt/y LCE and 24,000 mt/y LCE, respectively, potentially making the United States the fourth largest lithium producing country in the world [31].

While these developments could potentially push global lithium production capacity over 1 million mt/y LCE by 2025, which may be sufficient to meet near-term demand, several lithium projects have faced setbacks due to permitting issues caused by environmental and social concerns, higher costs due to inflation, labor shortages, and supply chain constraints. For example, Chile has the second largest estimated lithium reserves [15] in the world, at 49.5 Mt, trailing only Bolivia with 122 Mt (USGS 2023) [15]. However, the Chilean constitution prohibits the mining of lithium, considered a strategic resource, due to its potential use in nuclear fission applications [32]. The only two exceptions that would permit lithium mining are via a decree by the President or if a site was developed prior to 1979 and grandfathered [33]. The Chilean government has been attempting to revise this language, but no final document has been released yet. In the United States, the Thacker Pass project has raised concerns, as is estimated to disturb more than 6,000 acres of land (and potentially more when accounting for tailings piles), and the lithium extraction method (sulfuric acid leaching) is water-intensive, requiring an estimated 2.2 million gallons per day (MGD) of fresh water [34]. Furthermore, the project has prompted several protests and petitions over concerns that the open pit mine will disturb Native American lands considered sacred by the Paiute and Shoshone tribes [35]. In Western Australia, the Mt. Holland mine has experienced delays, most recently due to supply chain and labor shortages, resulting in a 20 % increase in project costs. Wesfarmers, one of the joint owners of the facility, has seen their share of capital costs rise from $950 million to $1.2 to $1.3 billion [36].

The supply-and-demand dynamics of lithium are further exacerbated by changing interest rates, new and expiring federal incentives, and consumer demand for electric vehicles. For example, China ended its federal incentives for purchasing a new electric vehicle on January 1, 2023, which is expected to slow consumer demand growth in China from 95 % year-over-year to 22 % [37]. Conversely, the United States is providing federal incentives of up to $7,500 for purchasing a new electric vehicle through 2032, via the Inflation Reduction Act. While it is widely recognized that increasing amounts of lithium will be required to support the electrification of the transportation sector, energy storage systems, and other lithium-dependent technologies, the exact manner and timeframe of this increase remain uncertain.

Considering the uncertainties surrounding lithium extraction technologies and supply sources, it is crucial to investigate and identify potential opportunities for diversification. Exploring alternative methods such as direct lithium extraction (DLE) and unconventional sources like geothermal brines could offer numerous advantages. For instance, utilizing DLE and repurposing disturbed lands or existing infrastructure at geothermal sites could help mitigate potential environmental and social impacts associated with new mining operations,

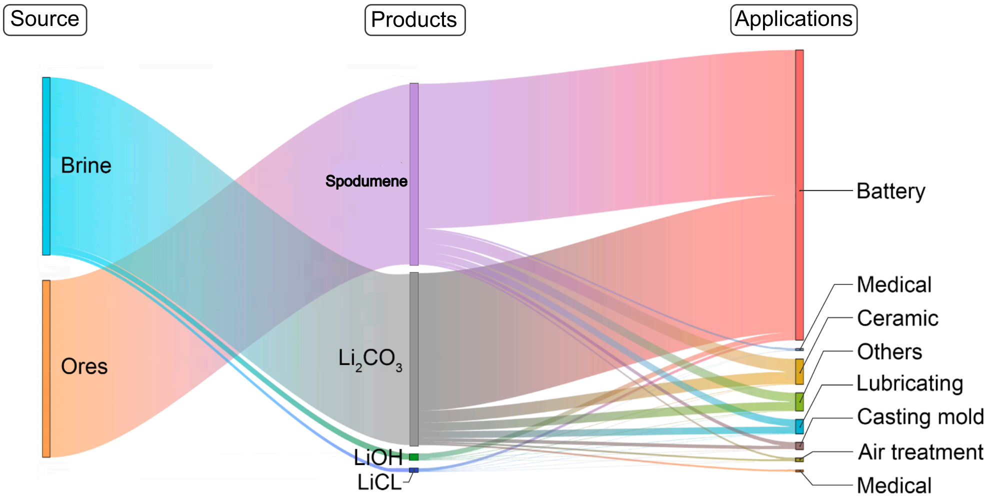


Fig. 1. From source to end-use application of lithium.

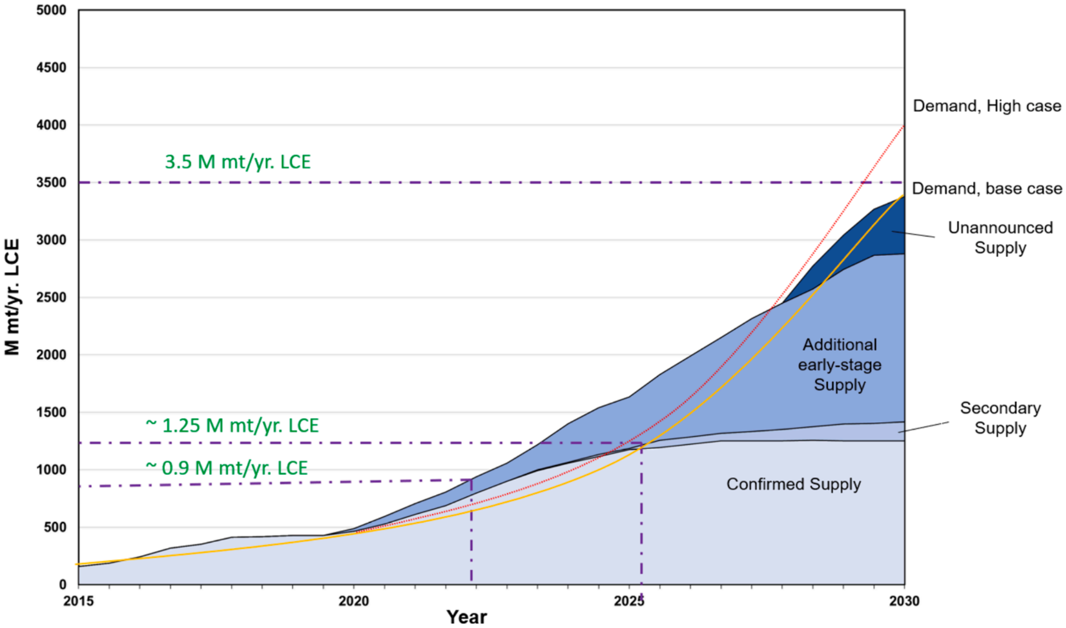


Fig. 2. Global lithium supply and demand. Adapted from [22]. Secondary supply stands for reuse and recycling of used Li-Ion batteries. Confirmed supply stands for supply from well-established lithium producing countries. Additional early-stage supply stands for new projects with recently mapped lithium resources around the world, including conventional brines, hard rock assets, and some confirmed geothermal and oilfield projects in Europe and North America.

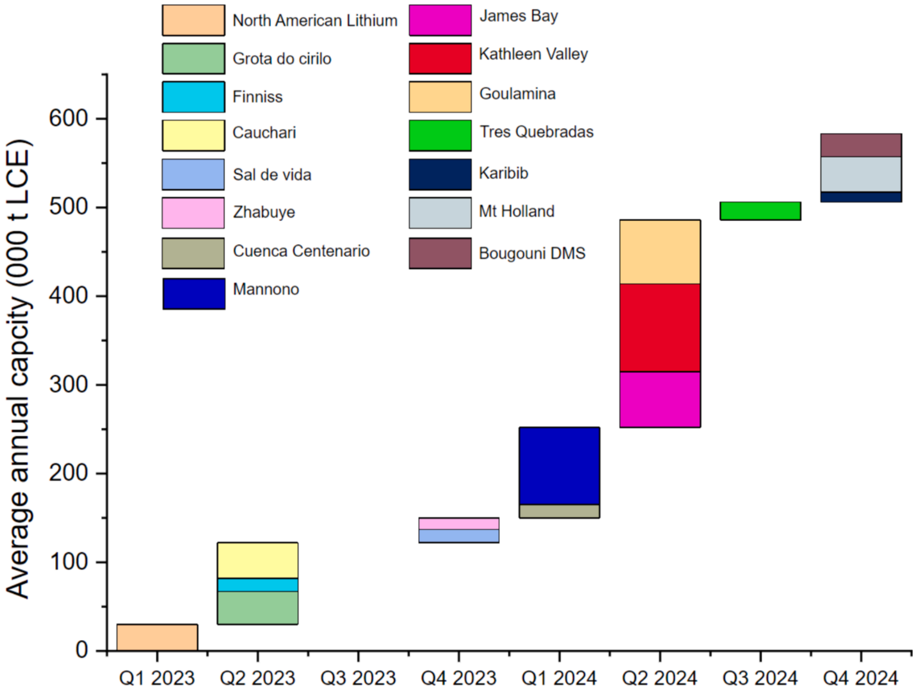


Fig. 3. Production capacity of most new projects to be commissioned in 2024. Adapted from [30].

and provide a more equitable approach to lithium extraction. Additionally, leveraging existing sites may streamline permitting processes, expedite facility construction, reduce costs, and accelerate new lithium supply to the market.

Geothermal, salt lake, and produced water (oilfield) brines also offer an attractive alternative to traditional ores with their rich mineral content, accounting for 62 % of total lithium resources. However, geothermal brines are also highly concentrated in arsenic, mercury, and boron due to the deep contact of hot water with the rocks which raises ecological and environmental concerns [23–28,38]. Seawater, on the other hand, represents another alternative feedstock with a vast reserve of approximately 230 billion tons of lithium globally [24,39]. However, the low concentrations of lithium ions (Li^{+}) in seawater make the recovery processes economically impractical due to the high costs involved. The presence of other impurities and ions further complicates the extraction of lithium directly from seawater. Nonetheless, these challenges also present opportunities for recovering lithium from such unconventional sources.

Generally, four main steps are involved in recovering lithium from brines [40]. These include the removal of Mg^{2+} and Ca^{2+}; removing Na^+ and K^+ and increasing Li^+ concentration to the appropriate level; removing SO_4^{2-}, Br^- and other ions; and finally, converting Li^+ to lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH). Traditional methods to extract lithium from water resources include solar evaporation and chemical precipitation. However, lithium has also been recovered from salt lake brines using a variety of separation processes, including precipitation, solvent extraction, ion exchange, selective semipermeable membranes, electrochemical-based processes, and evaporative crystallization [41]. Therefore, there is a need to provide a comprehensive comparison of these technologies from various aspects. While several notable review articles on this topic exist, this review paper distinguishes itself from other studies on lithium extraction technologies [42–51] by offering a thorough and global viewpoint that spans multiple scales, sources, and methods. This work provides a comprehensive and in-depth examination of the economic and environmental elements of these technologies. Previous review articles on lithium recovery only considered available technologies from the lens of one or two specific feedstocks, such as salt lake [46,47,50], oilfield brines [51], and geothermal brine [49] or a sole specific technology such as solvent extraction [45] or electrochemical recovery technologies [48], and gave less attention to sustainability and commercial readiness. Furthermore, in recent reviews such as Khalil et al. [43] and Meng et al. [44], although they delved into a range of lithium feedstock and explored various technologies for lithium recovery, the reviews lacked context for large-scale production of lithium based on increasing demand. In this review paper, we shed light on identifying the most viable technologies for recovering lithium from diverse brine sources. We comprehensively analyze various lithium recovery techniques, spanning from bench-scale experiments to large-scale industrial processes. We investigate solvent extraction, chemical precipitation, membrane-based processes, and electrochemical methods in great detail, weighing their respective strengths and weaknesses. Our aim is to provide an unbiased and rigorous evaluation of these technologies, taking into account the primary obstacles that each method faces, as well as their associated benefits and opportunities. Uniquely, this paper also discusses how these technologies can be integrated to enhance efficiency and sustainability, offering insights into potential synergies that are typically overlooked in the existing literature. Additionally, we assess the technology readiness level (TRL) of each method and review real-world and industrial projects, identifying the gap between academic research and industrial application, which other reviews have not addressed.

2. Lithium recovery technologies for unconventional feedstocks

2.1. Solvent extraction

Solvent extraction — also known as *liquid–liquid extraction* or *chemical extraction* — is a promising approach for lithium recovery from brines with its high product yield and low operating costs. The extraction process consists of extractant, co-extractant, and diluent, and involves using specific organic solvents that can dissolve high concentrations of lithium chloride (LiCl) while exhibiting high selectivity for excluding undesirable ions (Fig. 4) [43,52]. Tributyl phosphate (TBP)-$FeCl_3$-kerosene is the most commonly used extractant/co-extractant/diluent combination, whereas other systems and extraction configurations (*e.g.,* neutral extraction, ionic liquid, crown ether, supported liquid membrane, and other synergistic systems) are also proposed to boost extraction efficiency [53]. Despite its operational advantages, the solution's acidity and the concentration of Cl^- pose limitations due to favoring the reverse reaction that prevents the mechanism for Li^+ and TBP from forming a macromolecular compound for extraction. This high requirement of Cl^- increases the complexity of the process, ultimately restricting the widespread use of solvent extraction only to brines with a very high Mg^{2+}/Li^+ ratio [54–56]. Moreover, divalent ions such as Mg^{2+} and Ca^{2+} must be eliminated to keep the solvent extraction step effective, and lithium must be pre-concentrated [51]. Consequently, solvent extraction stands out as a valuable technology for extracting lithium from salt lake brines compared to dilute feedstocks [54]. Numerous studies have used liquid–liquid extraction systems for recovering lithium from salt lake brine and produced water [57–64].

2.1.1. Neutral extraction systems

The first neutral system used n-butanol and TBP as extractants with $FeCl_3$ as co-extractants which is shown to recover 99.42 % of the lithium from salt lake brine, demonstrating this technology's ability to achieve high lithium recovery [46,65]. However, TBP deterioration and equipment corrosion are easily triggered when these systems use high

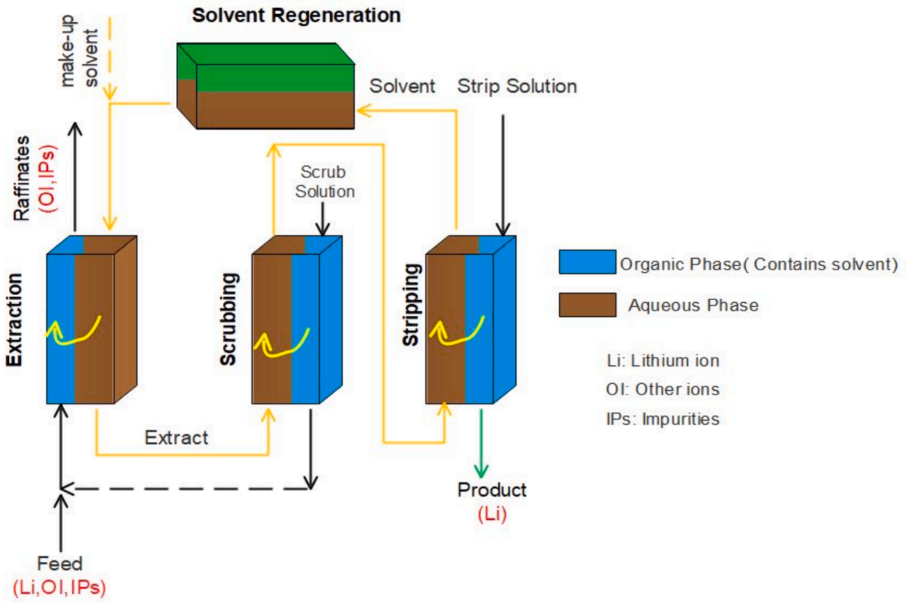


Fig. 4. Schematic of a solvent extraction system.
Adapted from [52].

concentrations of hydrochloric acid (HCl) that range from 6 to 8 M to strip lithium by exchanging Li^+ with H^+ [51]. Moreover, the loss of Fe^{3+} is another challenge as it affects the selective extraction of lithium, resulting in a lower extraction capacity [66]. This can be overcome by using different chlorides such as $ZnCl_2$ and $CrCl_3$ as co-extractants, instead of $FeCl_3$. Additionally, if the proportion of TBP in the organic phase is less than 80 %, organic polymerization will occur, resulting in organic loss and environmental pollution, which will reduce the process efficiency [46]. Neutral systems have also been used for lithium recovery from oilfield brine. Jang et al. used 1 M Di-2-ethylhexylphosphoric acid (D2EHPA) as an extractant and removed over 94.4 % of Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} ions in the first stage, which targeted divalent cations. In the second stage of lithium recovery, they achieved a lithium extraction efficiency of 41.2 % using 1.5 M D2EHPA and 0.3 M TBP [62]. However, these extraction systems consume large amounts of organic reagents, especially volatile organic compounds, which are known to cause adverse effects on the environment and human health [67]. To remedy this, a newer generation of solvent systems, such as ionic liquid and synergistic solvents are used.

A synergistic or multicomponent solvent system is another type of solvent extraction that aims to combine two types of extractants to substantially boost extraction efficiency and/or selectivity [52]. Several studies have shown that the combination of solvents can enhance the performance of lithium recovery. D2EHPA and tri-n-octyl phosphine oxide (TOPO) are well-known examples of synergistic mixes that can be used together with other solvents and improve selectivity and recovery [68]. One of the first studies in synergistic solvent extraction dates to 1993, when a mixture of D2EHPA and TBP was used to extract lithium from geothermal brine. The synergistic effect was observed when the lithium recovery from D2EHPA alone reached 52 % whereas using D2EHPA together with TBP increased the recovery rate to 88 % [69]. These systems were only applicable to brines with low sodium concentrations. Zhang et al. [58] also combined HBTA and TOPO along with kerosene as a diluent and reached a lithium extraction of 95 %. After that, lithium was entirely stripped by 2.5 M HCl solution, which is at a concentration lower than conventional sources. Several studies have shown that using a syngenetic solvent extraction system can also avoid the formation of a third phase, a common issue in most traditional solvent extraction systems [58,61,70]. However, it is vital to say one negative aspect of these systems is that they contain fluorine, which is a known toxic compound that can cause environmental pollution [71].

2.1.2. *Ionic liquid systems*

The benefits of ionic liquids include low flammability, high heat stability, variable viscosity, and low volatility. In liquid–liquid extraction systems, they are used as both replacements for volatile organic solvents and as additional co-extractants [65,72]. Several studies have successfully indicated the improvement in lithium separation and shown that the ionic liquid can be compatible with traditional solvents [60,73–76]. Shi et al. [77] used an ammonium ionic liquid (tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate) for the extraction of lithium from an aqueous solution. It was observed that in a single interaction, a concentration of HCl greater than 0.5 M was able to recover around 99.37 % of the loaded lithium ions. Hence, using ionic liquids can significantly decrease the amount and concentration of HCl required in the stripping section compared to the traditional solvent extraction process, which helps avoid rapid corrosion of the equipment. Zhang et al. [57] observed that using an ionic system benzoyltrifluoroacetone (HBTA), TOPO-kerosene would require 3 M of HCl in the stripping section to recover nearly 100 % lithium, while in the traditional system (TBP-kerosene-$FeCl_3$) 6 M of HCl is used to strip the lithium to an equivalent recovery ratio [78]. Zante et al. [64] used ionic liquid systems to recover lithium from simulated oilfield brine. The initial step involved dissolving divalent metals in n-dodecane using DEHPA (1 M) in five consecutive extraction cycles. By using an ionic liquid extracting agent [Aliquat-336][DEHPA] (1 M) in the second stage, 83 % of the lithium was removed in a single extraction cycle.

Although ionic liquids exhibit high recovery rates, their primary drawback lies in their cost. Ionic solvents such as Cyanex 272 and D2EHPA are \$119.4 to \$160/kg and \$15 to \$30/kg [79,80], respectively, while conventional solvents such as $FeCl_3$ have an average price of \$2.5/kg [81]. This makes ionic liquids best suited for low-throughput processes that extract high-value metals from lower-volume sources [49,82]. Ionic liquids are also restricted by their physical characteristics, such as viscosity and solubility in water, where only a subset of them is appropriate for use in the extraction process [82,83]. Components of ionic liquids are also often lost in the extracted solution since their extraction procedures frequently include ion exchange, which might have adverse effects [49]. Following hydrolysis of the fluorinated anions, the water phase can be contaminated with hydrofluoric acid, which makes it more difficult to regenerate and reuse ionic liquids. New research is focusing on functionalized ionic liquids or task-specific ionic liquids as these solvents are attached by a metal-coordinating group to either its cationic or anionic component, enabling their reuse [77]. For instance, Zhou et al. [84] used a hydroxyl-functionalized ionic liquid [OHEMIM][NTf_2] and TBP as co-extraction reagent and extractant, respectively, and achieved an extraction efficiency of 94.2 % for Li^+ while only using 1 M HCl as the stripping agent. This system has also been stable even after seven reuse cycles of the solvent, and the change in the Li+ recovery efficiency is maintained at 4.4 %.

2.1.3. *Crown ether systems*

Crown ethers and their derivatives have also been used to separate lithium due to the structure that allows for the formation of multidentate complexes, which are ideal for the selective extraction of alkali metals. Lithium bonds weaken with increasing crown ring size, and the order of selectivity for alkali metals via crown ether depends on the size of the cavity [85]. The oxygen atoms in crown ethers function as a strong base and preferentially bond to the Li^+, which is a strong acid [65].

Combining crown ether extraction with ionic liquid extraction or supercritical fluid extraction are two examples of how this method might be used in lithium recovery from brine [20,49,86–89]. Pálsdóttir et al. [87] synthesized 3-methylene-14-crown-4 and a novel fluorinated 14-crown-4 for supercritical carbon dioxide extraction of lithium from brine. The maximum extraction efficiency of 38 % was obtained, which is relatively low compared to other available solvents. Further, recent notable reviews by Stringfellow [49,85] argued that the selectivity of crown ethers for lithium in complex solutions had not yet been demonstrated, and their production is quite costly. There is also a lack of information regarding the extent of pretreatment needed (*i.e.*, the elimination of base metals) prior to crown ether extraction of lithium. Research efforts in this area should focus on improving the extraction efficiency and selectivity towards lithium ions, understanding the pretreatment needs, and ways to make them compatible with conventional solvents to reduce costs.

2.1.4. *Supported liquid membrane (SLM)*

Up to now, all aforementioned liquid–liquid extraction strategies have resulted in the loss of organic extractant into the brine, causing brine pollution and posing severe threats to the ecosystem. Lithium extraction by SLM offers a solution to the issues that arise during liquid–liquid extraction [90–92]. The organic extractant or carrier is dissolved in a suitable diluent to form the liquid membrane, and this carrier selectively reacts with the chemical species to be extracted. SLMs can be built in one of three distinct forms: a flat sheet SLM, a hollow fiber SLM, or a spiral wound SLM [93] (Fig. 5a). Numerous studies explored the extraction of lithium and other rare earth metals from brine using the SLM technology [65,92,94–96]. Ma et al. [94] worked on combining LIX54 with TOPO and kerosene to extract lithium in an SLM, and the Li^+ extraction efficiency system was greater than 95 % at a pH of 12.5 with 1 M H_2SO_4 serving as the stripping solution. The stability of this system was its biggest disadvantage. After three days, the study showed that the

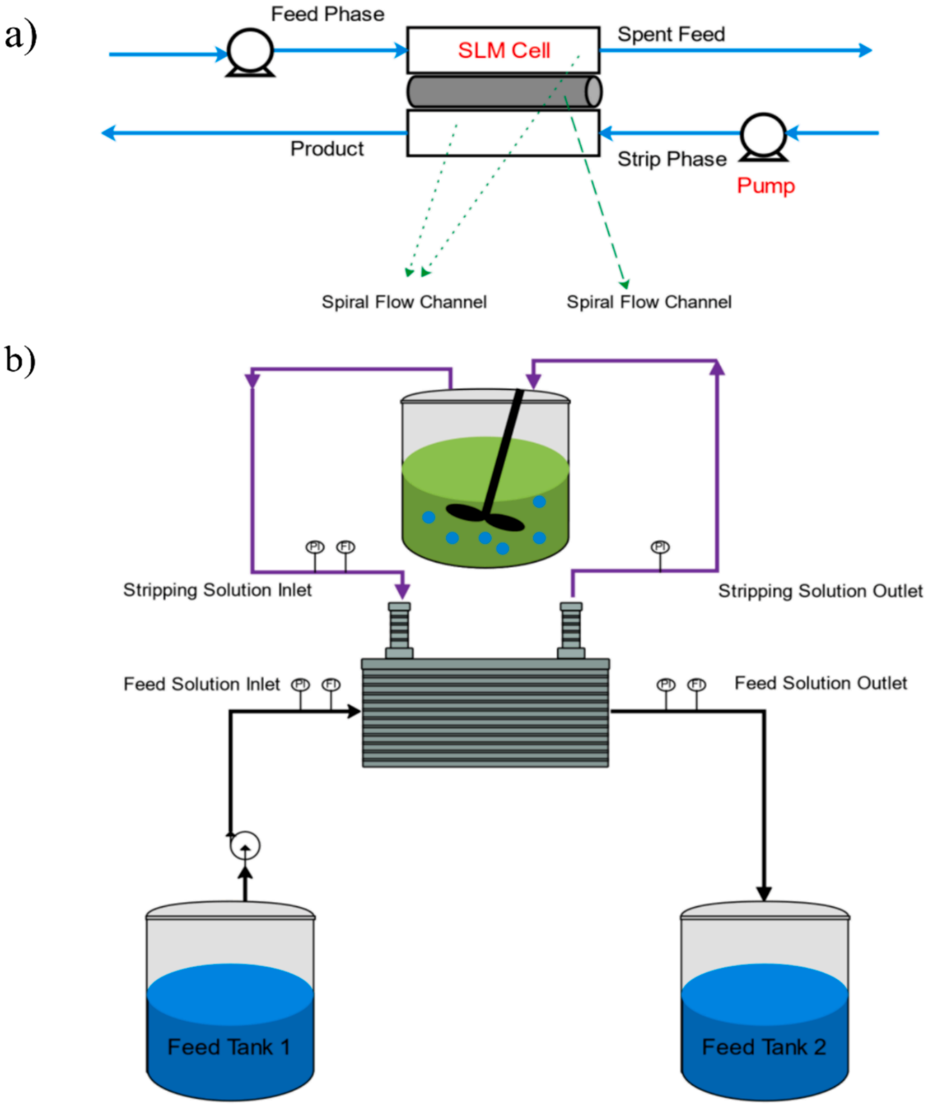


Fig. 5. Supported liquid membrane solvent extraction systems: (a) a simple schematic of the SLM system [94]; (b) the modified SLM system. Adapted from [98].

flux decreased by half its starting amount, compromising the performance of the system.

One way to improve the stability of these systems is to investigate newer system configurations (Fig. 5b). Almerajabi [97] discovered that emulsion pertraction technology (EPT) configuration can be more stable and avoid quick decay of performance with time. This is because the loss of the organic phase from the pores of the membrane solid support into the aqueous phase (the main cause of deterioration in the performance of these systems) would be less in this configuration. In another study, a hollow fiber SLM is shown to extract 82 % of lithium using 0.75 M D2EHPA and 0.75 M TBP in kerosene [95]. This study also used a low concentration of HCl solution (0.1 M) as a stripping agent, which shows another benefit of these systems.

SLM solvent extraction systems offer a multitude of advantages. It is possible to extract and strip chemical species continuously and simultaneously and to extract chemical species from dilute solutions via uphill transport against the concentration gradient. The SLM method has the potential for easy commercial scale-up in addition to its other benefits, which include low cost, high efficiency, minimal product contamination, reduced extractant consumption, and no phase separation issue [93].

2.1.5. Comparison of solvent extraction systems

Table 1 summarizes the key findings regarding solvent extraction systems, outlining the challenges and advantages associated with each system. Despite their wide use, traditional solvent extraction systems have the main issue of corrosion due to high concentrations of HCl stripping solution. Although this can be overcome by using newer systems and solvent types such as SLMs or ionic liquids, these methods still need to be developed for use at an industrial scale. The high production cost of these novel systems and solvents is their main hurdle in replacing traditional solvent extraction on a larger scale. Future research may focus on ways to identify alternative agents, such as replacing HCl which serves as the main striping agent in all methods with H2SO4 as employed in SLMs, or use of CO_2 as a stripping agent in a synergistic solvent extraction system [71], to make these systems more environmentally sustainable and stable. Finally, in the case of oilfield produced water, increasing the lithium concentration is necessary, divalent ions must be eliminated prior to solvent extraction, and organic contaminants can greatly reduce the extraction effectiveness.

2.2. Chemical precipitation

Chemical precipitation is a technique used to extract ionic

Table 1
Summary of major solvent extraction systems for lithium recovery.

System	Disadvantages	Advantages	Commonly Used Solvents	Common Stripping Agents
Traditional & synergistic solvent extraction	• Corrosion • Loss of solvents • Formation of third phase	• High recovery ratio	HBTA-TOPO; TBP-$FeCl_3$	HCl
Ionic liquid	• High price • Limited usage (*e.g.,* viscosity)	• Direct extraction of lithium	[C4mim] [NTf_2]) [C4mim] [PF6])	HCl
Crown Ether	• Expensive	• High selective reactivity with lithium	Cyanex 923	HCl
Supported liquid membrane (SLM)	• Performance deteriorates with time	• Low requirements of extractants • Simultaneous extraction and stripping	TBP, D2EHPA, TOPO	H_2SO_4 HCl

components from aqueous wastes by reducing their solubility by adding counter-ions [99], and it is extensively used for recovering lithium from brine [100–105]. The precipitation method is considered one of the first techniques that have been used in large-scale plants. A scheme of chemical precipitation for the removal of ions is shown in Fig. 6a [106]. There are several benefits associated with precipitation techniques, including their ease of use, low cost, and potential for industrialization. These techniques have been extensively explored over the past few decades for economically and scientifically effective lithium extraction from brines [100].

Yet, this method deals with some challenges. Co-precipitation of magnesium (Mg) is the fundamental problem in lithium precipitation. For instance, using a conventional precipitation process for many brines with a high ratio of Mg^{2+}/Li^{+} (*i.e.,* greater than 20) requires a high chemical reagent to precipitate lithium, resulting in high operational costs. Mg is regarded as the most disruptive element during the extraction of lithium from brine [43,102]. Hence, scientists have presented various solutions to this problem. New precipitation techniques, such as aluminate precipitation and Mg precipitation methods, have been applied to recover lithium from brines [49,100]. This section categorizes chemical precipitation into carbonate, aluminate, and Mg precipitation.

2.2.1. *Carbonate and carbonization precipitation*

Carbonate and carbonization are suitable for a low ratio of Mg^{2+}/Li^{+} (less than 10). The carbonate precipitation process involves using solar energy to evaporate and concentrate lithium-containing brine in an evaporation pond. Lithium is first precipitated as Li_2CO_3 by sodium carbonate (Na_2CO_3) after boron is removed by acid treatment, followed by the precipitation of Mg impurities by lime or calcium oxide [43]. For the synthesis of battery-grade lithium carbonate, boron is the most problematic contaminant; hence, as much of it as possible must be eliminated from the lithium-containing solution prior to lithium carbonate precipitation [107]. Although this method is relatively inexpensive as it takes advantage of solar evaporation, the process can take as long as 13 months. Carbonization precipitation via lithium bicarbonate ($LiHCO_3$) is another available process. $LiHCO_3$ is produced when Li_2CO_3 reacts with CO_2 and H_2O and has high solubility. This technique is effective but limited to carbonate-type salt lakes with low Mg^{2+}/Li^{+} mass ratios [100]. A combination of these two is used to recover lithium from brine. In a study by Xu et al. [108] on salt lake brine, iron, magnesium, and calcium were all extracted using different precipitants such as lime milk, NaOH, and oxalic acid. The final precipitation yielded a high purity (99.6 %) of homogeneous Li_2CO_3. The operating temperature was 80 °C. Also, previous studies [108,109] and a recent review article [43] indicated that achieving the appropriate temperature for the brine solution is vital for the precipitation process, but this is difficult to implement on a large scale as it requires a significant amount of energy for heating. Also, carbonate and carbonization precipitation methods are only suitable for low Mg^{2+}/Li^{+} ratio (*i.e.,* less than 10) feeds. For feedstocks with concentrations above 5,000 mg/L Mg^{2+}, there is an opportunity to recover it as a by-product such as magnesium oxalate and

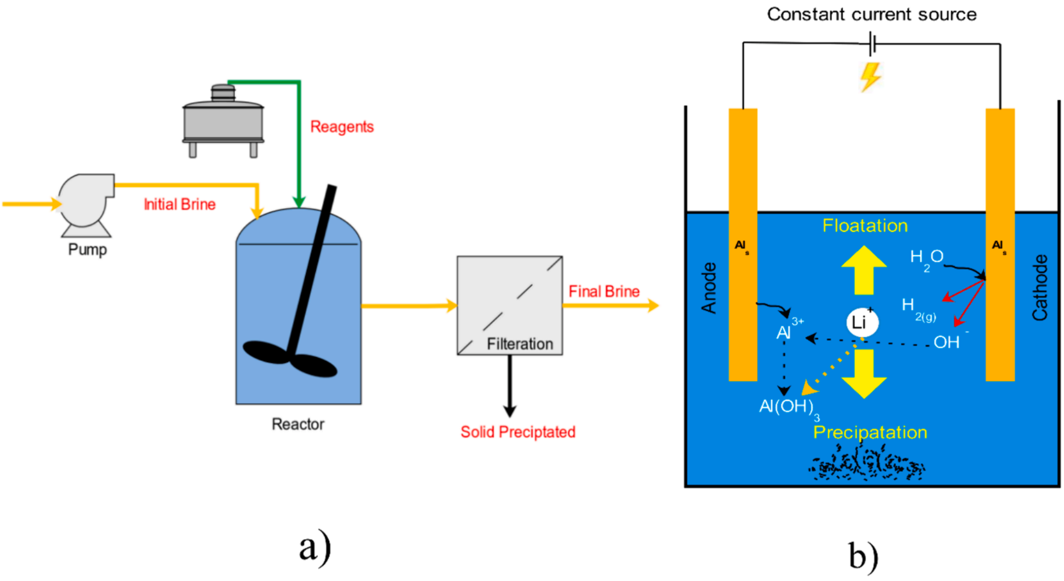


Fig. 6. Schematics of (a) Conventional chemical precipitation [106]; and (b) New generation electrocoagulation process with aluminum anodes for precipitating lithium.
Adapted from [113].

this will further boost process economics while reducing the amount of lithium lost in the process. Thus, numerous concepts have been developed recently to manage high-Mg brines, including aluminate precipitation [3].

2.2.2. *Aluminate precipitation*

One other type of precipitant that can be used for a high Mg^{2+}/Li^{+} ratio is aluminate precipitants. Lithium recovery from brines with a high Mg^{2+}/Li^{+} mass ratio is shown to be highly effective in a wide range of experimental studies employing aluminate precipitation methods [103,110,111]. In these cases, aluminum chloride ($AlCl_3$) and a strong base (NaOH or KOH) are added to lithium-containing solutions, in which they react with LiCl to form $LiCl{\cdot}2Al\ (OH)_3x{\cdot}H_2O$, as shown in Eq. (1). After a 3 to 6-hour reaction in a lab scale experiment, about 70–80 % of the lithium in the salt lake brines could be precipitated and recovered. During the process, various parameters such as Al^{3+} to Li^{+} ratio, pH, and temperature influence the performance of the lithium recovery [100]. Liu et al. [110] used aluminum-based material to recover lithium from a high Mg^{2+}/Li^{+} ratio solution. They recovered and precipitated nearly 78 % of the lithium at the optimum temperature of 90 °C.

$$LiCl + 2AlCl_3 + 6NaOH \longrightarrow LiCl \bullet 2Al\,(OH)_3 \bullet xH_2O + 6NaCl \tag{1}$$

In recent years, novel activated materials have been developed to increase the recovery rate and the efficiency of lithium extraction using aluminate precipitation from brine. For example, an Al-Ca alloy or an Al-NaCl mixture can recover up to 94 % of the lithium from a high Mg^{2+}/Li^{+} brine [43]. Furthermore, more than 90 % of the lithium can be recovered in an inexpensive and ecologically friendly way using engineered double hydroxides like lithium aluminum layered double hydroxide chloride [43]. Aluminate precipitation has been used for lithium recovery from oilfield brines [112]. Using $Al(OH)_3$ at 35 °C, with an Al^{3+}/Li^{+} molar ratio of 4.5, and an OH^{-}/Al^{3+} molar ratio of 2.6, 75.6 % of the lithium was extracted.

Another development in aluminate precipitation is the use of electrocoagulation technology with an aluminum anode to extract lithium from brines. In this method (Fig. 6b), hydroxide ions are produced at the cathode while metal ions are dissolved at the anode, resulting in the in-situ production of coagulants and lithium recovery. Electrocoagulation can be used on feeds with Li^{+} concentrations ranging from 200 to 1500 mg/L, which makes it ideal for operating with flexible feedstocks. This technology is also shown to be very cost-effective. A study conducted in China by Zhang et al. [113] showed that the entire operating cost per gram of lithium recovered was about $0.023/g lithium for the electrocoagulation precipitation process with an energy consumption of 0.064 kWh/g lithium, which is significantly less than the expense associated with an aluminate precipitation process which was about $0.108/g lithium with an energy consumption of 17.36 kWh/g lithium. Due to its ability to handle a wide range of feed concentrations, its cost-effective operation, and high recovery rates, the electrocoagulation process is anticipated to become the standard process for lithium recovery from unconventional sources at an industrial scale.

However, there are some challenges associated with aluminate precipitates the lithium loss is significant, and the precipitate must be processed to extract the metal. For example, reagents such as $AlCl_3{\cdot}6H_2O$, Na_2CO_3, and NaOH are added to salt lake brines to separate lithium from Mg in feedstocks with a high Mg^{2+}/Li^{+} mass ratio (*i.e.,* 19) for creating magnesium–aluminum-carbonate layered double hydroxide materials ($MgAlCO_3$-LDHs) [114]. This approach resulted in a lithium recovery of around 95 % and the precipitated $MgAlCO_3$-LDHs. The production of $MgAlCO_3$-LDHs is complex, and it is possible that some ions, such as Al^{3+}, will be introduced into the solution. Because of this, it would be advantageous to discover a new Mg precipitant that can effectively separate lithium from the mixture while still allowing for the reuse of the lithium and Mg resources that are recovered [115].

2.2.3. *Magnesium (Mg) precipitation*

The primary challenge with the aforementioned precipitation technologies is that they are only concerned with extracting lithium, leaving the Mg unused and discarded back to the environment. This results in significant pollution and the loss of a precious Mg^{2+} source that can serve as a viable by-product, for instance in the form of magnesium oxalate. The Mg precipitation technique has emerged as a means to improve lithium recovery while broadening the range of products obtained from unconventional feedstocks [43,114–116]. For example, under optimum reaction conditions, 98 % of the Mg^{2+} was precipitated using ammonium oxalate and Na_2CO_3 [43]. Unfortunately, this also led to lithium loss, and nearly 70 % of lithium was retained by the precipitated solid. Oxalic acid was also used to recover lithium from salar brine with an Mg^{2+}/Li^{+} ratio of 21 [117] using precipitation. The results show that pure magnesium oxalate (99.5 %) was attainable, but lithium was intercalated into the monoclinic structure of magnesium oxalate, leading to a loss of 10–30 % lithium [117]. In another study, magnesium oxalate with a purity level of 99.5 % was obtained by adding Na_2CO_3, after removing the calcium and magnesium oxalate from the brine. However, the lithium loss was still high in the precipitate, reaching 30 % [118].

To reduce the loss of lithium, researchers investigated newer types of magnesium participants with the capacity to selectively precipitate co-ions [109,114–116,118]. Sodium metasilicate nonahydrate was used as an Mg precipitant reagent. The precipitant effectively precipitated Mg^{2+} from the solution without affecting Li^{+} recovery; the precipitate entrained only trace amounts of Li^{+}, which co-precipitated with Mg^{2+}, leaving behind a substantial amount of Li^{+} in the solution. 86.73 % of the lithium was recovered in the solution, 99.94 % of the magnesium was precipitated, and the Mg^{2+}/Li^{+} mass ratio in the solution decreased from 30 to 0.022 in the solution [115]. Another new type of precipitant is $NH_4MgPO_4{\cdot}6H_2O$, an appealing technological development in Mg precipitation called struvite precipitation. In one study, a struvite precipitation technique was developed and implemented to separate Mg^{2+} and Li^{+} in a salt lake brine using tri ammonium phosphate trihydrate. Excellent Li^{+}/Mg^{2+} separation efficiency was observed in the precipitation tests conducted in the simulated brines. Under ideal circumstances, they could retrieve 99.71 % of the Mg^{2+} in the precipitates, with a minor lithium loss (2.70 %) when using diluted old brine. Also, it is shown that using natural sedimentation resulted in a Li^{+} recovery of around 90 % in the same study, while rapid and direct filtering resulted in a recovery of over 99 %. Direct filtering was found to prevent lithium adsorption onto the precipitates [116].

2.2.4. *Comparison of precipitation techniques*

An overall comparison of different methods in chemical precipitation is summarized in Table 2. Although theoretically possible, direct lithium extraction from geothermal brines via precipitation may not be feasible. Chemical reagent prices and potential waste disposal issues are affected by the non-selective nature of these reactions and many competing co-precipitates (such as calcium carbonates and iron hydroxides). Furthermore, the lithium extracted via precipitation must undergo many post-extraction purification and processing to be suitable for use in batteries or other applications [85]. One possible prediction for the future of this technology is to benefit from using CO_2 in the production of Li_2CO_3 to make the process more environmentally friendly. This was demonstrated in a few studies where chemical precipitation and solvent extraction can be combined to achieve this goal [104,108,119,120]. Generally, when the Mg^{2+}/Li^{+} ratio exceeds 10, substantial amounts of precipitants are required to selectively remove the Mg^{2+}, which will increase the cost and generate significant amounts of solid waste. Given that the Mg^{2+}/Li^{+} ratio in oilfield brine is usually above 20 and the high salinity in this brine decreases the precipitator's ability to recover Li^{+} selectively, lithium recovery from oilfield brine using precipitation could be costly [121].

Table 2
Summary of major precipitation methods for lithium recovery.

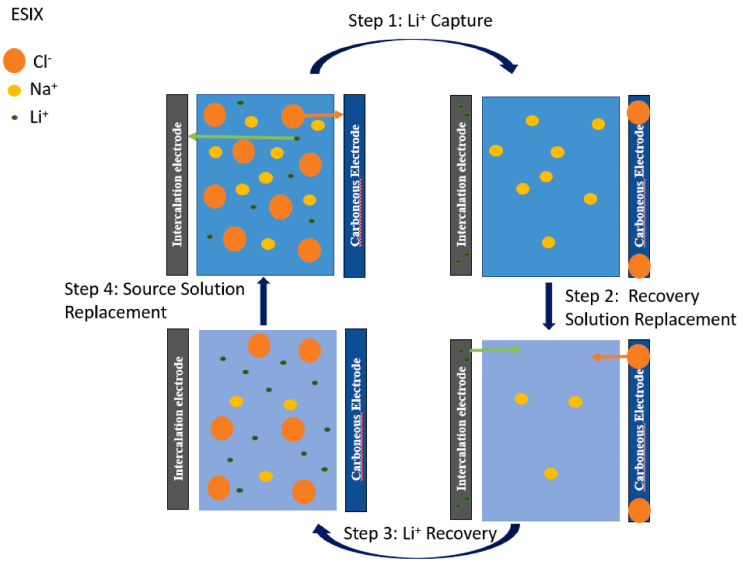
Type of precipitants	Applicability	Reagents	Disadvantages	Advantages
Carbonate and carbonization	Low Mg^{2+}/Li^{+} ratio (less than 10)	Lime, NaOH, Na_2CO_3	• Time-consuming • High energy consumption	• Facile industrialization • Low cost
Aluminate	For both low and high Mg^{2+}/Li^{+} ratio	$AlCl_3$, Al-Ca Alloy, NaOH	• High alkali consumption • Environmental hazards • High energy consumption for EC	• High purity Li_2CO_3
Magnesium	High Mg^{2+}/Li^{+} ratio (greater than 20)	Oxalic acid, Na_2CO_3	• Lithium loss	• High removal rate of Mg^{2+}

2.3. Electrochemical methods

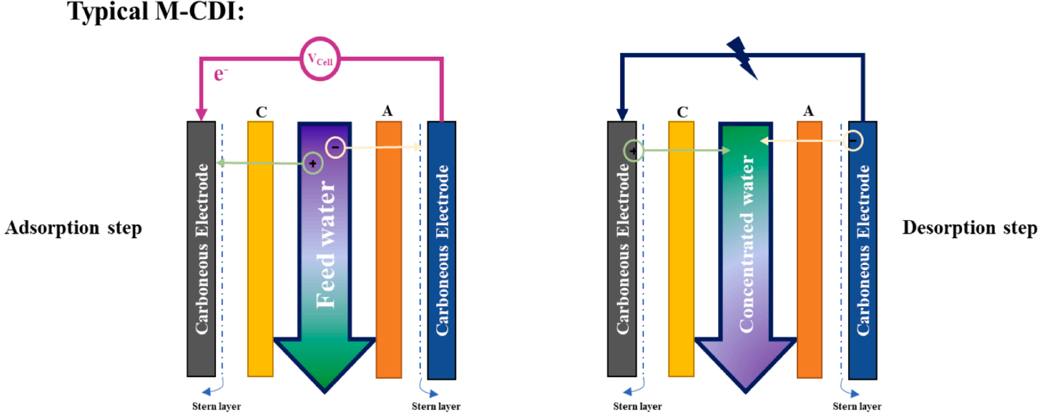
Capacitive deionization (CDI) and electrochemical ion pumping/exchange systems (EIXS) are representatives of electrochemical processes for lithium recovery. As shown in Fig. 7, a bevy of research on these two processes, which includes electrode design, membrane incorporation, and optimization of process parameters, has been done in recent years [122–127] across various feedstocks ranging from brine [128] to seawater [129]. This section provides insights into possible energy compensation pathways for the electrochemical system toward lithium recovery by integrating with other processes. Fig. 7 shows the schematic of these systems.

2.3.1. Capacitive deionization (CDI)

2.3.1.1. Current state-of-the-art CDI system toward selective lithium recovery. CDI is a promising electrochemical process that can be utilized to recover lithium from low-salinity synthetic brines [130]. An external power source will trigger the electron flow towards the cathode and attract the Li^{+} in the bulk solution by electrostatic attraction effect. It is followed by reversing the current or making it into short-circuit to release the Li^{+} back to the recovery solution. The performance of a CDI system tailored for lithium recovery is a function of feed salinity. Studies have shown that the normalized energy requirements for brine treatment were at 0.0017 kWh/m^3, while for seawater, they were 0.077 kWh/mol due to the higher salinity complexity of real-world seawater compared to the synthetic lab samples [131–133]. Additionally, higher



a) ESIX



b) CDI

Fig. 7. Schematic of electrochemical technologies: (a) EISX (b) CDI.

salinities tend towards lower lithium recovery efficiencies (*e.g.,* 70 % for simulated geothermal brine [126] and 45 % for simulated brine [134], which has been attributed to limited electrode adsorption sites. Furthermore, studies have shown that Li^+ recovery from CDI-based system can shorten the time of transformation of Li^+ to a usable source down to days [135,136].

To enhance the selective performance of lithium, electro-sorption efficiency, and recovery rate, hybrid capacitive deionization (H-CDI) and membrane capacitive deionization (M-CDI) are more analyzed because of their specific selectivity towards Li^+ over other divalent ions. Specifically, H-CDI is based on replacing cathode electrode materials from carbonaceous materials to intercalation-based ones (*e.g.,* λ-MnO_2, $Li_3V_2(PO_4)_3$ and $LiFePO_4$) to enhance Li^+ selectivity [137–139]. Fundamentally, the selectivity based on the intercalation electrode is contributed by the faradaic reaction to adsorb and desorb lithium towards/from the node of the structure of faradaic materials [136]. Other than typical pristine MnO_2-based faradaic electrodes, some elemental doped MnO_2 (*e.g.,* Ni and Co-doped) show stronger conductivity and efficiency towards lithium recovery. The mechanism underlying the enhanced performance of doped MnO_2 electrodes involves the facilitation of electron transfer processes and the modification of the electrode surface properties, which improve the interaction between lithium ions and the electrode. Ni and Co doping can introduce structural defects and increase the surface area of MnO_2, leading to more effective ion exchange and higher lithium recovery efficiencies [140,141]. These doped electrodes also exhibit improved stability and cycling performance, which are critical for the long-term operation of CDI systems. The spinel structure of λ-MnO_2 can stay stable even when the pH and temperature fluctuate. The intercalated electrode shows significant selectivity for lithium over monovalent and divalent ions, however, Na^+ and K^+ still have inferring effects when the concentration in the brine goes higher compared to the amount of lithium in the brine [136]. Currently, H-CDI shows higher selectivity in the recovery solution of Li^+/Mg^{2+} (2.14–181) [126,142,143] with a range of energy consumption (0.047–0.583 kWh/mol Li^+) [126,144]. Compared to conventional CDI since the activated carbon lack selectivity towards Li^+ along with the limited data of energy consumption reported [143,145,146]. To further promote the specific recovery of Li^+, M-CDI was adopted by incorporating a cation exchange membrane and an anion exchange membrane with conventional CDI. Initially, applying an ion exchange membrane aimed to increase the separation efficiency between cations and anions and facilitate the ion transport toward electrodes, which can lower energy consumption [136,147,148]. Recently, the combination of hybrid CDI with CEM/AEM was tested out to enhance the lithium recovery efficiency. The results show that the selectivity of Li^+ over divalent ions was enhanced with lower energy consumptions (2.95–57.7 for selectivity and 0.0018–0.077 kWh/mol of lithium ions) [134,136] compared to the hybrid CDI system [126,149].

2.3.1.2. Challenges of the CDI system toward a pilot-scale electrochemical system. Even though the CDI system is showing an initial promising recovery of Li^+ from low salinity brine with lower energy consumption than electrodialysis (0.254–2.25 kWh/mol Li^+) based on different Li^+ contents in the feeding solution [143,150].The application of CDI is limited by the scalability. The problems impeding the scalability of CDI are limited adsorption capacity and compromised ion permeability and selectivity (Table 3). These limitations are faradaic processes (also known as parasitic electrochemical charge transfer), leakage currents, and ohmic losses, which are the primary reasons that energy efficiency decreases (maybe by 20–30 %) after months of operation [151,152]. Another constraint towards adsorption capacity limitation is the complexity and concentration ratio of the feed source. High complexity composition and high initial interfering ions (*e.g.,* Na^+, K^+, and Mg^{2+}) can significantly compete for the adsorption sites with Li^+ in the feed solution [153]. For example, higher Mg^{2+}/Li^+ ratio (>20) composition will compromise the Li^+ recovery efficiency due to the compromised Li^+ transport. Moreover, the fouling issues mainly resulted from the organic/inorganic foulants (*e.g.,* barium sulfate and natural organic matter) existing in most feed sources. Fouling lowers the flux of ions and necessitates the operation of higher voltages [154]. Fouling may also negate the benefits of membrane modification strategies as it will cover unique chemistries and surface features that were intended to improve membrane performance [155].

Table 3
Summary of electrochemical methods and their challenges.

System	Electrode Modification Strategy	Advantages	Disadvantages	Applicable sources
CDI	Carbonaceous materials/ capacitor electrode as cathode	• High specific Li^+ adsorption, • Low energy consumption	• Low selectivity Li^+ • Low recovery performance with high ratio Mg^{2+}/Li^+ • Water • Electrode parasitic effects	Geothermal brine
	Faradaic electrode as cathode (H-CDI)	• High selectivity towards Li^+ • Energy efficient • Redox capacity	• Low recovery • Sensitive adsorption capacity to the current density fluctuation	Geothermal brine
EIXS	Faradaic electrode/ capacitor electrode as anode	• High selectivity Li^+ • Low energy consumption	• Frequent flushing and replacement of electrode • Current density fluctuation electrode material loss	Salt lake/ Geothermal brine
M-CDI	The selection of electrode in M-CDI is similar to the CDI and EIXS system, Membrane selection: Donnan exclusion effect and size sieving materials	• High cation/ anion separation • High selectivity towards Li^+ • Lower energy consumption than CDI	• Fouling • Materials corrosion/loss	Salt lake/ Geothermal brine

Another challenge for the CDI is that the size of hydrated Li^+ (diameter: 3.82 Å) is larger than undesired ions, such as the hydrated Na^+ (diameter: 3.58 Å) and K^+ (diameter: 3.31 Å) [156]. The larger size impedes lithium adsorption due to reduced diffusion and sorption into the membrane electrode [157]. Moreover, higher valence ions (*e.g.,* Mg^{2+} and Ca^{2+}) have a stronger affinity towards the electrode and will tend to be selected over monovalent ions [158]. Such challenges have impeded the widespread implementation of CDI on the industrial scale. To address these challenges, faradaic electrodes (*e.g.,* λ-MnO_2) and membrane incorporation and modification (*e.g.,* ZIF-8 and MXene) [158] have been studied to enhance selectivity towards lithium. These are based on the charge difference between divalent and monovalent ions. For example, ZIF-8 was used to provide sub-nanometer channel to facilitate lithium-ion diffusion and the sulfonate ($-SO_3^-$) group of MXene have a stronger affinity towards lithium over other cations.

2.3.2. Electrochemical ion exchange system (EIXS)

2.3.2.1. Current state-of-the-art EIXS towards selective lithium recovery.

Like other electrochemical lithium recovery methods, EIXS does not produce lithium in a directly usable form. The mechanism of EIXS is very similar to the CDI, which is dependent on an external power source triggering the electron flow towards the cathode and then attracting Li^+ in the bulk solution. The most significant difference between EIXS and CDI is that the EIXS was fed with a stagnant water source in a container and manually moved the set-up from the adsorption container to the recovery container. One of the benefits that EIXS compared to chemical precipitation is EIXS can keep Li^+ in the recovery solution until a high enough concentration (5000 mg/l) [122] is reached, there is no need to use time-consuming solar drying steps to extract Li^+ such as traditional lime soda evaporation process [159]. Studies have shown that the adoption of EIXS reduces the time to produce a usable product from years of sunlight to hours [131].

Current studies focus on the advancement and modification of anode materials to facilitate this recovery process. This is because the cathode of EIXS is mostly used as a faradaic electrode, especially λ-MnO_2 based, to selectively adsorb Li^+ from the brines. The spinel structure of λ-MnO_2 can provide stable chemical resilience and the cavity at the node of the structure is specifically designed for Li^+ extraction [160–162]. Recently, the most attractive strategy of EIXS to improve the selectivity without incorporating membrane into the system is using Li^+ exclusive electrodes (*e.g.,* nickel hexacyanoferrate (NiHCF)) [122]. This type of derivative of Prussian blue material, a class of cyanide-based coordination polymers with a distinct cubic shape and open framework structures [141], shows adsorption of interfering ions (*e.g.,* Na^+, K^+ and Mg^{2+}) during Li^+ recovery steps, which can efficiently enhance the purity of lithium products in the recovery solutions. This is because this lithium-exclusive electrode is used as an anode and has a specific affinity to attract interfering ions in the solution. This way, when electron flow is reversed from the cathode to the anode, the interfering ions adsorbed by the cathode can be additionally attracted from the recovery solution to the anode and further enhance the selectivity of lithium over other ions in the recovery steps. The selectivity of EIXS fed with synthetic solutions shows 1.63–36.6 [131] among monovalent ions and 1.13–315 [131,163,164] among divalent ions while energy consumption was reported to be within 0.001–0.017 kWh/mol of Li^+ [130,131,164]. It's noteworthy to point that one of studies are expressing that operation energy cost (*e.g.*, pumping energy: 0.2–1.7 kWh/mol) can be considered negligible while the energy consumption from galvanostatic tests were reported within the range of (0.002–0.01 kWh/mol) based on different initial lithium concentration in the feeding solution [165]. This information is critical to bring the operation energy cost into consideration, which was rarely reported in most electrochemical based studies. Except for the electrode-wise, advanced membranes like sulfonated HKUST-1 and carboxylated polyethylene terephthalate (PET) have shown promise for lithium recovery in electrochemical ion exchange systems. Sulfonated HKUST-1 membranes utilize the affinity of sulfonate groups for lithium ions to enhance selectivity and transport, while the efficiency of the carboxylated PET membranes is influenced by surface charge density and pH levels [166]. Additionally, rGO-SDDS (sulfonated 4,4′-diaminodiphenyl sulfone)-rGO membranes, integrating sulfonated compounds between graphene sheets, exhibit specific selectivity for lithium against multivalent cations. These membranes leverage unique mechanisms such as surface charge effects and functional group interactions to optimize lithium recovery from complex brine solutions [167].

2.3.2.2. Challenges of EIXS towards a pilot-scale electrochemical system. In EIXS, multiple recovery steps are repeated within a single lithium capture/release cycle to increase the amount of recovered lithium [163]. Power consumption usually refers only to the first cycle, so lower operation power consumption occurs on almost every cycle [168]. Also, the volume of the recovery solution is generally kept low to increase the concentration of recovered lithium. If multiple cycles are required for extraction to μL volumes (approximately 5 enrichment cycles), more than 1000 cycles would be needed to reach half of the expected concentration of Li^+ (~5000 mg/L) at factory scale considered as sufficient Li^+ source [169,170]. Similar to the release process, the pump energies associated with multiple steps in the cycle must be fully understood before large-scale implementation. Since the source and recovery solutions in the EIXS system are stored in two separate tanks or the same tank, flushing maintenance between the two solutions is required. Also, the high salinity of the feed solution would compromise the electrode stability because of parasitic effects and fouling generation at the surface of the electrode. The typical cycles that electrodes can last in the research would be around 8–100 cycles [131,171–173]. It is worth pointing out that the cycle values here are all dependent on the times the researchers conducted, which do not represent the actual cycle life since some researchers did not conduct many cycles. In addition, EIXS has high requirements for applied current stability. Otherwise, the system will behave erratically and affect its efficiency.

2.3.3. Comparison of electrochemical techniques

The electrochemical processes (CDI-based and EIXS) are compared with their advantages and disadvantages, as shown in Table 3, to evaluate each electrochemical technology. Based on the literature review results, the feeding salts and recovery products considered are mostly LiCl. The anions such as CO_3^{2-} and OH^- were not well studied and tested with the above electrodes and membrane modification papers. Furthermore, since the geothermal and salt lake brines have relatively high lithium concentrations compared to seawater, these are more suitable for electrochemical recovery techniques. To enhance the efficiency of lithium recovery and generate final lithium products for LiB usage, post-treatment (*e.g.*, chemical precipitation and bipolar membrane electrodialysis) of effluent from electrochemical techniques should be conducted.

2.4. Electro/pressure-driven membrane processes

2.4.1. Performance parameters of electro-membrane processes

The performance of typical electro-membrane processes including electrodialysis (ED), selective electrodialysis (SED), and bipolar membrane electrodialysis (BMED), are evaluated by using key parameters such as lithium recovery (R_{Li}), lithium-ion flux (J_{Li}), separation coefficient of lithium ($F_{M\text{-}Li}$) and specific power consumption (SPC) [173–176],

$$J_{Li} = \frac{V_C\left(C_{Li,c} - C_{Li}^0\right)}{A \cdot t} \tag{1}$$

$$R_{Li}(\%) = \frac{100 \cdot \left(C_{Li,c}^f - C_{Li,c}^0\right)}{V_0 \cdot C_{Li}^0} \tag{2}$$

$$F_{M-Li} = \frac{\left(C_{M,c}^f - C_M^0\right)}{\left(C_{Li,c}^f - C_{Li}^0\right)} \tag{3}$$

$$SPC = \frac{E\int_0^t Idt}{V} \tag{4}$$

$$\eta_{Li} = \frac{(n_{t,c} - n_{0,c}) \cdot Z \cdot F}{N\int_0^t I\,dt} \cdot 100 \tag{5}$$

where:

V_C is volume of concentrate (m^3)
$C_{Li,c}$ is concentration of lithium in concentrate (mol/m^3)
C_{Li}^0 is concentration of lithium in dilute (mol/m^3)
A is membrane area (m^2)
t is experimenting time (h)
V_0 is initial volume in dilute (m^3)

$C_{Li,c}^{f}$ and $C_{Li,c}^{0}$ are final and initial lithium concentrations in the concentrate, respectively (mol/m^3)

$C_{M,c}^{f}$ is concentration of other competitive cations in dilute at the end of experiment (mol/m^3)

$C_{Li,c}^{f}$ is final concentration of lithium in concentrate concentration (mol/m^3)

$n_{t,c}$ and $n_{0,c}$ is lithium mole in concentrate at the end of experiment and at the beginning, respectively.

E is electrical potential (V)

I is current (A)

V is volume of feed solution

N is number of cell and F is Faraday constant (96,485 C/mol)

2.4.2. *Electrodialysis*

Electrodialysis (ED) is an electro-membrane process using alternating cation and anion exchange membranes to remove ions from solution using an applied electrical potential [174]. In this process, cations pass through cation exchange membranes (CEMs) and are rejected by anion exchange membranes (AEM) while anions pass through anion exchange membranes and are rejected by cation exchange membranes, simultaneously [175]. This selective transport of ions is made possible by the charged functional groups in the membranes. The ions are recombined downstream to create a concentrate while the now deionized feed is referred to as the dilute [176]. Recently, given the emergence of monovalent selective ion exchange membranes, monovalent cation and anion exchange membranes have been used for the selective separation of lithium from aqueous solutions in ED to separate lithium from magnesium efficiently due to the abundance of resources having a high Mg^{2+}/Li^+ ratio, and this process is named selective electrodialysis (SED). Fig. 8 shows the configuration and mechanism of this technology.

SED has been used to separate Li^+ from aqueous solutions (especially in case of high Mg^{2+}/Li^+ ratio) due to its high selectivity against other divalent ions. Several studies [150,177–179] have been conducted using commercial monovalent permselective CEMs to separate lithium from brines containing other cations and/or anions such as Mg^{2+}, Ca^{2+}, K^+, Na^+ SO_4^-, Cl^-, and HCO_3^-. This is reversed to the order of hydrated radius of size. Mukherjee and Sengupta also showed that hydrated ionic radius determines the selectivity of different ions [177]. However, the effect of anions on the recovery of lithium was not investigated in this study.

Chen et al. [177] studied the application of SED for the recovery of lithium from synthetic brine solution containing a mixture of monovalent and divalent cations namely Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. The experimental setup consisted of eleven commercial CEMs (Astom Corporation, CIMS) and ten AEMs (Astom Corporation, ACS). The researchers observed that the presence of certain cations in the synthetic brine solution negatively affected the recovery of lithium via SED. This study shows that K^+ had the greatest negative effect on lithium recovery, followed by Na^+, Ca^{2+}, and Mg^{2+} respectively due to the difference between the hydrated radius of ions. However, the effect of anions on the recovery of lithium was not investigated in this study.

In a study by Ji et al. [178], the effect of both cations (Mg^{2+}, K^+, and Na^+) and anions (SO_4^{2-} and HCO_3^-) on the recovery of lithium using artificial brine of chloride type using SED containing the same commercial ion exchange membranes was examined. The study produced similar results to the Chen et al. [177] study, with the increase of the ratio of K^+ and Na^+ in the feed leading to a decrease in the recovery of lithium. The strength of the effect of K^+ was greater than that of Na^+ in this study as previously revealed. Interestingly, the lithium recovery and Li^+/Mg^{2+} ratio increased slightly in the presence of HCO_3^- because hydrolysis of HCO_3^- is greater than ionization of HCO_3^-. Therefore, the pH of the solution increases in dilute compartment and the formation of $MgHCO_3^+$ occurs. This contributes to the separation of Li^+ and Mg^{2+} ions as it leads to a reduction in the free Mg^{2+} concentration and limited mobility of $MgHCO_3^+$ ions, which have significant steric hindrance. Although researchers get promising results with SED equipped with commercial membranes for lithium extraction from aqueous solutions using synthetic salt solutions, it is important to note that these results may not directly translate to real brine solutions. Therefore, further research was needed to investigate the feasibility of SED using real brine [150,179].

Nie et al. [179] used SED consisting of commercial Selemion ASA and Selemion CSO monovalent ion exchange membranes to separate lithium from potassium-recovered old brine from East-Taijiner Salt Lake. They diluted the brine with water 1.4 times to prevent magnesium saturation before SED. A constant voltage of 20 V was applied, and 90.5 % lithium was recovered within 3.5 h. Although this result was remarkable, it was obtained with the help of pretreatment before SED. In another study, the feasibility of recovery of lithium from different natural brine sources via SED was studied using East Taijinar, Yiliping, and West Taijinar Salt Lake brines. East Taijiniar was found most feasible to extract lithium. At the optimum voltage (10 V), 76.45 % lithium was recovered with 0.66 kWh/ (mol lithium) energy consumption with commercial Astom CIMS and Astom ACS ion exchange membranes [150].

The performance of the SED process is not only affected by the properties of the feed solution but also affected by operating conditions such as temperature, applied electrical potential, and flow rate. Therefore, further research is essential to optimize operating conditions to maximize the recovery of lithium and minimize energy consumption [179–183]. One study demonstrated that an increase in applied voltage and linear velocity enhances the lithium recovery as expected since an

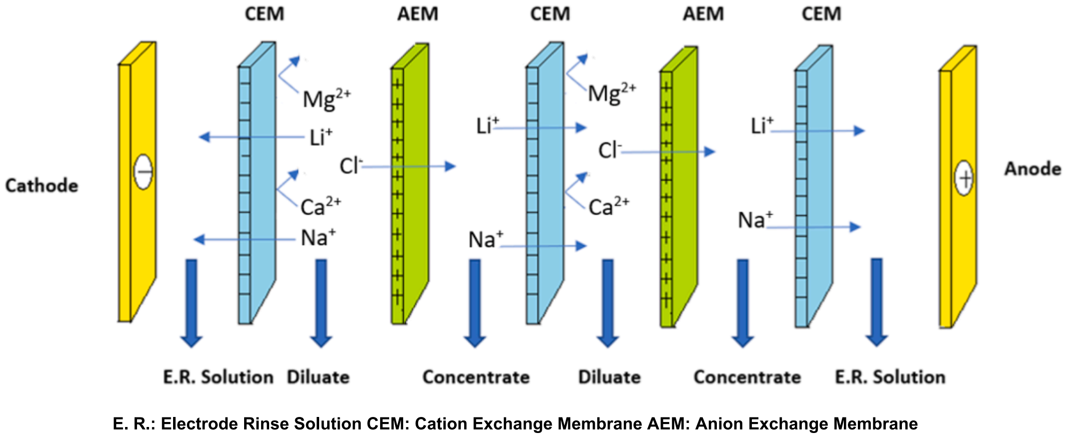


Fig. 8. Selective electrodialysis for recovery of lithium.
Adapted from [177].

increment in linear velocity helps to prevent partial adsorption on the membrane surface and an increment in applied potential helps to accelerate ion movement through the membrane in electro-membrane systems [175,180]. Moreover, it was revealed that the recovery of lithium via SED is more favorable under acidic feed solution. It was discovered that lithium recovery increases when the pH of the sample solution is between 1.8 and 4.7. However, this correlation ends when the pH was increased to between 5.9 and 7.8. This shows that only moderate concentrations of H^+ ions can enhance current density and mass driving force. However, when the number of H^+ ions exceed a certain limit, there might be competition between H^+ and Li^+ ions. This competition between H^+ and Li^+ ions could lead to a decrease in the lithium recovery [180].

Nie et al. and Zhao et al. [181,184] conducted studies to investigate the effect of temperature on the recovery of lithium using a simulated Salt Lake brine solution. Nie et al. [184] observed that the recovery of lithium decreased from 95.6 % to 73.5 % during 3 h of operation time with the increase of temperature from 15 °C to 30 °C. The researchers claimed that the drop in lithium recovery, caused by an increase in the conductivity of the feed solution, resulted in a decrease in the potential gradient, which is the driving force for electromigration. Although mass transfer by diffusion becomes favorable with a decrease in the viscosity of the feed solution with temperature increment, lithium recovery dropped due to the more prominent effect of electromigration compared to diffusion. On the other hand, a study done by Zhao et al. [181] showed that the lithium recovery increases with temperature in all different binary cation systems (Na^+/Li^+, K^+/Li^+, Mg^{2+}/Li^+, Ca^{2+}/Li^+). For instance, lithium recovery increased almost twice with the increase in temperature using feed solution including binary Na^+, Li^+ and Cl^- ions. This is attributed to the increase in permeability of ion exchange membrane and Brownian movement at high temperature. Moreover, it was concluded that change of membrane pore size and hydration radius of ion determines result of competition between Na^+ and Li^+. In the same study, it was found that the lithium recovery increased from 37.00 % to 59.63 % in Mg^{2+}/Li^+ binary feed solution. However, they also found that temperature increment did not affect the separation of lithium from sodium, potassium, magnesium, and calcium. The increment in the lithium recovery was observed due to the swelling of high polymer chains and decreasing water molecule numbers controlled by hydrated ions in the feed solution. This controversy between the two studies may also stem from the difference between the behavior of ion exchange membranes used in these studies. Zhao et al. [181] used Astom CIMS and CSO membranes while Nie et al. [184] used Asashi Selemion CSO and Selemion ASA. Further studies using different kinds of ion exchange membranes are needed to fully understand the effect of temperature on the recovery of lithium.

In addition to the commercial ion exchange membranes for the recovery of lithium from aqueous solutions, homemade ion exchange membranes were also designed and synthesized to achieve higher lithium recoveries and purities reducing the transport rate of other cations and anions in the feed solution [182,183,185]. One approach to increase the selectivity of lithium in the membrane is to incorporate nanomaterials. MOF(ZIF-8)/polypropylene homemade CEMs were synthesized to enhance the selectivity of lithium from aqueous solutions by tuning pore size and pore chemistry at the sub-atomic scale, which can enhance the effect of size exclusion. Moreover, this MOF film was fabricated on a flexible polypropylene membrane support, unlike other membranes in the literature, to avoid limiting its use solely to lab-scale applications. The synthesized film demonstrated a selectivity ratio of Li^+/Mg^{2+} is 3.87 [182]. However, lithium separation from monovalent ions remains a challenge since the transport mechanism mainly relies on partial dehydration-hydration process due to the tradeoff between low dehydration energy of K^+ and fast ion transport of dehydrated Li^+. Sharma et al. [185] designed lithium selective CEMs using sulfonated poly (ether ether ketone) and lithium selective nanomaterial (magnesium doped lithium manganese nanostructure) to overcome the challenge of separation of lithium from other ions. This nanomaterial was chosen due to its high lithium adsorption capacity. The ion exchange capacity for lithium increased with incorporation of nanomaterial compared to Mg^{2+}, K^+ and Na^+ ions due to the higher lithium exchange by nanomaterial, presence of large number of ion exchange sites for Li^+ and larger hydration radii of Li^+ than other cations. In ED, 64 % of lithium was recovered with $4.82Li^+/Mg^{2+}$ separation under 4 V applied potential from a synthetic salt solution containing 2000 mg/L feed solution (1280 mg/L Li^+). Hence, employing lithium selective nanomaterials particularly may give promising results increasing separation of lithium from other monovalent and divalent cations. Besides nanomaterial incorporation into CEMs, the use of zwitterion membranes configured with both anionic (SO_3^-, COO^-) and cationic groups ($^+NR_4$) instead of CEMs was also considered to improve lithium recovery. It was hoped that the cationic group improves permselectivity and anionic group may increase flux. However, membranes incorporated with SO_3^- show difficulties in separating lithium from even divalent due to the strong electrostatic interaction. Hence, COO^- group is preferred to use rather than SO_3^- due to its chelating and crosslinking capability with various functionalities such as –OH and NH_2 unlike other studies in the literature. Zwitterion membranes were synthesized using amino isophthalic acid (AIPA) and the fixed quaternized groups. The study revealed a notable Li^+/Mg^{2+} selectivity of 8. Furthermore, lithium flux increased from 1.66×10^{-10} mol/cm^{2}s to 33.46×10^{-10} mol/cm^{2}s corresponding to an increase of AIPA from 10 % to 20 % under 2.12 mA/cm^2 current density [186]. Recently, the modification of commercial monovalent CEMs to selectively separate lithium ions from other ions has been explored. The modification of monovalent CEMs via crown ethers (CEs) was investigated due to the nanoscale cavity structure of CEs, which gives them the capability of binding specific metal ions and forming stable complexes through electrostatic interactions, providing channels for targeted ions. Yin et al. [187] modified the CR671 membrane (a monovalent CEM from Veolia Water Technologies & Solutions) with 2-OH-15-crown-5 ether (15CE) to enhance the separation of lithium from both magnesium and sodium in brine. The modification includes a two-layer coating process, beginning with an initial layer of polydopamine (PDA) to enable the subsequent application of a second layer, increasing the hydrophilicity of the CR671 membrane. The second layer consisted of polyethyleneimine (PEI) and 2-OH-15-crown-5 ether (15CE), which created channels for selective lithium transport through crosslinking with 1,3,5-benzenetricarbonyl trichloride. The modified membranes showed 90 % and 80 % lithium recovery in Na^+/Li^+ solutions and Mg^{2+}/Li^+ solutions, respectively. The current efficiency of SED was determined to be 22.7–38.7 % for Na^+/Li^+ solutions and 17.0–39.4 % for Mg^{2+}/Li^+ solutions, depending on current densities.

Due to the difficulties to separate lithium from brine solutions containing high amounts of magnesium (such as $Mg^{2+}/Li^+ \geq 50$), another approach to enhance lithium recovery is to use liquid membrane electrodialysis, a combination of liquid membrane extraction and electrodialysis [183,188]. Liu et al. [183] designed a liquid membrane composed of an ionic liquid system as the Li^+ carrier and 2 solid cation-exchange membranes to sandwich the carrier. In the process of electrodialysis, cations from the feed solution in the anode chamber move toward the cathode. However, anions in the cathode chamber cannot move to the cathode due to the blocking of cation exchange membrane. Ideally, only Li^+ ions can be recognized among all cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) and migrated in the liquid membrane. Subsequently, Li^+ undergoes electromigration within the liquid membrane, and electrochemical stripping occurs at the interface between the receiving solution and CEM. The Mg^{2+}/Li^+ ratio decreased from 50:1 to 0.5:1 at 4.375 A/m^2 current density for 12 h. Zhao et al. [188] prepared the sandwiched liquid membrane consisting of two cation exchange membranes and a Li^+ loaded organic liquid film. TBP+ClO_4^- was the preferred organic liquid among the four other liquids due to its moderate working environment and sufficient performance. According to the results, the Mg^{2+}/Li^+ ratio was reduced from 100 to 2 in the brine at 3 V and 20 °C. Since the results are promising, this approach can also be used to separate lithium from brine containing high amounts of magnesium due to its ability to be highly adaptable and have low specific power consumption (SPC).

In another study, the idea of using fast ionic conductors instead of monovalent selective CEMs to their capability to obtain perfect lithium against other monovalent and divalent ions such as K^+, Mg^{2+}, and Na^+ was presented. Morita et al. [189] used $Li_{0.29}La_{0.57}TiO_3$ (LLT) as a separation membrane in electrodialysis. However, only 40 mg of lithium was extracted with 0.0043 mg/h average extraction speed after 72 h when they used brine water containing 166 mg of lithium. This is an important role because H^+ may adsorb on the LLT surface in acidic and neutral solutions to prevent Li^+ permeability. Therefore, this technique is more suitable to extract lithium from used lithium-ion batteries or mixed alkaline solutions rather than brine.

2.4.3. Bipolar membrane electrodialysis

The bipolar membrane electrodialysis (BMED) process is a combination of conventional ED and bipolar membranes [174]. Bipolar membranes consist of two layers namely cation and anion exchange layer separated by hydrophilic interface in which water dissociates H^+ and OH^- ions. The benefits of technology are to desalinate feed solution, extract lithium as LiOH, and produce acid simultaneously without using extra reagents. Fig. 9 shows the process and mechanism of the BMED. Several studies have been conducted to recover lithium as lithium hydroxide from aqueous solutions [190–196].

Bunani et al. [175] and Ipekci et al. [191] studied the feasibility of BMED including commercial ion exchange membranes to extract lithium as lithium hydroxide and boron as boric acid from pretreated synthetic geothermal water prepared by using lithium tetraborate pentahydrate ($Li_2B_4O_7{\cdot}5H_2O$). However, it was revealed that a notable disparity exists between the quantity of separated lithium from feed solution and the amount of lithium and boron recovered as LiOH and H_3BO_3, respectively. This difference is attributed to the partial adsorption on the membrane surface. The separation efficiencies of both lithium and boron were found to be over 90 % [191].

The feasibility of generating hydrochloric acid and lithium hydroxide from a simulated lithium chloride solution using BMED was also explored in other studies [193,194]. The results showed that when the LiCl concentration is lower than 4 g/L, BMED is not a feasible technology due to the higher solution resistance resulting in higher energy consumption [193]. Additionally, increasing initial acid and base concentrations to improve the yield of HCl and LiOH may not be a good way due to the increment of mass transfer from the feed compartment into the acid and base compartment and OH^- ion leakage in the CEM [191–194]. Gonzalez et al. [194] show that LiOH concentration in a concentration range of 3.34–4.35 wt%, with 96.0–95.4 % purity is possible. In addition, electrical consumption and LiOH contamination with chloride ions were two important factors influencing the purity of the solution.

In another study, BMED was used to treat the lithium extraction process further to convert lithium sulfate to lithium hydroxide to investigate the feasibility of this technology in the battery industry, which requires higher purity of LiOH. An increase in the initial LiOH concentration in the base compartment and a decrease in the initial H_2SO_4 concentration in the acid compartment reduced sulfate transfer from acid and feed solutions to base solution. This work shows that BMED technology has the potential to replace the current chemical precipitation to produce LiOH (99.9 % purity) from Li_2SO_4, by eliminating the use of alkali-intensive steps [192].

Unfortunately, many studies were conducted using synthetic feed solutions including only lithium even though it was clearly known that migration of Li^+ decreased in the presence of other cations such as K^+ and Na^+ due to the ion competition [175,191–194]. Therefore, further research was carried out to see the lithium recovery as LiOH in the presence of anions and other cations. In one study, it was discovered that the lithium migration rate was 5.1 mmol/m^{2}s using pure LiCl while it dropped to 2.09 mmol/m^{2}s with increasing Na/Li molar ratio of feed solution was 1.3. It was revealed that the coexisting K^+ has a greater impact compared to Na^+. Moreover, the presence of SO_4^{2-} in the feed solution resulted in significant lithium leakage to the acid compartment [195]. In addition, BMED requires extensive pretreatment to generate soft brine to avoid scaling and fouling caused by silica and hardness. Typically, BMED requires silica concentration less than 10 mg/L and hardness <10 mg/L in feed brine.

To increase lithium recovery and prevent divalent ion migration coming from the feed solution, bipolar membrane electrodialysis coupled with monovalent selective ion exchange membranes (BMSED) was used. Qiu et al. [196] used two different kinds of commercial monovalent CEMs (Astom CIMS and AGC CSO) and AEMs (Astom ACS and AGC ASV). In this study, pretreated salt lake brine containing 1803 mg/L Li was used as feed solution, and 1211 mg/L Li was recovered with ASTOM CIMS and ASTOM ACS membrane pair. However, the recovered amount of lithium decreased to 1146 mg/L when AGC CSO and AGC ASV membrane pair was used. Moreover, the amount of Ca and Mg in the base compartment was 1.43 mg/L Ca and 0.12 mg/L Mg with ASTOM CIMS/ACS pair while 1.04 mg/L Mg and 3.82 mg/L Ca was detected with AAGC CSO/ASV pair. Therefore; CIMS/ACS membrane pair was more favorable than CSO/ASV in terms of both lithium recovery and Ca and Mg rejection. Hence, the increase in Ca^{2+} and Mg^{2+} rejection resulted in less impurity in the LiOH base compartment.

Even though the feasibility of BMED to separate lithium from aqueous solutions was investigated, with several studies using artificial salt solutions (primarily containing only lithium), the effect of real salt

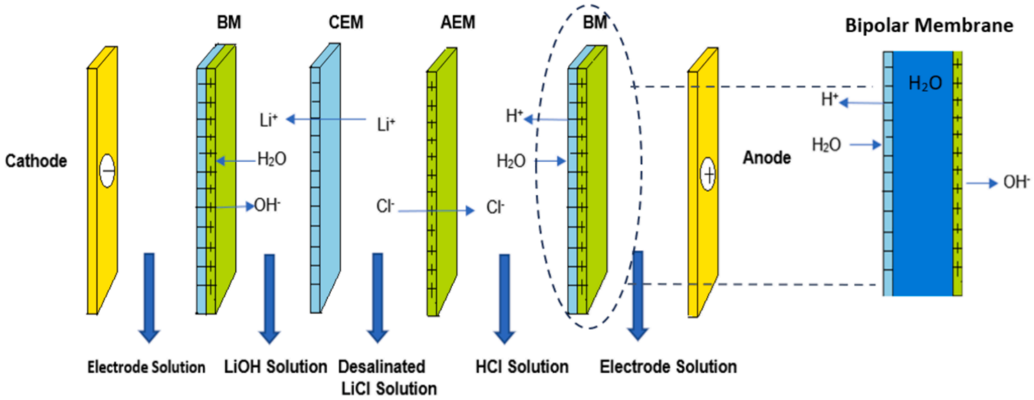


Fig. 9. Bipolar membrane electrodialysis for separation of lithium from brine. Adapted from [194].

lake solutions as feed solutions and the effect of temperature on the recovery has not been investigated. Therefore, further studies are required to understand the mass transfer mechanism in presence of other ions, membrane fouling and scaling potential during treatment of real brine should be investigated. Additionally, the fabrication of customized ion exchange membranes can be explored to increase the separation efficiency of lithium in BMED process.

2.4.4. Nanofiltration

Nanofiltration (NF) is a type of membrane filtration in which a semi-permeable membrane with a pore size typically less than 2 nm is used to separate particles and molecules based on their size and charge (Fig. 10). NF is indeed very similar to reverse osmosis (RO), which dominates the desalination market today, but NF operates at comparatively lower pressures and utilizes membranes that are less tightly packed than RO membranes. Lithium separation via NF, without the use of additional chemicals, reduces the energy and environmental impacts of traditional lithium recovery methods, making the process appealing [197–201].

Several types of NF membranes have been investigated for lithium recovery. Some NF membranes are designed to separate divalent ions from monovalent ions, making them potentially valuable for lithium-containing solutions with a high Mg^{2+}/Li^{+} ratio. It is known that positively charged NF membranes show better performance in terms of separation of $LiCl/MgCl_2$ due to the Donnan exclusion [197,198]. Therefore, in many cases, positively charged NF membranes were fabricated by using positively charged monomers. Recently, the use of polyethyleneimine (PEI), a positively charged monomer, has become popular to make NF membranes positively charged [197,199]. Li et al. [197] synthesized a positively charged NF membrane via interfacial polymerization of trimesoylchloride (TMC) and branched poly(ethylene imine) (BPEI) on the crosslinked polyetherimide support. To increase the selectivity of lithium, synthesized NF membranes were modified with ethylenediaminetetraacetic acid (EDTA) due to its capability to complex with divalent ions. The separation factor of Li/Mg was obtained as 9.2 with 6 $L\ m^{-2}\ h^{-1}\ bar^{-1}$ for the $LiCl/MgCl_2$ feed solution with a Mg^{2+}/Li^{+} ratio of 24. This result was achieved within 36 h of filtration when employing the optimal EDTA-modified NF membrane. Even though this membrane shows promising results in separating lithium from magnesium, the permeation of the membrane should be enhanced to reduce the cost of the processes. Therefore, piperazine-grafted carbon nanotubes and polyethersulfone (PES) three-channel capillary ultrafiltration (UF) membrane as a substrate were used to synthesize positively charged PEI based NF membranes with high water flux and good lithium separation efficiency in another study. When tested with simulated salt lake brine having an Mg^{2+}/Li^{+} ratio of 21.4, the membrane showed high rejection of $MgCl_2$ at 95 % and lower rejection of LiCl at 18 %, resulting in a 1.3 Mg^{2+}/Li^{+} ratio in the permeate solution with a high water permeance of 34 $L\ m^{-2}\ h^{-1}\ bar^{-1}$ [199].

In addition to conventional liquid/liquid interfacial polymerization, a new approach – gas/liquid interfacial polymerization – has been developed to synthesize positively charged NF membranes, leveraging the known Janus structure of polyamide. Specifically, one side of the membrane, facing the amine monomers, becomes positively charged, while the other side becomes negatively charged. Therefore, this method involves the interfacial polymerization between amine monomers (in the gas phase) and acyl chloride monomers (TMC in the liquid phase) to create a positively charged polyamide structure. To synthesize positively charged NF membranes, ethylenediamine (EDA) was selected as the amine source due to its high volatility and reactivity with TMC. The synthesized NF membranes exhibited good Mg^{2+}/Li^{+} separation performance, with a separation factor as high as 28 and a water permeance of 10 $L\ m^{-2}\ h^{-1}\ bar^{-1}$ with simulated brine solution ($Mg^{2+}/Li^{+} = 20$). Moreover, these NF membranes maintained the same selectivity, retaining 90 % of their water permeance at the end of seven days [202].

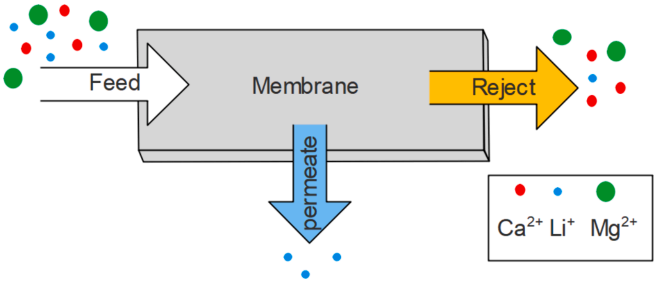


Fig. 10. Nanofiltration for lithium separation from aqueous solutions. Adapted from [199,201].

Several commercial NF membranes, such as DK, DL, NF270, and NF90, have been tested for lithium separation as well as a reverse osmosis low-pressure membrane (LPRO), XLE. Somrani et al. [203] tested NF90 and XLE membranes. It was found that NF90 is more efficient for lithium separation from diluted brine compared to XLE mainly due to its higher hydraulic permeability to pure water [203]. The study by Li et al. [200] involved testing of DK membrane with a molecular weight cut off 150–300 Da in different operating conditions such as different operation pressures (1.5–3.5 MPa), feed temperatures (293–313 K), multi-ion presences (sodium, calcium, and potassium), and concentration ratios (1.5, 2, 3 and 4) via circulating the concentrate back to the tank for lithium separation. The results showed that the yield of lithium and its separation from magnesium increase with increasing pressure but separation of lithium from other cations decreases with increasing temperature. This decline in lithium fraction can be attributed to more open membrane pores due to thermal expansion at elevated temperatures. The yield of lithium reached 99 % when the concentration ratio was 4, although the separation efficiency decreased. The experimental findings indicate that higher concentration ratio causes more magnesium to pass through the membrane while rejecting lithium, which decreases the separation efficiency. The main reason for this is that lithium depletion during the concentration process leads to more magnesium penetration to maintain electro-neutrality. The main reason for this is that lithium depletion during the concentration process leads to increased magnesium penetration to maintain electro-neutrality Hence, Mg^{2+}/Li^{+} ratio increases in the permeate [200]. To enhance the lithium separation, commercial membranes (DK, DL, NF270) were modified with PDA and PEI. Lithium permeability reached about 95 % at the flux of 21.33 $L\ m^{-2}\ h^{-1}$, and the Mg^{2+}/Li^{+} ratio was reduced from 30 to 4.1 compared to the unmodified NF270 membrane after facile polymerization. However, modified DK membranes suffered from pore narrowing and broad pore size distribution, leading to reduced permeability and lithium recovery [201].

To modify the surface of NF membranes, chemical grafting of an imidazolium-type ionic liquid (IL) onto the surface of the nascent polyamide membrane was also fabricated and tested with simulative brine ($MgCl_2/LiCl$ binary solution with Mg^{2+}/Li^{+} ratio is 20). 1-(3-aminopropyl)-3-methylimidazolium bis (trifluoromethanesulfonyl) imide ([MimAP][Tf_2N]) was selected to modify the NF membrane surface, because the grafted [MimAP][Tf_2N] could endow the membrane surface with hierarchically structured pores and higher positive charge density. For simulative brine, the Mg^{2+}/Li^{+}ratio was reduced from 20 to 3.5, and the selectivity of lithium over magnesium was 8.12 for the optimized membrane [198]. In another study, surface modification of a PEI-based NF membrane was conducted using a different ionic liquid-based monomer, the triple-quaternary ammonium-based ionic liquid (TQAIL), N1-(6-amino(hexyl)-N1, N1, N6, N6-tetramethyl-N6-(6-(trimethylammonio)hexyl)hexane-1,6-diaminium bromide. The resulting membranes exhibited good fouling resistance, but the selectivity of Li^{+}/Mg^{2+} and water permeance dramatically decreased with an increase in the Mg^{2+}/Li^{+} ratio in the feed solution [204]. These studies show promising results for the separation of lithium from magnesium; however, the selectivity is poor due to the low surface charge density and non-uniform pore size distribution. It is, therefore, crucial to develop new methods to tune pore size distribution and surface charge density. Accordingly, in recent years, several homemade membranes were designated and tested to improve the selectivity and water permeance of NF membranes for the lithium recovery.

One approach to increase Li^+/Mg^{2+} selectivity without decreasing the permeance of the membrane was to incorporate nanomaterials into the support membrane to modify the support membrane and create a bridge/connector between the support and the active layer of the membrane [205–207]. An example of this approach is a study involving synthesizing a polyamide membrane with single wall carbon nanotubes (SWCNTs) on PES support and grafting branched PEI containing a large number of amine groups on the membrane surface to increase its positive charge density, resulting in a high Mg^{2+}/Li^+ separation factor of up to 33.4 and 98.5 % $MgCl_2$ rejection for simulated brine [207]. To increase the water permeance of NF membranes and keep the Mg^{2+}/Li^+ separation factor, multi-walled carbon nanotubes(MWCNTs) were used in addition to SWCNTs. Novel potassium carboxylate functionalized MWCNTs (MWCNTs-COOK) were incorporated into the PES ultrafiltration support membrane. The MWCNTs-COOK in the PES substrate worked as a “connector” and influence the formation of the polyamide layer as a result of the interfacial polymerization of PEI and TMC. With the 0.012 wt% MWCNT loading, a significant difference between the rejection of magnesium and lithium was observed as 87 % while flux was 11.46 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ [206]. Another approach to exceeding the trade-off between water permeance and selectivity is to synthesize a non-polyamide membrane via self-polymerization of MPD assisted by Cu^{2+} which helped to enhance polymerization, and crosslinking while serving as a positive-charge center in the NF membrane. The optimized membrane showed a high water permeance of 16.2 ± 2.7 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ with 8.0 ± 1.0 selectivity, exceeding the trade-off [208]. In another research, a strong electrolyte monomer, quaternized bipyridine (QBPD), was also used for surface modification of PEI-based NF membrane to circumvent the trade-off. The pure water flux (96.6 $L\,m^{-2}\,h^{-1}\,bar^{-1}$) was 8.2 times higher when modified NF membranes were used. The flux of the modified membrane was 81.6 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ while the Mg^{2+}/Li^+ ratio decreased by 8.5 from 50 [209].

Despite all efforts to make the surface of the NF membrane positively charged to increase the separation efficiency of lithium and decrease the Mg^{2+}/Li^+ ratio, approaches such as narrowing the pore size distribution of the membrane and making the membrane surface negative were also considered. For this purpose, ceramic membranes were modified by dip coating the membranes with BTESE, followed by calcination at 400 °C, resulting in a narrow pore size distribution of 0.63–1.66 nm. The modified ceramic membranes exhibited a high permeability 9.5 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ for salt solutions, along with 74.7 % and 20.3 % rejection towards LiCl and $MgCl_2$, respectively. These results suggest that the modified ceramic membranes have the potential for efficient lithium recovery, particularly due to the excellent chemical stability of ceramic membranes as compared to their polymeric counterparts [198].

2.4.5. *Comparison of membrane-based technologies for lithium separation*

The ED, BMED, and NF processes are compared with their advantages and disadvantages as shown in Table 4 to evaluate each membrane technology. Compared to NF, the recovery and selectivity of lithium are higher and the energy consumption is low in SED [184]. SED can also concentrate lithium concentration within a short time (30 min to 6 h) depending on feed composition and operating conditions (*e.g.*, electrical potential, flow rate, temperature). Although BMED seems advantageous compared to these two technologies due to its capability of producing base (LiOH) as the final product, direct use of this technology suffers low purity of the final product due to the presence of the other monovalent ions (K^+/ Na^+) in the feed.

2.5. *Adsorption*

Adsorption is a common technique for selectively recovering lithium from aqueous solutions. Recently, several types of inorganic-metal-based (lithium-aluminum layered double hydroxides (LiAl-LDHs), lithium titanium oxide type lithium-ion sieves (LTO-LISs), and lithium manganese oxide type lithium-ion sieves (LMO-LISs)) and metal–organic frameworks (MOFs), as well as crown ether-based adsorbents have been tested and reported for lithium recovery [210–219]. The lithium-aluminum layered double hydroxides (Li/Al-LDHs) have gained significant attention from researchers due to their efficient lithium recovery from brines with high Mg^{2+}/Li^+ content and low Li^+ content, as well as their easy synthesis and regeneration. These adsorbents are composed of two-dimensional aluminum hydroxide layers united by van der Waals forces, hydrogen bonds, and electrostatic contact. Li^+ ions are present in the octahedral spaces in the hydroxide ions. However, the low reusable stability resulting from excessive deintercalation and the inherited low Li^+ adsorption capacity of Li/Al-LDHs remain the main challenges [210,211,220].

2.5.1. *Li/Al-LDHs adsorbents*

Paranthaman et al. [221] used Li/Al-LDHs produced by coprecipitation to extract Li^+ from geothermal water. To preserve the structural integrity of the adsorbents during desorption, they chose a low concentration of pure LiCl solution as the desorption solution to prevent the structural collapse of adsorbent into gibbsite $Al(OH)_3$ phase. In the end, more than 91 % of the Li^+ in the brine was recovered with Li/Al-LDHs without significant adsorbent loss [221]. Apart from using low-concentrated pure LiCl eluent solution during desorption, a new strategy, doping of superparamagnetic nanoparticles (Fe_3O_4 or γ-Fe_2O_3) to Li/Al-LDHs has been adapted to achieve controllable adsorbent recovery with external magnetic fields to minimize adsorbent loss [210,211,220]. However, it was discovered that the adsorption capacity of Li/Al-LDHs decreased with the addition of Fe_2O_3 content due to the reduced Li/Al-LDHs components and strengthened pore blocking) [210]. In further studies, these nanomaterial doped adsorbents were tested for long-term use, but it was found that the adsorption capacity and crystal

Table 4
Advantages and disadvantages of each membrane-based separation technology.

Method	Advantages	Disadvantages	Energy Requirement	Complexity
SED	• Low operating cost • High recovery • High Li/Mg selectivity • Environmentally friendly	• Scaling • Requires a recovery unit • Requires pretreatment	SPC: 1.9–160 kWh/kg Li	Moderate
BMED	• High Permselectivity • Acid-base production without using toxic chemicals • Environmentally friendly	• Pretreatment of the feed solution is necessary to produce high-quality acid and base	SPC:0.0077–9.45 kWh/kgLi	Moderate
NF	• Low or moderate Li/Mg selectivity	• Requires a recovery unit • High operation cost • Energy-intensive • Fouling and scaling	–	Moderate

structure of Fe_2O_3 doped Li/Al-LDHs (MLi/Al-LDHs) did not further change even after 8 adsorption–desorption cycles [211]. Later, some simulations were done to understand the effect of Fe doping on the structural integrity of adsorbent, and results showed that Fe-doping increases the binding energy of host layers, thus increasing the structural stability of adsorbents. In one study, it was found that the decrease in lithium adsorption capacity of the adsorbent was only 2.5 % after 30 adsorption–desorption cycles when Fe-doped Li/Al-LDHs adsorbent was used to recover lithium from brine [220]. Luo et al. [222] worked with granulated Li/Al-LDH to extract lithium from salt lake brine. To increase the adsorption capacity of the adsorbent, the porosity of the adsorbent was tried to be enhanced. The preparation of granulated lithium adsorbents included the synthesis of the precursors $NH_4Al_3(SO_4)_2(OH)_6$ and γ-AlOOH, the lithiation of the precursors, and granulation of powder lithium adsorbents by crosslinking sodium alginate in $CaCl_2$ aqueous solution. In this study, both $NH_4Al_3(SO_4)_2(OH)_6$ and $Li_2Al_4(OH)_{12}SO_4\cdot xH_2O$ are utilized as host materials for lithium intercalation. However, the mechanism of lithium intercalation is different for $NH_4Al_3(SO_4)_2(OH)_6$ and Li-Al-Li/Al-LDHs. In Li/Al-LDHs, both lithium cations and anions simultaneously enter the structure, with lithium cations occupying the octahedral sites in the Al $(OH)_3$ layers and anions intercalating into the interlayer spaces. In contrast, for $NH_4Al_3(SO_4)_2(OH)_6$, lithium ions enter into the puckered interlayers formed by SO_4 tetrahedra and AlO_6 octahedra. The adsorption capacity has been determined to be 9.16 mg/g after 10 cycles of adsorption and desorption [222]. In another study, Li/Al-LDHs with different interlayer water contents were designed to understand the relationship between interlayer water content and Li adsorption performance of adsorbent in high Mg^{2+}/Li^{+} ratio brines. It was discovered that adsorption capacity increased from 1.05 mg/g to 7.89 mg/g as interlayer water content increased from 5.52 % to 18.18 %. Moreover, it was established that there is no relationship between the structural integrity of adsorbent and interlayer water content, however, it was concluded that interlayer content causes less interlayer spacing to enhance adsorption selectivity [223].

2.5.2. *LMO-LISs adsorbents*

Manganese-based adsorbents (LMO-LISs) are other types of adsorbents which are widely investigated due to their excellent selectivity towards lithium and high adsorption capacity. However, their weak mechanical properties because of their powder form limit the industrial use of these adsorbents as well as their poor chemical stability due to their weak metal–oxygen bond. To minimize the effect of these disadvantages, several approaches have been tested, such as composite adsorbent synthesis using microporous silica beads, polyvinyl chloride (PVC), and nonwoven fabric; metal doping; surface coating of the adsorbent; utilizing a different eluent rather than HCl; and membranization [212,213,224–228]. Composite adsorbents can adsorb lithium, but their capacities are mainly limited due to the loss of active sites for lithium adsorption [227]. Recently, epoxy resin (E-12) has been adopted to prepare cylindrical granular adsorbent to prevent loss in adsorption capacity. Researchers determined the adsorption capacity of E12 adopted Mn-based adsorbent as 30.2 mg/g in batch experiments. The continuous adsorption–desorption experimental results showed that the adsorptive capacities for lithium in LiCl solution and sampled brine were 21.3 mg/g and 17.2 mg/g, respectively [228]. Several metals such as Al, Ti, V, Fe, Co, Ni, Mg, Ba, Zn, Cu, Ge, Nb, etc., have been used to replace manganese in order to improve the stability of LMO-LISs. Among these metals, Al^{3+} has shown great potential due to its similar radius to Mn^{3+} (0.57 Å for Al^{3+} compared to 0.66 Å for Mn^{3+}), and the Al-O bond energy is greater than that of the Mn-O bond. This leads to the shrinkage of spinel cells and an increase in the valence of manganese, thereby improving the stability of the structure by suppressing Jahn-Teller distortion [229–233]. Zhang et al. [229] prepared Al-doped lithium manganese oxides $Li_{1.6}Al_xMn_{1.6-x}O_4$ by sol–gel synthesis and solid-state reactions. Protonated samples were obtained through further acid treatment. The results indicated that Al doping not only increased the stability of Al-doped LMO-LISs but also enhanced the adsorption capacity of the adsorbent. The findings demonstrated that, compared to the undoped counterpart, Al-doped $H_{1.6}Mn_{1.6}O_4$ had a higher lithium absorption capacity, reaching approximately 32.6 mg/g. Moreover, the adsorption capacity of Al-doped acid-treated LMO-LISs did not change significantly (26.8 mg/g). Manganese dissolution loss was found to be 1.92 % after 4 cycles of adsorption–desorption experiments. Ohashi et al. [234] modified the surface of spinel-type manganese oxide ($Li_{1.33}Mn_{1.67}O_4$) adsorbent in a pH-controlled environment using different oligomeric metal-hydroxide precursors. Their results showed that the surface of the adsorbent was covered with 10–20 nm metal oxide layers (7.1 % wt. Al or 11.8 wt% Ni). Metal-oxide coated $Li_{1.33}Mn_{1.67}O_4$ showed lower manganese dissolution and higher lithium extraction than the raw $Li_{1.33}Mn_{1.67}O_4$. The reason behind this was the suppression of Mn (III) disproportionation reaction by precipitated metal oxide on the surface of the adsorbent. Marthi et al. [235] tried to use of a different eluent ($(NH_4)_2S_2O_8$ at 80 °C instead of HCl. Before replacement, it was observed that a 30 % loss in adsorption capacity was observed after only five adsorption–desorption cycles. However, this loss was reduced to 0.6 % with a $(NH_4)_2S_2O_8$ eluent. Moreover, 95 % of lithium was extracted from salt-lake brine. Qui et al. adapted membranization by using cellulose acetate (CA) membranes with polyvinyl alcohol (PVA). They considered that the porosity of cellulose acetate can contribute to creating lithium diffusion channels, promoting the insertion/extraction of lithium, and that PVA can increase mechanical and chemical stability due to the poor mechanical properties of CA. Therefore, they prepared a polyvinyl alcohol (PVA) reinforced cellulose acetate membrane-$Li_4Mn_5O_{12}$ (PVA/CAM-$Li_4Mn_5O_{12}$). The results showed that the adsorbent has low Mn loss and good cyclability, allowing it to be reused up to 8 times [212].

Although LMO-LISs have some challenges, as briefly discussed above, they have not only been used for the recovery of lithium from typical brine solutions but also for the recovery of lithium from produced water containing oil and other major cations such as Na^{+}, Ca^{2+}, Mg^{2+}, in addition to lithium due to their exceptional lithium adsorption capacity and high lithium selectivity. Seip et al. [236] used manganese-based adsorbent (LMO-LIS) for the recovery of lithium from produced water. They revealed that adsorbent loss is due to the decrease in the pH of the solution during adsorption. Additionally, the possibility of a manganese reduction in the adsorbent structure due to organic molecules present in the brine has been speculated. Therefore, pretreatment to remove organics was suggested before adsorption. Later, Trian et al. [237] also used LMO-LISs to extract lithium efficiently from produced water. They found that lithium adsorption capacity strongly depends on the pH of the produced water. The adsorption capacity of lithium was stable and showed only a slight decrease (5.35 % for raw produced water and 3.53 % for pre-treated produced water) after four adsorption–desorption cycles.

2.5.3. *LTO-LISs adsorbents*

Titanium-based adsorbents (LTO-LISs) are also promising candidates to extract lithium via adsorption. Unlike LMO-LISs, LTO-LISs have structure stability in acidic solutions and minimal adsorbent loss due to the stronger Ti-O bond. Therefore, several studies have been conducted with LTO-LISs [214,215,238–245]. For instance, Wang et al. [245] synthesized H_xTiO_3 (HTO) to extract lithium from the high Mg-containing ($Mg^{2+}/Li^{+} \approx 54$) brine. The maximum adsorption capacity of Li^{+} was 36.34 mg/g, and the separation factors of Li^{+} to Mg^{2+} reached 4783 in the brine, which contained Na^{+}, K^{+}, Li^{+} (~1.56 g/L), high Mg^{2+} (~58.5 g/L), high Ca^{2+} (~55 g/L) and high concentrated anions at the initial pH 8.8, 25 °C for 24 h. Furthermore, the lithium adsorption capacity was found to be 33 mg/g after six adsorption–desorption cycles, showing good stability of the H_xTiO_3 structure. Since the synthesis of LTO-LISs is costly, efficiently recovering the adsorbent is crucial. Therefore, iron-doping has been attempted in further studies to recover

HTO adsorbent from brine by magnetic separation. These adsorbents showed a high adsorption capacity, and they were separated easily from the solution [243,246]. The saturated adsorption capacity of the iron-doped HTO in brine (Li^+1.56 g/L, pH=8.8) was 34.8 mg/g [247]. Given the promising results of LTO-LISs in lithium separation, several synthesis procedures for these adsorbents have been extensively investigated and compared. Hydrothermal synthesis, sol–gel method, and solid-state reaction are frequently mentioned as key synthesis techniques in the literature [241–243,245,248–252].

Hydrothermal synthesis requires high temperature and pressure for a long time. Sol-gel method requires controlled pH and temperature using chelating agents. However, the solid-state reaction requires simple mechanical mixing and calcination. Therefore, several studies have been conducted on solid-state reactions to synthesize those adsorbents even though adsorbents synthesized via solid-state reaction show relatively lower lithium adsorption capacity due to the agglomeration of tiny particles [241,248]. Gu et al. [248] utilized TiO_2 and $C_2H_3LiO_2{\cdot}2H_2O$ instead of Li_2CO_3 to synthesize Li_2TiO_3 adsorbent without agglomeration via solid state method. During the reaction of dehydrated $C_2H_3LiO_2{\cdot}2H_2O$, huge amounts of heat and gases are released, and this causes acceleration of nucleation process and elimination of agglomeration. Lithium adsorption capacity was found to be 24.5 mg/g and it did not change after 5 cycles of adsorption–desorption for West Taijinar Salt Lake. Wei et al. [238] synthesized HTO porous nanofibers using a combination of the solid-state method and electrospinning to increase the adsorption capacity of lithium by enhancing the exposure of adsorption sites. The synthesized HTO porous nanofibers showed a lithium adsorption capacity of 59.1 mg/g at pH 11 and excellent chemical stability. The adsorption capacity for Li^+ remained at 86.5 % after 6 cycles. Quian et al. [253] synthesized H_2TiO_3/cellulose aerogels (HTO/CA) with a porous network to prevent agglomeration and obtain high adsorption capacity without sacrificing the adsorption rate, considering aerogels provide conductive channels for hydrated lithium ions. The obtained results revealed that the maximum lithium adsorption capacity of HTO/CA was approximately 28.58 mg/g. Although nanosized LTOs have higher adsorption capacities, they are not suitable for practical applications mainly because of their small particle sizes (<500 nm). Therefore, immobilizing nanosized adsorbents by attaching them to stable support has been attempted. In another study, the relationship between the crystal phases of TiO_2 and the lithium adsorption capacity of the adsorbent was investigated. LTO-LISs were synthesized from amorphous, anatase, and rutile TiO_2 via solid-state reaction. The adsorbent derived from the anatase structure of TiO_2 showed the highest adsorption capacity (34.2 mg/g) due to its strong hydrophilicity. Moreover, the lithium adsorption capacity of the adsorbent remained at 31 mg/g even after eight adsorption–desorption cycles, and Ti loss was below 0.31 % from the first to the eighth cycle. After revealing that lithium adsorption capacity increases with hydrophilicity and considering that the hydrophilicity of the adsorbent depends on the density of hydroxyl groups, the lithium adsorption mechanism of this adsorbent was investigated. It was shown that lithium adsorption on H_2TiO_3 involves the breaking of surface O−H bonds and the formation of O−Li bonds instead of simple ion exchange between Li^+ and H^+ [254,255]. Later, the utilization of surfactant to tune the hydrophilicity of the adsorbent has been adopted. Sun et al. used double surfactants of triblock copolymer PEO_{106}-PPO_{70}-PEO_{106} and hexadecylamine in the synthesis of HTO adsorbent. The maximum lithium adsorption capacity was found 31.68 mg/g at pH 12.3 when both surfactants were used in the synthesis [256].

Unlike Li/Al-LDHs, LTO-LISs have slow lithium extraction kinetics (typically 12–24 h) Therefore, it is important to accelerate Li^+ adsorption rate. Li et al. used the hydrothermal method to synthesize ultrathin nanosheets-assembled $Li_4Ti_5O_{12}$ porous microspheres with hierarchical mesoporous structure considering that the mesoporous structure significantly contributes to the specific surface area of HTO and exposed more adsorption active sites, thus accelerating the adsorption rate of Li^+. The adsorbent showed a good Li^+ adsorption capacity of 43.20 mg/g within 25 min for solution containing 500 mg/L lithium and high selectivity for Li^+ from high Mg-containing aqueous solutions [257]. Adsorption with Ti_2O_3 adsorbents has also been investigated by several researchers for lithium recovery from produced water (oilfield brine). In one study, the recovery of lithium from simulated shale gas-produced water (similar to Marcellus shale gas-produced water) was evaluated by a combination of precipitation and adsorption. Before adsorption via Ti_2O_3 adsorbent, the solution was pre-treated with Na_2CO_3 for precipitation. The lithium recovery and lithium adsorption capacity were determined to be 54.4 % and 25.4 mg/g, respectively [258,259].

2.5.4. MOF-based adsorbents

In addition to inorganic metal-based adsorbents, researchers have also studied adsorbents based on metal–organic frameworks (MOFs) and crown ethers [166,216,217,260]. MOFs, formed through the coordination of metal ions or clusters with multi-chelated organic ligands, have been widely used in adsorption due to their high surface area and numerous metal sites. Considering the good adsorption capacities of MOFs, several studies on lithium extraction using MOF-based adsorbents have been conducted [216,217,260]. Jiang et al. [260] prepared a cuboid rod-shaped three-dimensional framework termed TJU-21, composed of fluorine-pillared coordination layers of Fe–O inorganic chains and benzene-1,3,5-tricarboxylate (BTC) linkages. The adsorbent showed good lithium adsorption capacity and chemical stability. Moreover, lithium adsorption capacities were found to be 13 mg/g, 37.4 mg/g, and 18.8 mg/g for pretreated Da Qaidam brine, Uyuni brine, and Yiliping brine, respectively. However, most MOF-based adsorbents are synthesized via hydrothermal methods, which require costly synthesis procedures, harsh reaction conditions, and excessive use of toxic organic solvents [261–263]. Therefore, Wei et al. [216] studied the cooling crystallization technique to synthesize adsorbents at ambient pressure and below 100 °C. Their results showed that there is no significant difference between the lithium adsorption capacities of MOF-based adsorbents synthesized via the hydrothermal method and those synthesized via the cooling crystallization technique. Additionally, introducing stimuli-responsive compounds into MOF to avoid chemicals in the adsorbent regeneration process has been tried. For this purpose, a polymer-functionalized MOF adsorbent (a crosslinked poly(N-isopropylacrylamide-co-acryloylamidobenzo-18-crown-6)-functionalized MOF-808), denoted pNCE/MOF-808, has been synthesized and thermally regenerated at 45 °C. The synthesized adsorbent showed an adsorption capacity of 7.22 mg/g and excellent selectivity, with ratios up to 29.4 for Na^+/Li^+ and 34.4 for K^+/Li^+ in a mixed solution containing 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl [217].

2.5.5. Crown ether-based adsorbents

Crown ether-based adsorbents recently gained attention due to their annular chelator properties and high regenerability [65,264–266]. Crown ethers suitable ring size can be well coordinated with positive ions such as alkali metal ions. A plurality of C-O dipoles in the molecule can coordinate with different metal ions to form different complexes as the size of the ring changes. Moreover, the inner diameter of 12-crown-4 (12C4) is 0.15 nm, which is like the size of Li^+ (0.152 nm). However, 12C4 is liquid at ambient temperature, so recovery of them is difficult. Therefore, they need to be immobilized or grafted on solid materials. In the literature, several studies have been conducted to combine macroporous membranes and crown ethers to synthesize membrane adsorbents. Since these membrane materials such as PVDF or PSF suffer from a lack of lithium selectivity due to the limited number of specific lithium binding, ion imprinted membranes technology (IIMT) using crown ethers has gained attention to enhance lithium selectivity [218,219,267].

For instance, Sun et al. [266] synthesized macroporous polymer-ion imprinted macroporous membranes (IIMMs) using PVDF as membrane matrix and crown ether (CE, 12-crown-4) as function monomer by using phase-inversion technique. The maximum lithium adsorption capacity was obtained as 27.1 mg/g. Even though PVDF is a promising candidate to be used as support due to its excellent chemical and thermal stability, the hydrophobicity of PVDF makes these membranes prone to fouling. Therefore, TiO_2 incorporated PVDF membrane was used as support to prevent fouling by improving the hydrophilicity of PVDF. The maximum lithium adsorption capacity of the adsorbent was determined as 132.00 mg/g after immersing in 300 mg/L LiCl with good lithium vs other ions (Na^+, K^+, Ca^{2+}, $Mg^{2+)}$ selectivity [218]. In one study, PES was used as a membrane matrix with CE (12-crown-4) to create highly selective multilayered lithium-imprinted membranes (Li-IIMs) with enhanced hydrophilicity and stability. The optimal relative selectivity coefficients of Li^+/Na^+ and $Li^{+/}K^+$ reached up to 1.85 and 2.07, respectively, at a low effective working concentration of the target ions (50 mg/g). The results showed that rebinding capacities reached up to 90.3 % of the initial binding after 5 cycles of adsorption/desorption and declined to 88.1 % after another 5 cycles a month later [219]. In a study by Li et al. [268] 4‘-aminobenzo-12-crown-4 (AB12 C4) ethers were grafted onto a chloromethylated polysulfone (CMPSf) membrane via an in-situ surface grafting process through nucleophilic substitution between amino groups on AB12 C4 ethers and chloromethyl groups on the CMPSf membrane surface to activate the crown ethers. The synthesized membrane adsorbent showed a maximum lithium adsorption capacity of 51.99 mg/g. The selectivity of Li^+/K^+, Li^+/Na^+, Li^+/Ca^{2+}, and $Li^{+/}Mg^{2+}$ was found to be 38.43, 33.13, 27.11, and 3.42, respectively. In another study, Liang et al. [302] used magnetic carbon nanospheres as a support due to their good mechanical stability, biocompatibility, and magnetism. The adsorbent (Li^+-IIP-Fe3O4@C) structure was designed with carbon nanospheres (Fe_3O_4@C) as the carrier and 2-hydroxymethyl-12-crown-4 as the adsorption unit. Additionally, 2-hydroxymethyl-12-crown-4 grafted onto the polymerized methacrylic acid-Fe_3O_4@C surface was cross-linked by ethylene glycol methacrylate. The results revealed that the adsorption capacity of Li^+-IIP-Fe_3O_4@C for Li+ decreased slightly from 13.84 to 12.62 mg/g after six adsorption–desorption cycles, representing only an 8.8 % decrease. This slight decrease is attributed to damage of the adsorption sites caused by using HNO_3 as an eluent during desorption. Moreover, Li^+-IIP-Fe_3O_4@C showed good regeneration performance, with recovery rates ranging from 96.12 % to 97.27 % over six adsorption–desorption cycles.

Polymeric high internal phase emulsion (polyHIPE) foams have been evaluated as a support due to the opportunity to shorten diffusion paths and enhance mass transport by incorporating chemical functionality on the surface of macropores. Therefore, microporous polymer foam (polymeric glycidyl methacrylate, PGMA) with abundant epoxy groups via high internal phase emulsions (HIPEs) templates were fabricated. Subsequently, 2-methyl-12-crown-4 ether (2M12C4), an organic ligand, was used to fabricate immobilized porous adsorbent (PGMA-CE) for Li+ recovery. Although PGMA-CE showed promising selectivity for lithium, the low density of CE groups resulting from the reaction between epoxy groups and CEs, and the low stability of hydroxyl groups, which can be denatured during treatment, have been observed. Therefore, another approach has been adopted to address these problems: introducing crown ether (CE) functionality onto the surface of the porous foam by growing a “brush” of polymer chains from surface-initiating sites [269–271]. Bai et al. prepared 2-(allyloxy) methylol-12-crown-4 ether (2AM12C4) functionalized polymer brushes (chloromethyl functionalized porous polymer (PVBC)-g-PCE) from microporous polymeric high internal-phase emulsion (PolyHIPE) using UV-initiated surface polymerization. The maximum lithium adsorption capacity was found to be approximately 3.5 mg/g at pH 6. The selectivity of Li^+/Na^+, Li^+/K^+, $Li^{+/}Mg^{2+}$, and Li^+/Ca^{2+} was found to be 3.10, 9.06, 3.79, and 12.3, respectively [272]. In further studies, the utilization of hybrid polymer nanosheets has been suggested by researchers. However, they are not extensively discussed in any field regarding selective separation due to their complicated and costly synthesis. Recently, Zhou et al. proposed a single-step Pickering double emulsion method rather than traditional two-step emulsification. They combined crown ether (CE) with polymer nanosheets to efficiently extract lithium via adsorption. Benefiting from specific “size-match” complexation, the adsorbent exhibited excellent selectivity towards Li^+ even in the presence of competitive cations [273].

2.5.6. *Comparison of adsorbents*

Several types of adsorbents have been tested in terms of lithium recovery from aqueous solutions. The advantages and disadvantages of each types of adsorbents are stated in Table 5. In general, Li/Al-LDHs have fast extraction kinetics but low adsorption capacities due to their structure. On the other hand, LMO-LISs and LTO-LISs exhibit slow extraction kinetics but possess higher lithium adsorption capacities compared to Li/Al-LDHs. However, the adsorption capacity of LMO-LISs and LTO-LISs strongly depends on the pH of the solution, increasing with pH, whereas LTO-LISs and crown ether-based adsorbents achieve maximum adsorption capacity under neutral pH conditions. For industrial applications, adjusting the pH of the feed solution is challenging; hence, these adsorbents are suitable for naturally alkaline solutions. Furthermore, the stability of LMO-LISs remains a significant challenge that must be addressed in the future. Although LTO-LISs do not face severe stability issues, their synthesis is more costly compared to Li/Al-LDHs. Crown ether-based adsorbents show promise due to their relatively high adsorption capacity, but improvements in lithium selectivity are necessary. Simplifying and making the synthesis procedure cost-effective for industrial use is also crucial. Moreover, further studies using real brine solutions are needed. MOFs are also promising due to their tunable chemistry, high surface area, and porosity. However, their complex synthesis procedure and mechanical stability issues currently limit their industrial application.

Table 5
Comparison of different types of adsorbents used for lithium recovery.

Adsorbent Type	Advantages	Disadvantages
LiAl-LDHs	• Fast extraction kinetics • Low preparation cost • High stability and regenerability • Environmentally friendly • Good performance at neutral pH	• Poor lithium selectivity • Low adsorption capacity
LTO-LISs	• High adsorption capacity • Moderate preparation cost • Moderate stability and regeneration • Good lithium selectivity • Good environmental safety	• Slow adsorption kinetics • Good performance at alkaline pH conditions • Performance dependence on pH • Costly synthesis
LMO-LISs	• High adsorption capacity • Good lithium selectivity	• Slow adsorption kinetics • Poor stability and regeneration • High preparation cost • Poor environmental safety
Li-IIPs (Crown ether-based)	• Moderate adsorption capacity • Good performance at neutral pH • Moderate stability • Moderate extraction kinetics	• Poor Selectivity • Poor Reusability
MOF-based	• Tunable chemistry • High porosity and surface area • High selectivity	• Costly • Water stability can be challenging

2.6. Hybrid systems

In addition to the aforementioned methods for lithium recovery from brine, researchers have also explored the possibility of using a combination of diverse techniques in order to achieve higher efficiency in lithium recovery. Most of these studies focused on the integration of membrane technologies with other lithium recovery methods.

Jiang et al. [274] introduced an integrated membrane process for Li recovery from brine. Pre-concentration using ED and precipitation via Na_2CO_3 were proposed to make the process feasible via concentrating Li in the brine and preventing scaling. A novel technique, electro-electrodialysis bipolar membrane (EEDBM), a combination of electrolysis and bipolar membranes, was then introduced to produce LiOH and increase the current efficiency. Their suggested procedure included the following steps: (1) precipitation of Mg^{2+} and Ca^{2+} using Na_2CO_3, (2) preconcentration of the filtered solution containing Li^+, Mg^{2+}, and Ca^{2+} via ED, (3) fractional crystallization to get rid of remaining Ca^{2+} and Mg^{2+} ions as well as Na^+ ions from the ED concentrate, and (4) production of LiOH via EEDBM. The authors also assessed the cost of the integrated process at the lab scale, noting that crystallization and pre-concentration via ED account for 0.25–0.3 % and 10–40 % of the costs, respectively. They mentioned that the final step (EEDBM) cost is significantly higher than the pretreatment and preconcentration steps due to the high cost of bipolar membranes. The EEDBM process cost is estimated to be $2.59/kg at a current density of 30 mA/Cm^2 to produce LiOH with 95 % purity.

Qiu et al. [196] proposed a hybrid process that primarily combines SED and BMSED technologies to produce LiOH from salt lake brine with a high Mg^{2+}/Li^+ ratio (≈456). The proposed process involves five steps: (1) SED to separate Li^+ from divalent ions, mainly Mg^{2+} and Ca^{2+}, (2) further purification of SED concentrate by adding $H_2C_2O_4$ to precipitate MgC_2O_4 and CaC_2O_4, (3) ion exchange via cation exchange resins to further decrease Mg^{2+} and Ca^{2+} content, (4) SED to concentrate LiCl, and (5) after evaporation, LiCl solids with a small amount of $MgCl_2$ and $CaCl_2$ were used as BMED feed to produce LiOH and HCl. The produced HCl was intended to regenerate the cation exchange resins. In this suggested mechanism, the Mg^{2+}/Li^+ ratio decreased from 456 to approximately 49 after the second SED treatment before evaporation. In the final step, a 0.3 M LiCl solution ($Mg^{2+}/Li^+ \approx 0.195$) was fed into BMSED; LiOH with 99 % purity at a current density of 6 mA/cm^2 was obtained, reducing the ratio of Mg^{2+}/Li^+ to 0.0001.

In another study [275], the production of Li^+ hydroxide from Salt Lake brine with $Mg^{2+}/Li^+ > 30$ ratio was targeted by combining BMSED with NF, RO, and ED processes. The goals of the integrated process were determined as follows: (1) Li separation from divalent ions (such as Mg^{2+} and Ca^{2+}) via NF, (2) enriching the Li^+ content of NF permeate via RO-ED, (3) precipitation of Mg^{2+} and Ca^{2+} ions via Na_2CO_3 and NaOH before BMSED to prevent fouling of ion exchange membranes in BMSED, (4) LiOH production via BMED, and (5) production of LiOH via the evaporative crystallization. RO-ED and dual-stage NF processes before BMED were found to be effective ways to enrich the Li^+ content of the solution by separating Li^+ from Mg^{2+}. The Mg^{2+}/Li^+ ratio was reduced to below 0.5, and Li^+ was concentrated to above 14 mg/L. Moreover, the current efficiency and energy consumption of BMSED were found to be 36.05 % and 6.20 kWh/kg Li with 99.6 % purity.

Some studies also focused on membrane distillation (MD) and its integration into different lithium recovery technologies [276,277]. Gulied et al. [277] used direct contact membrane distillation (DCMD) and ESIX to recover lithium from seawater brine. They were able to recover 91.8 % of lithium from the source solution. Kalmykov et al. [276] did a simulation study on lithium recovery from geothermal brine using a hybrid precipitation system, membrane distillation, and membrane extraction. The system, with a saline solution holding 140 kg in the loop and a membrane module measuring 2.5 m^2, can produce a maximum of 1.4 kg of lithium ions. In addition to membrane systems, chemical precipitation, and solvent extraction are integrated with other lithium recovery systems [104,106]. In a study by Chen et al. [104], they proposed a CO_2 mineralization and solvent extraction to magnesium from high Mg^{2+}/Li^+ ratio brine. The integrated system has the advantage of CO_2 capturing, and the magnesium conversion rate reached 67.41 % under ideal conditions, and the magnesium-to-lithium ratio dropped from 20 to 5.4.

3. Cross-comparing technologies: identifying promising approaches for various feedstocks

So far, we analyzed and evaluated individual technologies in their respective domains. Table 6 shows the lithium concentration and the main advantages and disadvantages of lithium recovery from various feedstocks. Now, we are cross-comparing technologies and identifying the ones that are most relevant and promising for each feedstock. In this context, Table 7 provides a comparison of all technologies by outlining their underlying mechanisms, their primary challenges, and the applicable feedstocks for each respective technology and their respective Technology Readiness Levels (TRLs). These levels are assessed based on data from industrial projects and evaluations of real-world implementations. Further details are elaborated in Section 4.

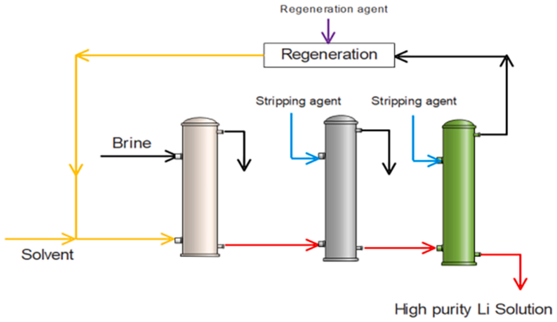
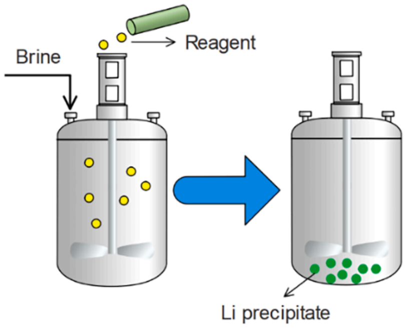
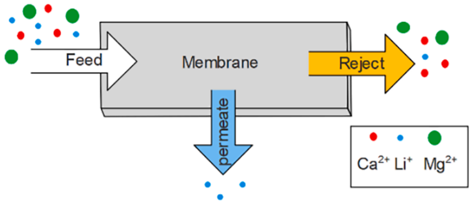
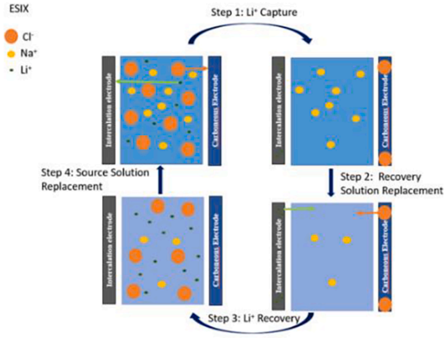
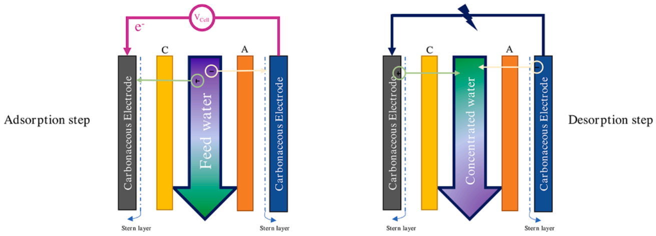
Table 6 shows the characteristics of different brine feedstocks. The most important feature in brine is the Na^+ and Mg^{2+} content. High Mg^{2+} is a major technological obstacle and it would also cause fouling for the membrane. On the other hand, Na^+ would deteriorate the final purity of products. So, it is vital to remove both of them efficiently. For high lithium sources such as salt lake (40–3020 mg/L) and geothermal brines (25–1000 mg/L), solvent extraction, chemical precipitation, EIXS, and CDI are useful. Solvent extraction and chemical precipitation technologies have already been commercialized and enable the larger-scale recovery of lithium. However, both methods face significant challenges in solvent loss and the use of chemical agents, which can have adverse effects on the environment. On the other hand, EIXS and CDI are more environmentally benign while having low energy consumption. Yet, their full potential for large-scale lithium recovery has not been realized due to current density fluctuation issues, fouling, and electrode material loss or corrosion. SED and BMED technologies have also been tested at aqueous solutions, including over 100 mg/L lithium concentrations, with SED showing promising results in recovering lithium from salt lake brines. However, both membrane technologies require feedstock pretreatment and are sensitive to scaling and the Mg^{2+}/Li^+ ratio in the feed solution. Overall, electrochemical and membrane-based techniques still need further testing in real geothermal brine and salt lake solutions to gain a better understanding of their recovery performance under complex chemistries, and new materials need to be researched

Table 6
Characteristics of various brine resources.

Feed	Li Concentration (mg/L)	pH	Advantages	Disadvantages
Seawater	0.1–0.2	7.5–8.5	Most abundant lithium resource	Low lithium content makes the recovery economically impossible
Salt lake	40–3020	6–9.3	Natural solar evaporation	Limited to specific regions & High Mg contents
Geothermal	25–1000	5–9	Geothermal energy	Many competing ions in the brine & high temperature
Oilfield Brine (Produced water)	0.3–500	4.3–7.45	Considerable amount of lithium & less land is required	High amounts of oil, H_2S

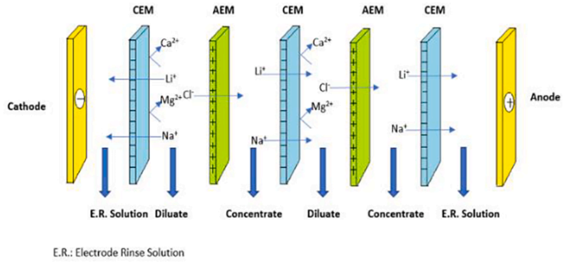
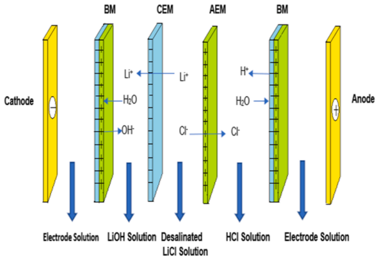
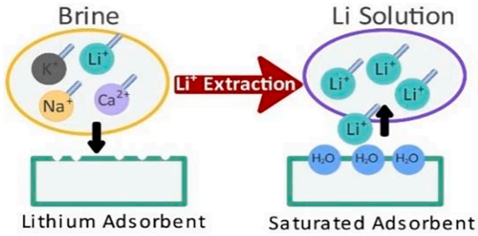
Table 7

Summary of technologies for lithium recovery. In this table, SE: Solvent Extraction, CP: Chemical Precipitation, NF: Nanofiltration, BMED: Bipolar Membrane Electrodialysis, SED: Selective Electrodialysis, CDI: Capacitive Deionization, EIXS: Electrochemical.

Technology		Feedstocks	Main Challenge	TRL
	SE	Salt lake, Geothermal & Oilfield brine	Solvent loss & corrosion	Pilot
	CP	Salt lake, Geothermal & Oilfield brine	Environmental pollution & lithium loss	Commercial
	NF	Applicable to the diluted brine solutions	Not Applicable to high Mg^{2+}/Li^{+} ratio	Pilot
	EIXS	Seawater, Salt lake & Geothermal brine	Electrodes corrosion, Upscaling necessitates a sizable area for storing and repositioning tanks holding the source and recovery solutions.	Experimental
	CDI	Seawater, Salt lake & Geothermal brine	Sensitive performance to the current density fluctuation, Fouling	Experimental

(*continued on next page*)

Table 7 (*continued*)

Technology		Feedstocks	Main Challenge	TRL
	SED	Seawater & Salt lake brine	Scaling	Experimental
	BMED	Pretreated/ concentrated Li brines	Pretreatment of feed solution	Experimental
	AD	Salt lake, Geothermal, Oilfield & Seawater brine	Additional processing steps and regeneration, Poor mobility	Commercial

and developed to overcome technological issues currently faced by these new-generation technologies. We observe that only a few recovery techniques are applicable for direct lithium extraction for seawater due to the low concentrations of Li^+ present in this feedstock. CDI is the most feasible option for recovering lithium from low-salinity sources among these technologies. However, it is important to note that the challenges previously discussed for CDI and other electrochemical systems remain relevant when applied to seawater feeds. The deterioration of electrodes has become a significant concern as more cycles are required to extract lithium from these diluted feedstocks. SED and BMED technologies are also cost-prohibitive in recovering lithium from aqueous solutions with low lithium content. For SED, the other challenge is Ca^{2+} content in the feed solution due to the precipitation of calcium if the Ca^{2+}/Li^+ ratio exceeds 10 in the feed solution. Therefore, the pretreatment of the solution or using NF can be applied to high-Ca feeds.

We also used radar plots to make a more quantitative comparison between technologies and assess the overall performance and commercial viability of each technology (Fig. 11). We evaluated the performance of each technology using five different metrics listed in Table 8, including recovery, environmental friendliness, levelized cost of recovery, operation duration, and commercial maturity, in the range of 0 to 4. For a fair comparison, technologies are compared based on the feedstock type: (a) seawater, (b) oilfield brine, (c) geothermal brine and salt lake ($Mg^{2+}/Li^+ < 10$) and (d) salt lake ($Mg^{2+}/Li^+ > 10$). For seawater, we compared only adsorption and chemical precipitation, while for oilfield brine, we also included solvent extraction. This selection is based on the fact that most studies on these two resources focus on solvent extraction, chemical precipitation, and adsorption. In these figures, a larger area signifies a more advantageous technology.

The key finding in Fig. 11 is that the chemical precipitation, following adsorption, emerges as the most effective technology compared to the other methods. Membrane and electrochemical techniques exhibit high environmental friendliness by avoiding toxic or corrosive chemicals during recovery. In contrast, solvent extraction and chemical precipitation methods cannot be classified as environmentally friendly due to their reliance on such substances. Despite environmental concerns, chemical precipitation and adsorption are the only technologies currently commercialized on an industrial scale for all types of lithium resources. This is justified because chemical precipitation has a high recovery rate compared to other methods. In contrast, solvent extraction has the lowest operational cost and high recovery rate, as shown in Fig. 11. These systems also operate continuously and enable Li_2CO_3 production. Unfortunately, despite their environmentally friendly nature, SED, BMED, and NF suffer from commercial immaturity in lithium recovery due to their low recovery rate or purity.

As shown in the radar plots, each electrochemical system (CDI-based and ESIX) has outstanding environmental positives and is relatively low cost, but the recovery ratio is relatively low for lithium. This is because the fundamental mechanism of these two mainly depends on the electrode adsorption sites (pore sites and node sites), as discussed previously. Therefore, electrochemical systems are preferable to be used as pretreatment and lithium harvesting processes for the salt lake (40–3020 mg/L), and geothermal brines (25–1013 mg/L), which contain moderate to high Li^+ concentration in the feed source compared to the seawater (0.1–0.2 mg/L). Although CDI is a viable option for recovery of lithium from seawater, such low lithium content will compromise the balance between energy consumption and recovery efficiency. Another important point is that electrochemical systems are not suitable for use as Li-posttreatment, which is the final process before distributing to the LiBs company for direct use. This is because the current final products that can be used for LiBs are either LiOH or Li_2CO_3, which are not the common lithium products recovered (LiCl) in lab testing. In addition, OH^- and CO_3^{2-} are different from Cl^- considering the pH fluctuation and deterioration effects on electrodes. Therefore, based on the current research review results, electrochemical systems still require other processes such as BMED and CP to replace the Cl^- ions

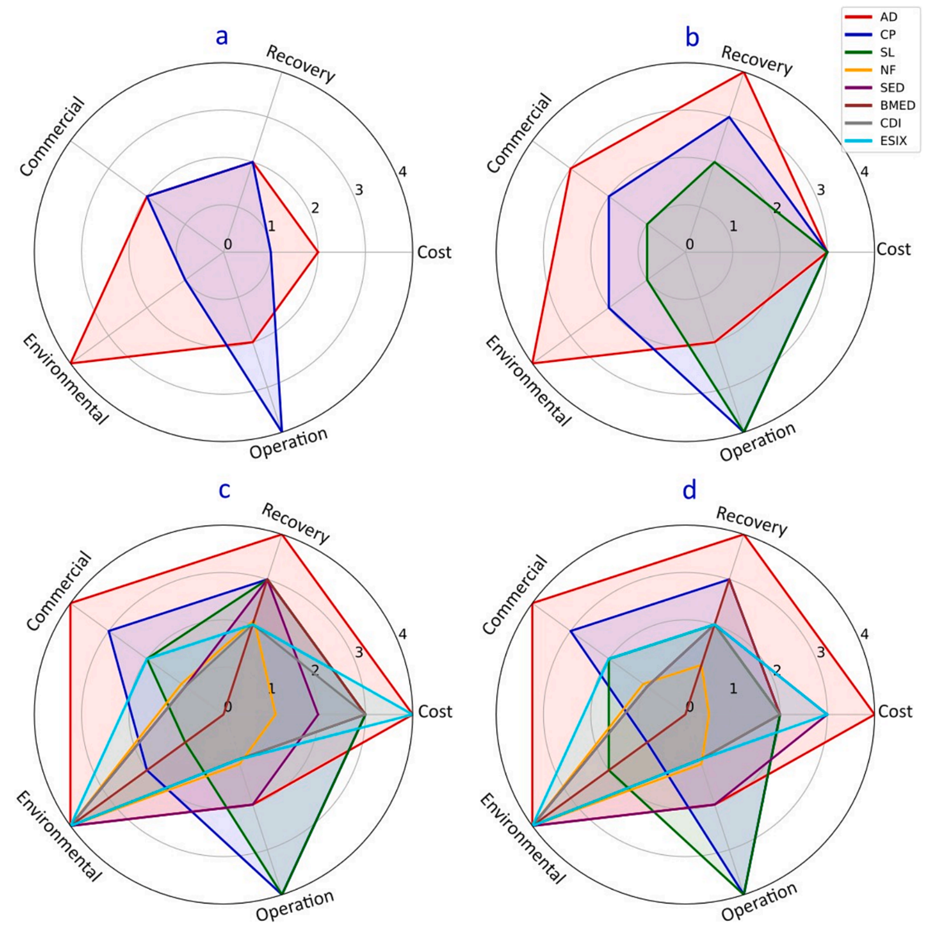


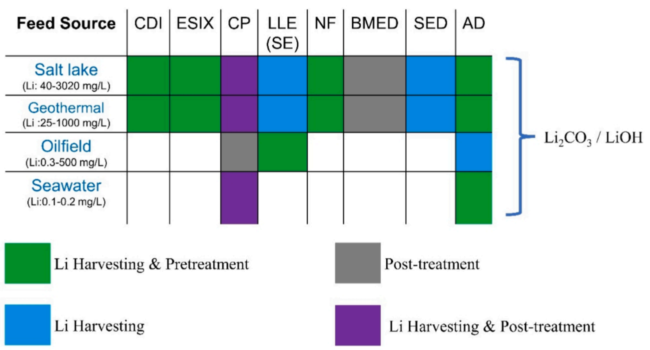
Fig. 11. Radar plots comparing different lithium recovery technologies: (a) Seawater brine, (b) oilfield brine, (c) geothermal and salt lake brine ($Mg^{2+}/Li^{+} < 10$), and (d) salt lake brine ($Mg^{2+}/Li^{+} > 10$).

Table 8
Metrics for comparison of technologies.

Metric	Environmentally friendly	Recovery	Operation Duration	Commercial Maturity	Cost ($/kmol)
0	Toxic/Corrosive waste and hazardous chemical without reuse system	less than 45	Min	Lab scale (Simulated Brine)	100>
1	Toxic/Corrosive waste and hazardous chemical with reuse system	45–65	Hours	Lab scale (Real Brine)	11–100
2	Nontoxic, Corrosive, waste without reuse of some of chemical or solvents in the process	65–90	Days	Pilot Scale (Simulated)	1–10
3	Nontoxic. Corrosive, waste with reuse of some of chemical or solvents in the process	90–95	Months	Pilot Scale (Real Brine)	0.3–1
4	No use of harmful chemical	95–99.9	Continuous	Industrial Scale (Real brine)	0–0.3

with either OH^- or CO_3^{2-} after recovery steps and additionally provide the recovered lithium for commercial use (*e.g.*, LiBs).

These comparisons also provide further insights into integrating different technologies for lithium recovery and allow us to develop a pathway specifically designed for unconventional feedstocks (Fig. 12). Lithium recovery requires three essential processing steps: pretreatment, extraction or harvesting, and post-treatment. The recovery technologies we have critically assessed can be leveraged to create process pipelines that benefit from their advantages at different stages of the lithium recovery process. For instance, chemical precipitation (CP) is a common post-treatment process for converting the harvested LiCl to Li_2CO_3 or other desired products. In addition, chemical precipitation has an untapped potential to selectively harvest lithium from high-concentration brines by reducing the solubility of ions. However, solvent extraction and chemical precipitation are not viable for direct lithium recovery from seawater due to the lower $Li+$ concentration in this feedstock. Also, no study has used these methods to directly recover lithium from seawater without concentrating on the solution first. For low salinity brines such as CDI seawater, apart from being used for harvesting lithium, membrane-based technologies such as SED and NF can serve as the pretreatment for seawater. On the other hand, BMED can only be used as a post-processing option to obtain the final product (mostly as LiOH) due to product purity problems in the presence of other cations. It is well-known that using BMED is not practical for feed solutions containing less than 4 g/L LiCl because it causes high energy consumption due to the high resistance of the solution. This makes this technology impossible to use directly for aqueous solutions with low lithium content.



Feed Source	CDI	ESIX	CP	LLE (SE)	NF	BMED	SED	AD
Salt lake (Li: 40-3020 mg/L)	🟩	🟩	🟪	🟦	🟩	⬛	🟦	🟩
Geothermal (Li :25-1000 mg/L)	🟩	🟩	🟪	🟦	🟩	⬛	🟦	🟩
Oilfield (Li:0.3-500 mg/L)			⬛	🟩				🟦
Seawater (Li:0.1-0.2 mg/L)			🟪					🟩

🟩 Li Harvesting & Pretreatment
⬛ Post-treatment
🟦 Li Harvesting
🟪 Li Harvesting & Post-treatment

Fig. 12. Integration of different processes for lithium recovery. Post-treatment is the process of converting LiCl to Li_2CO_3 or LiOH. Pretreatment involves the elimination of undesired ions, while lithium harvesting selectively recovers lithium from the solution.

4. Current status of full-scale lithium separation technology

This section explores current industrial lithium recovery projects and their practical applications. Fig. 13 illustrates the process of lithium recovery from various feedstocks, including salt lake, geothermal and seawater, and oilfield brine. We classify these sources into current sources (salt lake), emerging sources (geothermal and oilfield brine), and prospective sources (seawater).

As shown, DLE and conventional methods are two different routes to recover lithium. Both recovery routes involve several steps. Starting with pretreatments that are commonly employed to handle the variability in feed composition, which depends on factors such as location, pH, temperature, and impurities. These pretreatments entail the extraction and elimination of undesirable ions from the brine feedstock, including magnesium, potassium, and sodium. An optimal pretreatment technique should have the capability to maximize the lithium concentration. Some pretreatment technologies are softening, pH adjustment, ion exchange and membrane separation. The final step of lithium recovery is post-treatment. The main steps in post-treatment are concentrating lithium solution (LiCl) using evaporation and crystallization and then converting it to battery-grade LiOH or Li_2CO_3. Different conversion processes, such as chemical conversion of LiCl using Na_2CO_3 or electrochemical routes, will result in LiOH or Li_2CO_3. More details on pretreatment and post-treatments procedures are discussed in a recent review by Farahbakhsh et al. [42].

Fig. 13 also illustrates the processing routes for different lithium feedstocks using DLE and conventional methods. Beginning with seawater, despite containing about 230 billion tons of lithium, the low lithium concentration limits its large-scale use with existing technologies. Lithium production from seawater begins with desalination, followed by lithium recovery from the residual brine. In the case of geothermal brine, it is first used at geothermal power plants. This offers a sustainable method for clean electricity generation and lithium extraction with minimal environmental impact. Lithium extraction from these sources traditionally involves solar evaporation ponds and chemical precipitation, taking 12–18 months. Moreover, conventional methods are weather-dependent and unsustainable. However, DLE technologies are an alternative to conventional methods to recover lithium and are now being employed to shorten this processing time [278], with some DLE technologies being more widely utilized than others.

We further analyze the utilization of different DLE and conventional lithium recovery methods and identify the ones primarily employed commercially (Table 9). An examination of current projects for extracting lithium from different types of brine shows that traditional techniques, such as solar evaporation ponds, are still in use while adsorption and chemical precipitation are among the most commonly utilized DLE methods on a commercial scale. They are preferred due to their simplicity, effectiveness, high rates of lithium recovery, and capacity to handle brines with low lithium contents.

Although most of the projects are on salt lake brine, our evaluation shows an increasing emphasis on alternative sources of brine, such as geothermal and produced water. For these types of brine, adsorption is primarily utilized as shown in Table 9. Electrochemical methods are being actively investigated for the extraction of lithium from seawater (Qingdao Lithium Extraction Project). This indicates that future research and development endeavors may further enhance electrochemical methods for extracting lithium from seawater. Nevertheless, when it comes to salt lake and geothermal brines, the effectiveness of adsorption, chemical precipitation, and solvent extraction typically surpasses the possibility of producing lithium on a large scale by electrochemical methods. This is because these technologies have already proven to be successful.

Although DLE technology has been developed, traditional techniques of extracting lithium, such as solar ponds, are still utilized and not outdated. Currently, various ongoing construction projects (Mariana and Sal de Oro) employ these conventional approaches. An important observation made from studying different lithium extraction projects is

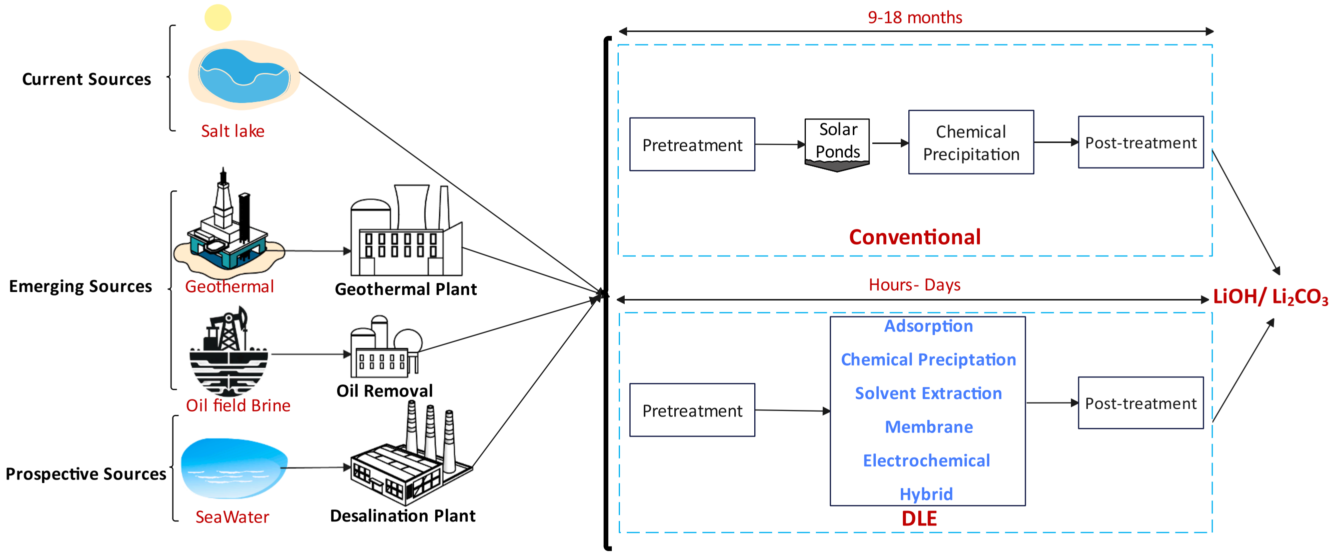


Fig. 13. Path of lithium recovery from different resources.

Table 9
Summary of lithium recovery projects from brine.

Project/ Company	Location	Technology	Brine	Stage	Ref
Yiliping Lake	Yiliping lake, Qinghai China	Adsorption (Sorbent-based)	Salt lake	Production	[278]
IBAT Modular Direct Extraction	Lake Charles, Louisiana USA	Hybrid (Adsorption-membrane)	Oilfield	Pilot	[279]
Clearwater Lithium Project	Alberta, Canada	Adsorption (Sorbent-based)	Oilfield	Pilot	[280]
Solvay	Belgium	Solvent Extraction	–	Pilot	[278]
Xinghua Lithium	Qinghai, China	Solvent Extraction	Salt lake	Production	[42]
Pure Energy Minerals	Canada	Solvent Extraction	–	Pilot	[281]
KMX Lithium Projects	–	Membrane	Geothermal and other brines	Pilot	[282]
Minmetals Yi Li Ping Salt Lake Project	Qinghai, China	Hybrid (membrane and evaporation)	Salt lake	Production	[283]
Fenix (Hombre Muerto)	Salar del hombre muerto, Argentina	Adsorption	Salt lake	Production	[284]
Silver Peak Min by Albemarle	Neveda, USA	Chemical Precipitation	Salt lake	Production	[285]
Cornish Lithium	Cornwall, UK	Testing different DLE	Geothermal	Pilot	[286]
Upper Rhine Valley from Vulcan Energy Resources	SW Germany	Adsorption	Geothermal	Production	[287]
Qingdao Lithium Extraction Project	Qingdao, China	Hybrid (Electrochemical and other technologies)	Seawater	Development	[288]
Galaxy Resources – Sal de Vida	Sal de Vida, Argentina	Evaporation, Chemical Precipitation (Conventional)	Salt lake	Production	[289]
Mariana	Salta province, Argentina	Evaporation, Chemical Precipitation (Conventional)	Salt lake	Construction (Large Scale)	[290]
Sal de Oro	Catamarca, Argentina	Evaporation, Chemical Precipitation (Conventional)	Salt lake	Construction (Large Scale)	[290]

that while certain technologies may prove effective in extracting lithium from similar sources, the choice of the right technology should be carefully customized to the unique characteristics of each project. This meticulous approach guarantees that the selected technology is perfectly in line with the specific environmental circumstances, resource composition, and economic factors of each project. As a result, it maximizes efficiency and sustainability in lithium recovery operations [283]. Finally, a comprehensive review of current lithium projects and research has pinpointed the future paths for extracting lithium from different brine sources. For lithium recovery from oilfield brine (produced water), the primary areas of study have been identified as adsorption, membrane technologies, and solvent extraction [121]. In the case of salt lake brine, the majority of research and commercial projects currently focus on chemical precipitation and adsorption. However, it is anticipated that membrane technologies will become the primary research focus for extracting lithium from this type of brine. Additionally, membrane technology is expected to play a significant role in lithium extraction from geothermal brine. Regarding seawater, while recovering lithium economically using these technologies remains challenging due to low lithium concentrations, electrochemical methods are seen as the most viable option for future advancements in this field.

5. Future directions & opportunities

Given the increasing demand for lithium, more research will be conducted on recovering lithium from secondary sources such as brines and seawater. The current commercially mature technology is adsorption and chemical precipitation. Chemical precipitation has traditionally been used with solar ponds, making lithium recovery time-consuming and spanning several months. Chemical precipitation reactions are also carried out at temperatures around 90 °C (depending on the precipitating agent), leading to high amounts of energy consumption typically supplied from non-renewable sources. Lithium recovery technology will likely move toward developing more environmentally friendly methods that will enable water conservation, energy efficiency, waste, and carbon footprint reduction. This can be achieved by integrating commercially mature technologies with emerging techniques such as CDI/ESIX, ED, BMED, or NF to create hybrid processes that leverage their advantages for enhanced recovery. However, research in emerging technologies still needs to address several technological bottlenecks. The CDI/ESIX electrodes should be enhanced, or new electrode materials should be discovered to increase their capacity for lithium harvesting applications. For NF, ED, and BMED, developing commercial lithium selective membranes will be crucial to increase the efficiency of lithium recovery. In the future, to make the lithium recovery process more economical and feasible at an industrial scale, new research directions should focus on the systems contextualization of integrated resource management techniques for the extraction of brine and the recovery of lithium. This will enable the recovery of other precious minerals, valuable by-products, and waste stream management, ultimately improving the entire value chain of energy-critical materials. Any technological advancement at the process level should also accompany techno-economic and cradle-to-grave or cradle-to-gate life cycle assessment calculations to quantify and understand any newly developed technology's economic and environmental impacts. This will further inform economic and environmental hotspots for future research and development that were not initially considered. Ultimately, a multiscale approach that spans from membrane and electrode development to industrial-scale production will contribute to a lithium recovery process that is more sustainable and efficient, improve the economic competitiveness of countries without major reserves, and accelerate the adoption of electrification and decarbonization strategies.

CRediT authorship contribution statement

Hasan Nikkhah: Writing – original draft, Investigation, Formal analysis. **Deniz Ipekçi:** Writing – original draft, Investigation, Formal analysis. **Wenjun Xiang:** Writing – original draft, Investigation, Formal analysis. **Zachary Stoll:** Writing – original draft, Supervision, Investigation, Formal analysis. **Pei Xu:** Writing – review & editing, Supervision, Funding acquisition. **Baikun Li:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Jeffrey R. McCutcheon:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Burcu Beykal:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A

Table A1

Summary of recent studies on recovery of lithium from various brine and seawater using DLE methods.

Technology	Source	Findings	Ref
Chemical Precipitation	Synthetic Oilfield brine	• **Condition**: Al^{3+}/Li^{+} • Molar ratio: 4.5; Temperature: 35 °C; contact time: 6 h • **Type of precipitant**: Al (OH)$_3$ • **Performance:** Recovery rate 75.6 %; Ca^{2+} removal rate: 93.5	[112]
Chemical Precipitation	Salt lake brine	• **Condition**: Initial Li^{+}: 5 g/L, Synthesis temperature 15 °C; synthesis time of 30 min. • **Type of precipitant**: Facet engineered Li$_3$PO$_4$ • **Performance:** Recovery rate 42.8 %	[291]
Chemical Precipitation	Salt lake brine	• **Condition**: Ratio of Al/NaCl is 3:7; Initial Li^{+}: 1 g/L, temperature 90 °C • **Type of precipitant**: Aluminum-based material • **Performance:** Precipitation rate 78.3 %; Mg^{2+}/Li^{+} mass ratio reached 0.02	[109]
Chemical Precipitation	Synthetic solution, geothermal water	• **Condition**: pH 12.5 for [133]: 50–100 mg/L; Initial Li^{+}: 10 mg/L, temperature 25 °C • **Type of precipitant**: Sodium aluminate solution as coprecipitating agent • **Performance:** Recovery rate 70.0 %	[292]
Chemical Precipitation	Dead Sea end brine	• **Condition**: Use evaporated brine; 7 g precipitant reagent; 450 rpm stirring speed; temperature: 40 °C • **Type of precipitant**: trisodium phosphate **Performance:** Recovery rate 40.0 %; Enriched lithium concentrations from 30 to 40 mg/L.	[293]
Chemical Precipitation & Solvent Extraction	Seawater brine (treated by nanofiltration)	• **Process Description**: A three-step process. 1- Divalent ion removal using [A336] [V10] diluted in p-cymene extraction system 2- lithium extraction using Mextral 54–100 and Cyanex 923, diluted in ShellSol D70 3- Ethanolic sodium hydroxide as precipitating agent for removal of impurities. • **Performance:** Total lithium carbonate yield of the process: 74 %; Near-quantitative extraction of 99.0 % Mg^{2+} and 99.2 % Ca^{2+} are removed; 98 % lithium extraction.	[294]
Chemical Precipitation & Solvent Extraction	Simulated geothermal fluid	• **Condition**: pH: 5.1–5.6; Li^{+}: 157–181 mg/L; Na^{+}: 20551–21000 • **Process Description**: Two steps process, 1- Precipitation using Ca (OH)$_2$ for removal of Mg^{2+} and silicate ions and Na$_2$CO$_3$ used to remove Ca^{2+} and other divalent ions. 2- Solvent extraction system of D2EHPA, TBP (1.5 M D2EHPA & 0.3 M TBP) and kerosene for removal of metal cation • **Performance:** 97.0 % Mg^{2+} and 98 % Ca^{2+} are removed; Lithium extraction efficiency of 87.7 %	[295]
Solvent Extraction	Oil field brine	• **Condition**: Li^{+}: 90.7 to 98.1 mg/L mg/L; O/A=1:1, Two stage process • **Solvents**: Extractant: D2EHPA; Co-extractant TBP; Diluent: Kerosene • **Performance:** Lithium extraction efficiency reached over 20 % after eight cycles; 99 % of calcium was removed.	[63]
Solvent Extraction	Salt lake brine	• **Condition**: Li^{+}: 350 mg/L; volume concentration of TBP=30 %, Fe3+/Li + molar ratio = 1.3 and O/A phase ratio = 1:1 • **Solvents**: Extractant: TBP; Co-extractant: FeCl$_3$; Diluent: diethyl succinate • **Performance:** Recovery rate 40.0 %; Separation factor lithium to magnesium: 347.8, Extraction efficiency: 65.53 %	[296]
Solvent Extraction	Simulated brine	• **Condition**: Li^{+}: 350 mg/L; 4 crossflows stages; n([Bmim]Bph$_4$)/n(Li^{+}) = 2.6, 50 % TBP/50 % CH$_2$BrCl (v/v), O/A=1:1) • **Solvents**: Extractant: TBP; Co-extractant: ([Bmim]Bph$_4$); Diluent: CH$_2$BrCl • **Performance:** Separation factor lithium to magnesium: 2754, Extraction efficiency: 99.47 %	[56]
M-CDI	Geothermal water	• **Condition:** Li: 12.6 mg/L, Na: 7363 mg/L, Mg: 38.2 mg/L; Operation time: 0.13hr; Constant voltage (2 V); Initial Li/Mg: 1.4:1 • **Material:** Lithium-manganese-titanium oxides as cathode and AEM with AC as anode • **Performance:** Removal capacity: 14 mg/g; Energy Consumption (kWh/mol): 5.606; 70 % efficiency recovery	[126]
M-CDI	Lab-made solution	• **Condition:** 30 ml/min, CV(1 V); Initial feeding water with 500 mg/L; Operation time: 10 mins • **Material:** Monovalent selective CEM with AC as electrode • **Performance:** Removal rate for Li: 10 %, Mg: 3.39 %; Energy Consumption (kWh/mol): 0.0018	[136]
Electrochemical ion pumping (EIPS)		• **Condition:** Li: 43 mM, Na: 757 mM, K:102; Current at 1C for recovery • **Material:** λ-MnO$_2$ as cathode and Nickel Hexacyanoferrate anode • **Performance:** purity from 4 % to 96 %; Li/Na = 0.053, Li/K=0.388, Li/Mg = 0.567; Energy Consumption (kWh/mol): 0.0036 with using NiHCF and 0.0041 with using Ag	[131]
EIPS	Salt lake (Atacama Chilie)	• **Condition:** Li: 43 mM, Na: 757 mM, K:102; Current at 1C for recovery	[122]

(*continued on next page*)

Table A1 (*continued*)

Technology	Source	Findings	Ref
		• **Material:** $LiFePO_4$ as cathode and NiHCF • **Performance:** Energy Consumption (kWh/mol):0.008	
EIXS	Salt lake	• **Condition:** 100 mM LiCl • **Material:** λ-MnO_2 film coated and BiOCl@Ppy coated • **Performance** Removal Capacity: 10.88 mg/g; Energy Consumption (kWh/mol):0.001	[164]
SED	Synthetic salt lake brine	• **Condition:** I = 5.9 A/m^2; T = 15.6 °C and T = 30 °C; Li^+:150 mg/L • **Membrane Type:** Asashi Selemion CSO and Selemion ASA • **Performance** Mg^{2+}/Li^+ = 150; R = 95.6 % (15 °C); SPC = 0.0019kWh/g; R = 73.5 % (30 °C)	[184]
SED	Salt lake brine	• **Condition:** E = 10 V; Li^+:34,705 mg/L • **Membrane Type:** ASTOM CIMS and ASTOM ACS • **Performance** Mg^{2+}/Li^+ = 36; R = 76.45 %; SPC = 0.66 kWh/mol	[150]
Multistage SED	Salt Lake brine	• **Condition:** I = 33 A/m^2-142.85 A/m^2; Li^+:7990 mg/L • **Membrane Type:** Selemion CSO and • Selemion ASV • **Performance** R = 90 %; Mg^{2+}/Li^+ ratio was reduced from 9.85 to 0.57; SPC = 2.65×10^{-2} kWh/mol Li^+	[297]
ED with fast ion conductor	Brine water	• **Condition:** E = 5V; 72 h; Li^+:166 mg/L • **Membrane Type:** Lithium lanthanum titanate (LLT, $Li_{0.29}La_{0.57}TiO_3$) conductor • **Performance:** Extracted lithium = 0.31 g; Average extraction speed = 0.0043 mg/h	[189]
SED	Simulated Salt Lake Brine	• **Condition:** 15.9 mA/cm^2 and 14.7 mA/cm^2 180 mL/min dilute and concentrate flow rate; Li^+:5000 mg/L • **Membrane Type:** Modified CR671 (15CE/PEI-PDA-CR671) • **Performance:** R = 90 % in Na/Li solution (4.1 g/kWh cm^2) and R = 80 % in Mg^{2+}/Li^+ solution (12.1 /kWh cm^2)	[187]
BMED	Synthetic salt solution	• **Condition:** E = 15 V and E = 30 V(optimum); Flow rate = 50L/h; Li^+:256 ± 33.11 mg/L • **Membrane Type:** Mega CEM and AEM • **Performance:** R = 57 % and SPC = 1.98 kWh/m3 (15 V); R = 74 % SPC = 5.66 kWh/m3 (30 V)	[298]
BMED	Synthetic salt solution	• **Condition:** E = 25,28,30,35 V; Li^+: 340 mg/L • **Membrane Type:** Neosepta CMB and Neosepta AHA • **Performance** R = 90.3 %(25 V), R = 94.1 % (28 V), R = 97.8 % (30 V), R = 97.7 % (35 V)	[175]
BMED	LiCl solution	• **Condition:** I = 80 mA/cm^2; Li^+:130 mg/L • **Membrane Type:** ASTOM CM-4 and ASTOM AM-4 • **Performance:** Feed was converted into 3.57 mol/L LiOH and 3.24 mol/L HCl	[193]
BMED	Pretreated salt lake brine	• **Condition:** I = 6 mA/cm^2; Li^+:1802.80 mg/L • **Membrane Type:** ASTOM CIMS and ASTOM ACS • **Performance:** 1211 mg/L Li^+;0.12 mg/L Mg^{2+}; 1.43 mg/L Ca^{2+}; SPC = 5.45 kWh/kg	[196]
NF	Synthetic salt solution	• **Condition:** Mg^{2+}/Li^+ = 30.0; pH = 6.7 ± 0.2; Li^+:392 mg/L • **Membrane Type:** QBPD modified PEI • **Performance:** Flux = 21.33 L m^{-2} h^{-1} bar; Mg^{2+} rejection = 86.7 %; Li + rejection = 5.34 %	[201]
NF	Simulated brine	• **Condition:** Mg^{2+}/Li^+ = 50.1; 0.6 MPa; 300 °C; Li^+:39.2 mg/L • **Membrane Type:** PDA/PEI modified polyamide • **Performance:** Flux = 81.6 Lm^{-2}h^{-1}bar; Mg^{2+} rejection = 98.5 %; Li + rejection = 46.2 %; Li/Mg selectivity = 33.4	[209]
NF	Simulated brine	• **Condition:** 6 bar; Li^+: 13.882 mg/L • **Membrane Type:** BTESE coated TiO_2 Membrane • **Performance:** Flux = 57 L m^{-2} h^{-1} bar; Mg^{2+} rejection = 20.3 %; Li + rejection = 74.7 %	[198]
NF	Simulated brine	• **Condition:** Mg^{2+}/Li^+ = 50.1; 5 bar; Li^+: 500 mg/L • **Membrane Type:** IL modified NF • **Performance:** Flux = 5.10 L m^{-2} h^{-1} bar; Li/Mg selectivity 6.70	[204]
Adsorption	Seawater	• **Synthesis Method:** Dissolution; regeneration, and freeze-drying • **Type:** H_2TiO_3/cellulose aerogels • **Performance:** Adsorption capacity of 24.29 mg/g at pH=10.25	[253]
Adsorption	Seawater	• **Synthesis Method:** Electrospinning • **Type:** CE/PVA microfiber • **Performance:** Adsorption capacity of 0.65 mmol/g at pH 8.32 at 30 °C; Li/Mg separation factor 516.94	[299]
Adsorption	Geothermal brine	• **Synthesis Method:** Calcination • Wet Spinning • **Type:** PSf/H_2TiO_3 • **Performance:** Adsorption capacity of 22.66 mg/g; Li/Ca selectivity factor >1408.16	[300]
Adsorption	Simulated geothermal brine	• **Synthesis Method:** Coprecipitation • Granulation • **Type:** Granular Li/Al-LDHs • **Performance:** 91 % recovery of lithium	[221]
Adsorption	Salt lake brine	• **Synthesis Method:** Coprecipitation • **Type:** Li/Al-LDHs • **Performance:** Adsorption capacity of 7.89 mg/g at 30 °C; Li/Mg selectivity 126.52	[223]

(*continued on next page*)

Table A1 (*continued*)

Technology	Source	Findings	Ref
Adsorption	Salt lake brine	- **Synthesis Method:** Hydrothermal - **Type:** H_xTiO_3 - **Performance**: Adsorption capacity of 36.3 mg/g at pH=8.8; Li/Mg separation factor 4783 at pH=8.8	[245]
Adsorption	Oilfield brine	- **Synthesis Method:** Coprecipitation - **Type:** $Li_{1.33}$ $Mn_{1.67}$ O_4 - **Performance**: Adsorption capacity of 17 mg/g	[212]
Adsorption	Synthetic salt solution	- **Synthesis Method:** Coprecipitation - **Type:** $LiMn_2O_4$ - **Performance**: Adsorption capacity of 51.9 mg/g	[301]

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