

Review

Lithium in a Sustainable Circular Economy: A Comprehensive Review

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Abstract: Lithium is a vital raw material used for a wide range of applications, such as the fabrication of glass, ceramics, pharmaceuticals, and batteries for electric cars. The accelerating electrification transition and the global commitment to decarbonization have caused an increasing demand for lithium. The current supply derived from brines and hard rock ores is not enough to meet the global demand unless alternate resources and efficient techniques to recover this valuable metal are implemented. In the past few decades, several approaches have been studied to extract lithium from aqueous resources. Among those studied, chemical precipitation is considered the most efficient technology for the extraction of metals from wastewater. This paper outlines the current technology, its challenges, and its environmental impacts. Moreover, it reviews alternative approaches to recover lithium via chemical precipitation, and systematically studies the effects of different operating conditions on the lithium precipitation rate. In addition, the biggest challenges of the most recent studies are discussed, along with implications for future innovation.

Keywords: lithium; lithium recovery; chemical precipitation; circular economy



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1. Introduction

Identified as “Energy Metal in the 21st Century”, lithium is one of the main components of electric vehicles, mobile phones, and laptops. The global demand for lithium (Li) is growing exponentially, not only due to technological evolution, but also because of environmental regulations, which are committed to reducing greenhouse gas emissions caused by fossil fuel cars [1–3]. The increase in electric vehicle manufacturing has increased the global demand for Li, and it is estimated to triple by 2025 [4–6].

There is increased interest in harvesting lithium from secondary resources such as wastewater. Recapturing waste and converting it into a raw material will further diversify lithium extractive sources, increase the metal’s availability, reduce material use, and make lithium production less resource-intensive. All of these factors support the circular economy, which is a popular concept being implemented around the world. A sustainable recovery process to harvest lithium from alternate resources is needed, and different approaches have been studied, including chemical precipitation, ion exchange, adsorbents, membrane-based processes, solvent extraction, and electrolysis-based systems [7–10].

Lithium extraction by adsorption and ion exchange methods has good performance and offers a simple design; however, most of the adsorbents used have poor regenerability,

have low adsorption capacity, and are suitable for lithium recovery in solutions with very low concentrations of Li [11,12].

The extraction of Li using membrane technology from aqueous sources still encounters many challenges due to the poor monovalent selectivity of the conventional membranes. This method only removes divalent ions, which narrows down its application with the aim of Li concentration for recovery [13]. Noteworthy factors, such as high cost, process complexity, membrane fouling, and low permeate flux have restricted their industrial use.

On another note, solvent extraction can selectively extract lithium in an individual metal system. However, the presence of other metal ions hinders the lithium extraction efficiency [10,14]. Additionally, this method involves prolonged extraction times and requires large amounts of solvent. The use of organic solvents creates serious environmental concerns, as huge leftover volumes of solvent would be generated [11,15].

Lithium extraction by electrolysis is another technology that has been studied. Yet, it is not widely used due to a large voltage being required to increase the Li recovery rate. The cost-effectiveness of this technology for large-scale production depends on energy efficiency and reliable electricity at low cost.

Interestingly, chemical precipitation is considered the most efficient technology for the removal of dissolved metal from aqueous sources. The method is relatively simple and inexpensive to operate [12]. The overarching aim of this paper is to review the technologies studied to recover lithium via chemical precipitation, along with the novel materials used, and discuss the effects of initial pH, temperature, and reaction time on the chemical precipitation rate.

2. The Nature of Lithium

Lithium (Li) is a soft, silver–white alkali metal. It is the lightest of all metals, with an atomic weight of 6939, and the 33rd most abundant element in the Earth's crust. Li has the lowest density and electrochemical equivalent of all solids: 0.53 g/cm³ and 0.259 g/Ah, respectively. These physical characteristics make lithium an exceptional material for batteries, as it offers high voltage, high energy density, and high heat capacity in comparison to any other metal [16–19]. Thus, Li known as an energy critical element and is being widely utilized in large-capacity rechargeable batteries, particularly Li-ion batteries (LIBs).

2.1. Sources of Lithium

Lithium can be found on Earth as a compound in igneous rocks, in brine aquifers, in lithium clay deposits, or dissolved in seawater. However, the two main economic resources of Li are brines and hard rock ores [20]. Around 40% of the global lithium production is from ores, and brines account for more than 60% of the production [18].

Worldwide ore-based lithium resources number more than 100. However, only three are commercially extracted from pegmatite ores. Pegmatite deposits contain Li minerals such as spodumene (LiAl(Si₂O₆)), petalite (LiAlSi₄O₁₀), and lepidolite (K(Li,Al)₃(Al,Si,Rb)₄O₁₀(F,OH)₂), among others. Spodumene is the most important lithium mineral for the market due to its high Li content. Lepidolite is the most widespread Li mineral. Lastly, petalite, which is geographically limited, as it is mainly found in Africa, is an important source of Li [21].

Pegmatite is an igneous rock, usually of granitic composition and characterized by interlocking mineral grains [22]. Even though there are various categories for granitic pegmatites, the pegmatites of greatest economic interest are the granitic LCT pegmatites. This group take its name from their geochemical trace element composition, which consists mainly of lithium, cesium, and tantalum [23,24].

Among the Li-rich pegmatite minerals, spodumene (LiAl(Si₂O₆)) is currently the main source of Li from ores and the most important for the market, due to its high lithium content and widespread availability; moreover, it is considered an easily exploitable deposit. Spodumene consists of lithium aluminum silicate, and its theoretical Li content is 8.1%, as LiO₂. At present, the largest lithium ore deposit is the mine of Greenbushes, a

spodumene deposit in Australia. Other spodumene deposits are in China, Russia, Canada, and Germany [25,26].

Petalite ($\text{LiAlSi}_4\text{O}_{10}$) is another commercial source of lithium. Petalite minerals contain 16.7% Al_2O_3 and 78.4% SiO_2 , and their Li content can vary from 1.4 to 2.2%, or 3.0 to 4.7% as Li_2O . Petalite is considered a lithium mineral of economic importance in Zimbabwe; however, large petalite ore deposits are also found in Canada, Brazil, and Australia [18,27,28]. The literature also reports a significant amount of petalite in Namibia, China, and Russia [5,18,29].

Most of the lithium is produced from spodumene and petalite, and to a lesser extent from lepidolite. Lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$), also known as lithium mica or zinvaldite, was one of the early ores mined for lithium, especially for salt production and glass fabrication. However, it has lost importance on the market due to its high fluorine content, which is around 9%. The theoretical Li content of lepidolite can vary from 1.39% to 3.58%, while this value is 3.0% to 7.7% in Li_2O . Even though this mineral is not widely found in pegmatites deposits, it is exploited and commercially produced in Zimbabwe, Canada, Namibia, Brazil, Portugal, and Argentina [18,27,30,31].

Lithium can be also found in naturally occurring salt-lake brines, which are also known as continental brine or salars. Such aquifers have the vast majority of land-based lithium in the world; nearly 70% of global lithium resources are hosted in continental brines [5,23]. Lithium extraction from continental brine is considered more economical than production from hard rock ores, and is between 30% and 50% less expensive. Therefore, it is the preferred source of Li for investors [22,23,32].

Continental brines are hypersaline aquifers, with salinity values of 1.7 to 24 times that of seawater, and they are characterized by high concentrations of dissolved ions. Continental brine deposits are normally found in underground reservoirs, contained in closed basins, with the surrounding rock formations being the cause of the dissolved elements in the brine [23,26]. Only a few places in the world have the geological characteristics and arid climate that allow the economic extraction of lithium, and currently the most developed and important brines for lithium extraction are in the salars of Chile (Salar de Atacama), Argentina, and Bolivia (Salar de Uyuni), known as the lithium triangle [12,25,33].

2.1.1. Waste a New Source of Lithium

Lithium recovery from secondary resources is crucial to meet the increasing demand for the metal and ensure the sustainability of the electrification transition with electric vehicles. In terms of sustainability, recovering Li from waste such as spent Li-ion batteries and wastewater provides a potential approach to diversify Li extraction sources and make lithium production less resource intensive.

Cathode active materials contain around 5 wt.% of lithium, or 360 kt, which is equivalent to 1900 kt of Li_2CO_3 [34]. The economic worth of lithium-ion battery recycling has been estimated as USD 22,000 per ton, based on the values of lithium and cobalt [35]. Unfortunately, less than 5% of the spent LIB waste is currently recycled [34]. Hence, substantial research has been conducted on recycling Li from spent LIBs.

The recycling process of LIBs involves physical and chemical methods. The physical separation includes disassembly, crushing, screening, magnetic separation, washing, heating treatment, etc. At present, hydrometallurgical processes, which involve leaching and reduction operations, are widely used as chemical methods to recover lithium. The major industrial processes to recycle Li-ion batteries are the Toxco process, the Sony–Sumitomo process, the Umicore process, and the Recupyl process [36]. However, lithium is only recovered by the Toxco and Recupyl processes; the other processes focus primarily on the recovery of cobalt and nickel [34,37].

The Toxco process (Canada) is designed for all types of lithium-containing waste [38,39]. This process uses cryogenic conditions, where the materials are first cooled in liquid nitrogen to reduce the reactivity [22,36]. Subsequently, the batteries are shredded and submerged

in an alkaline bath, where acid components are neutralized and lithium salts are dissolved. The dissolved Li salts are treated with sodium carbonate to produce lithium carbonate [40].

The Recupyl process (France) involves the mechanical separation of the batteries under an inert atmosphere to reduce the reactivity of lithium [22]. After the batteries are shredded and crushed, different fractions are obtained. The fine fraction is separated from the other and added to water. The lithium in the fine fraction dissolves in the water, and becomes rich in lithium hydroxide. The lithium is subsequently recovered by using either sodium hydroxide or phosphoric acid [36].

The literature reports additional lithium recovery processes, such as Accurec GmbH and AEA technology [22,38–40]. Accurec is a German pyrometallurgical process used to recycle batteries and recover Co–Mn alloy and lithium chloride. The method involves mechanical treatment to separate materials. After extracting electronic, plastic casing, aluminum, copper, and steel elements, the remaining electrode is agglomerated by adding a binder and is then pressed into briquettes. These pieces are then smelted in a furnace where two fractions are obtained, the Co–Mn alloy and lithium-containing slag. Lithium is extracted from the slag as either lithium chloride or lithium carbonate by acid leaching [22,38].

AEA technology is a patented method in the UK. The three main stages of the process are electrolyte extraction, electrode dissolution, and cobalt reduction. In this process, the spent LIBs are shredded in an inert and dry atmosphere. The electrolyte is extracted by an anhydrous solvent with a boiling point below the lithium salt decomposition temperature (~80 °C). Once the electrolyte is obtained, the cell pieces are immersed in solvent (N-methyl-2-pyrrolidone) at 50 °C to dissolve the binder—PVDF. The binder solution is filtered to separate other materials, such as residual copper, aluminum, steel, and plastic. The solvent is evaporated for reuse, and the residue (LiCoO₂ and carbon) is subjected to electrochemical reduction to obtain the lithium hydroxide solution [22,39,40].

Recent advances in the recycling of lithium-ion battery recycling are focused on hydrometallurgical processes. This method includes leaching, solvent extraction, precipitation, or electroreduction. In the leaching step, strong acids such as hydrochloric acid [41,42], sulfuric acid [41,43,44], nitric acid, and formic acid [37,45] are used, with sulfuric acid being the most common one. Hydrogen peroxide is used in the leaching process as a highly effective reducing agent, with which cobalt, nickel, and manganese are reduced to more soluble species. At the end of the recycling process, lithium is recovered and purified as a byproduct. Unfortunately, the use of inorganic acids results in the generation of a large amount of hazardous wastes with serious environmental impacts; therefore, as an alternative approach, organic acids have been explored as leaching agents in order to lessen the environmental footprint and make the recycling process more sustainable.

The use of organic acids mitigates the corrosion of equipment, minimizes the risk associated with the use of strong acids, and achieves more selective metal recovery. The most recent studies of the organic acid-assisted leaching methods included ascorbic acid [46], formic acid [47], tartaric acid [48], oxalic acid [49,50], and most recently, p-toluene sulfonic acid (PTSA), a strong organic acid [45,51]. However, the hydrometallurgical process with organic acids requires a sequence of separation and purification steps of Co and Li, making this method difficult, and resulting in product yield losses with the significant consumption of chemicals [45]. Therefore, continuous efforts are needed to find more effective organic acids, solve technical challenges, and simplify the subsequent procedures for the separation and recovery of Li.

Once the lithium is obtained in the leach liquor, the element is extracted by solvent extraction or precipitation. In first step, precipitation is used to eliminate impurities such as Cu, Al, and Fe from the leachate, followed by the solvent extraction of Co and Ni. After cobalt and nickel have been removed, lithium is precipitated by using Na₂CO₃ or CO₂ [52]. Section 3.2 contains recent studies on precipitant agents used to precipitate Li from leach liquor and wastewater from the cathode manufacturing process.

Produced water is the largest byproduct of the oil and gas sector, and thereby has significant financial and environmental implications [53,54]. Shale gas exploitation by

hydraulic fracturing and horizontal drilling in unconventional reservoirs has made possible the current flourishing of gas and oil production from shale reservoirs. However, the use of these methods results in large volumes of water being produced; in fact, it is estimated that the volume will reach 499–3585 million m³ globally by 2030 [55]. Furthermore, as wells age, there is a decrease in oil and gas production and a significant increase in the produced water. The volume of produced water could reach 98% in brownfields, leaving only 2% of oil/gas production [53]. Therefore, the growth of the market for the management and reuse of produced water is increasing.

Recent studies have revealed that produced water is a promising source of lithium, and harvesting this valuable metal from wastewater has attracted much attention from the oil and gas industry. For example, the Li concentration in Marcellus shale gas flowback and produced water is between 4 and 202 mg/L [55], Smackover brines in the U.S. contain approximately 500 mg/L of Li [7], and the Sichuan Basin (China) has an average Li concentration of 33 mg/L [55]. Oil fields such as Fox Creek and Valleyview in Canada have the potential to produce 362,000 and 385,000 metric tons of Li metal equivalents, respectively. The Smackover formation in the U.S. could potentially generate 750,000 metric tons of Li metal equivalents [7]. Therefore, produced water is a potential lithium resource. Li recovery from wastewater supports the circular economy concept by recapturing waste as a resource to manufacture a new material. Moreover, harvesting Li from produced water would not only alleviate the imbalance between supply and demand, but would also create new revenue for the oil and gas sector.

2.1.2. Global Availability

Prior to discussing the global availability of lithium, it is important to address the difference between reserves and resources and assess the available amount of lithium accordingly. Resources are geological stock that has been identified and could be mined with better technology, whereas reserves refer to the amount of lithium available for exploitation with the existing technological and socioeconomic conditions; therefore, lithium reserves are the existing sources for lithium production present in the world [30,33].

From the literature review, the consensus regarding the amount of lithium from different resources is estimated to be between 34 and 45 million tons, and the reserves available for lithium production are approximately 14 million tons. Christmann, Gloaguen [56] estimated the global lithium resources and reserves, on the basis of published data from exploration and mining companies. The compiled information contains data from 88 deposits in 22 countries, showing a total of 45.2 million tons of lithium resources and 12.22 million tons of reserves. Martin, Rentsch [26] reported above 14 million tons of available reserves and approximately 34 million tons of resources. Zhang, Hu [12] reported the resources of lithium by deposit type and its worldwide distribution. Accordingly, 26.9 million tons of lithium are found in brines, and 16.7 million tons are found in minerals, bringing the total amount of lithium resources to 43.6 million tons.

It is important to note that lithium resources have increased significantly owing to ongoing exploration, and now stand at roughly 89 million tons worldwide. New lithium resources have been identified in continental brines, geothermal brines, hectorite, oilfield brines, pegmatites, and searlesite. Moreover, recent governmental reports have revealed that over the past decade, 2021 had the largest lithium reserve volume—the total estimated reserves amounted to 22 million tons [57,58]. However, available resources need to be converted into reserves to meet the projected future consumption and ensure a reliable and diversified supply of lithium. Take into account the limited sources of Li, and we can see that it is essential to carry out Li recovery for a sustainable future. Figure 1 shows the global availability of lithium by author.

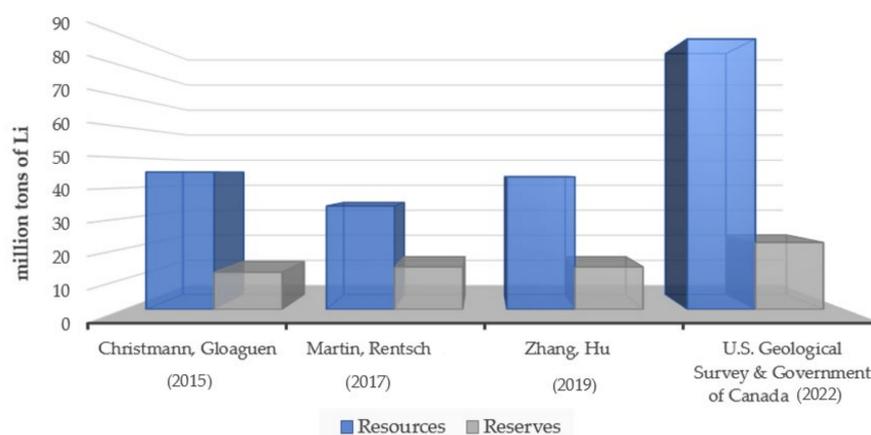


Figure 1. Lithium global availability [56–58].

2.1.3. Environmental Challenges

The processes of the extraction of lithium from brines include evaporation, crystallization, and precipitation. First, the brine is pumped out of the underground aquifer and transferred into evaporation ponds. Through solar radiation, the brine is evaporated for about one to two years [15]. During the evaporative process, some compounds such as sodium, potassium, and magnesium chlorides are removed by crystallization, at several stages of successive evaporation [5,22,59]. However, the main purpose of this stage is to increase the lithium concentration [60]. The concentrated brine is afterward brought to the carbonate precipitation phase, where residue magnesium impurities are first precipitated by calcium oxide. Subsequently, sodium carbonate is added to precipitate lithium as Li_2CO_3 . At the final stage, lithium carbonate is redissolved and reprecipitated to achieve high purity in the final product [12,15,61,62].

The use of evaporation ponds in lithium processing has raised concerns about the interaction and pollution of watercourses [59]. For instance, audit reports of the Salar de Atacama and other reports of the Uyuni Salar area (Bolivia) have indicated water contamination, increased sediment loads, landscape modifications with disturbance of the native biodiversity, and changes in the ecosystem structure, which might have negative effects on the health of local people [26,59,63].

The extraction of the brine from an underground aquifer creates an imbalance in the hydrological system, as most of the water is lost during the evaporation process and only a fraction of liquid is pumped back into the aquifer. The cone of depression (which is formed during brine extraction) expands laterally and downward, causing a reduction in the pressure gradient of the aquifer. This phenomenon causes freshwater aquifers in neighboring areas to migrate towards the brine aquifer. Therefore, usable water resources are diverted away from local communities, which is a matter of concern, as the depletion of water from these resources, especially in water-scarce areas, can negatively impact the ecosystem and locals [59,60,64]. For example, The Salar del Hombre Muerto, an Argentine Lithium brine, has brought several problems to the region. Local communities have reported that Li extraction operations have contaminated the waterways used by humans, livestock, and irrigation, along with the deterioration of the soil and air quality [59].

As a further matter, fresh water is largely used for the preparation of lime solutions and the purification of lithium carbonate [61]. Approximately 5 to 50 m^3 of freshwater is used per ton of lithium carbonate [65]. Regarding the overall sustainability of the process, there is a big question about the usage of freshwater in arid and water-scarce areas.

The evaporation processes of lithium brines produce large amounts of waste. Salt-lake brines are complex systems that contain numerous ions, and nearly all of them except lithium carbonate are removed as waste, which are currently being accumulated at the verge of the Salar. As an example, the production of 20,000 tons of Li_2CO_3 per annum

from a native brine, during a period of ten years, will generate a total amount of waste of $1.15 \times 10^7 \text{ m}^3$, and such a volume will require a disposal site of 11.5 km^2 [61]. The increased amount of waste generation is already a major issue worldwide. Additionally, land scarcity for waste disposal is a serious and growing concern [66]. Therefore, consider the contamination of land, air, and water, along with the negative impacts on human health and the environment related to land disposal.

Currently, brine is regulated as a mineral, so there is debate over the classification of lithium brine as water or mineral. Brine is classified as a mineral mainly because it is not fit for human consumption, and it is not economically feasible to make it freshwater for agriculture. However, current studies supporting the position that brine is a type of water show that by physiochemical and thermodynamic analysis, the water molecules in brine are similar in structure to the molecules in freshwater at a pressure of 1.2 atm. The study gave a scientific perspective to persuade regulators, investors, and other stakeholders to accurately classify brine as water and adopt corresponding practices during the Li extraction process, so as to minimize the negative impacts caused by the production process resulting from a misleading categorization [64,67].

Ore deposits are another important source of lithium, but with the highest impact due to the extraction process. The common procedures used for lithium beneficiation include the concentration of the spodumene by gravity separation, magnetic separation and froth flotation, and production of Li concentrate [18,30]. Heavy media separation is a preconcentration stage to separate spodumene from gangue silicates. Spodumene is slightly heavier than gangue minerals; therefore, it sinks while the others float. Subsequently, magnetic separation is used to remove iron gangue minerals. This step can be performed before or after froth flotation. The flotation stage is the most common practice used to concentrate lithium minerals from pegmatite ores. However, the surface chemistry of the minerals, among other factors, can affect the selective recovery of Li by flotation. Thus, pre-treatment of the spodumene is necessary in the separation process, to clean or modify the surface of the mineral for its flotation to be selective [18]. In what follows, a leaching treatment using sodium hydroxide is used to enhance the flotation recovery of spodumene [68]. The lithium is finally extracted from the spodumene by either acid or alkaline digestion. The final products are lithium carbonate and lithium hydroxide. The acid digestion is performed at temperatures above $250 \text{ }^\circ\text{C}$, using concentrated sulfuric acid [69], and alkaline digestion is at $1040 \text{ }^\circ\text{C}$ with concentrated calcium hydroxide [70]. In the case of H_2SO_4 , β -spodumene reacts with the acid and lithium is extracted in the water-soluble form of lithium sulfate, at $200\text{--}300 \text{ }^\circ\text{C}$ [29].

Important socio-environmental impacts are caused by lithium mining operations from spodumene ores. To begin with, there are the toxic emissions caused by blasting operations, which are conducted prior to ore extraction and processing [60]. The concentration of lithium in hard rock sources requires large amounts of spodumene ore to obtain economically significant quantities, resulting in substantial volumes of waste rock [71]. Furthermore, toxic tailings are among the waste products of the extraction and processing of the ore. For example, during the processing of spodumene concentrate with sulfuric acid, large amounts of reagents are used, which lead to large waste yields [29,30].

Apart from the large amount of toxic waste generated, there is a concern about unscrupulous business practices. For instance, in 2017, a survey report showed that around 2 billion pounds of hazardous waste was thrown into watercourses by mining companies, representing a severe risk to human health and aquatic life [15]. Regarding waterways, the ore-based production of lithium involves the high consumption of water—in fact, its use of freshwater is higher than in brine-based production [25,60].

The production of lithium from spodumene ores is a significant contributor to greenhouse gas emissions, as the electricity generation required is carbon-intensive. Additionally, the energy consumption is rather high. As shown in the life cycle analysis performed by [25], one of the reasons is that the means of generating energy during the extraction process from Australian spodumene ore rely only on fossil fuels (diesel). Moreover, the

subsequent processing of the spodumene concentrate into either carbonate or lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) at a Chinese facility is performed using coal for heat energy.

2.2. Lithium Applications

Lithium is mainly used in the fabrication of Li-ion batteries (LIBs). These batteries are the most promising rechargeable batteries owing to their unique qualities. LIBs are not only widely used in electronics and vehicles, but also in the wheeled, naval, and aviation sectors. Lately, lithium-ion batteries have attracted attention from industry, academia, and governments, as their use in energy storage systems offers a new means of grid energy storage. Li-ion technology has the potential to eliminate the need for costly peak power plants, and at the same time incorporates the usage of renewable energy sources [72–75].

Lithium is a versatile material used for a wide range of applications. The major Li products are used in the manufacture of lubricants, ceramics, glass, synthetic plastics, rubber, pharmaceutical products, and metal alloys [19,76]. Lithium stearate is used in automotive, military, industrial, aircraft, and marine sectors as a high-temperature lubricant grease. The lithium-based grease provides high resistance to water, does not react with oxygen, and does not solidify at low temperatures.

Lithium carbonate is extensively used in the fabrication of glass and ceramics to control thermal expansion and improve thermal resistance. In the production of synthetic rubber and plastics, Li is used as a catalyst [77]. Styrene-butadiene rubber (SBR) is widely used in the production of tires. In the production of SBR, n-butyl lithium, an organic lithium compound, is used as the initiator of the polymerization reactions. n-Butyl lithium, n-butyllithium, and sec-butyl lithium are used to produce polymers with thermoplastic properties [26]. Lithium has been used in the main pharmacological treatment for bipolar disorder; it has been also used for the production of flavors and fragrances [78].

In the metallurgical industry, Li is utilized as a flux to promote the melding and soldering of metals, as it absorbs impurities and inhibits the formation of oxides. Lithium–magnesium and lithium–aluminum alloys are widely used in the manufacturing of armored vehicles and in aerospace products, as these alloys are lightweight and strong. The composites of lithium with cadmium, aluminum, copper, and manganese are used in several aircraft components. The Mg–Li alloy is the lightest, most versatile material commercially available [77]. Lithium niobate and lithium tantalate wafers are used for the production of microchips for electronics [26].

Lithium chloride is utilized in industrial dehumidifier and drying equipment. Lithium bromide is an absorbent in industrial absorption chillers. Lastly, lithium and lithium peroxide are employed to reduce carbon dioxide from the air in submarines and spacecraft [26].

Electric Vehicles Market

Global warming, or climate change, is perhaps the biggest threat to this planet. For instance, the average global temperature has increased by 0.85 °C since the pre-industrialization period [79,80]. Greenhouse gases (GHG) are the major contributing factors to climate change and air pollution, and a significant source of GHG is the transportation sector. For example, according to United States Environmental Protection Agency (EPA), in 2020 transportation accounted for the largest portion (27%) of total U.S. GHG emissions, and among cars, trucks, commercial aircraft, railroads, and other sources, light-duty vehicles emitted more greenhouse gases than any other [81].

Electric vehicles (EVs) are considered a potential solution for a sustainable and low-carbon transportation system, and an important step to reducing emissions and mitigating climate change. EVs do not produce pollutant emissions, as their internal source of energy is an electric motor powered by electric batteries. Additionally, the powertrain offers the possibility of operating with zero emissions. EVs not only offer maximum protection for the environment, but also unique features and advantages. For example, EVs are quieter and overall smoother than gas-based cars. The main reason is that the electric motor provides high torque to the wheels, resulting in smoother acceleration and deceleration, together

with zero noise emissions, while operating. These vehicles have been efficiently designed to use the electric motor as a propulsion source and as a generator when decelerating or when moving by gravity. This type of “energy recovery” technology is an important feature in EVs, as it increases the overall energy efficiency of the car [82]. The electric motor of an electric car is smaller than an internal combustion engine, resulting in spacious interiors. With neither a gearbox nor a clutch, EVs make driving hassle-free.

Lithium plays an important role in the development of electric vehicles, as these are powered by Li-ion batteries. These batteries are the best available due to their superior qualities and cutting-edge technology. They have the highest energy density, volume, and mass. LIBs are the most efficient technology for energy storage, as a high density of Li ions can be stored with respect to the battery weight (energy density). By way of comparison, a Li-ion battery provides an energy density (300 to 500 Wh/kg) that is ten times greater than that of a lead-acid battery. Among other features, Li-ion batteries offer one of the highest coulombic efficiency levels (charge and discharge efficiency), a high voltage output, good high-temperature performance, light weight, easy recharging, durability, and the recycling of some of their components, which aligns with the principles of the circular economy, making this technology even more attractive [83,84].

A Li-ion battery consists of two mixed ion and electron conductors as the anode and cathode, which are separated by a separator and an ion-conducting electrolyte [85]. These batteries work on the principle of insertion reactions, where both electrons are atomic frameworks that host mobile lithium ions as charge carriers. Hence, when the battery is charging, lithium ions move from the cathode to the anode, and they move back during discharging [86]. The composition of the battery elements is an essential factor to achieve high performance in the battery, and alternative electrochemical arrangements are being developed in an effort to produce energy storage devices with a higher energy density.

The cathode is one of the critical components in LIBs and the main sources of the active lithium ions. To achieve high capacity and energy output, a significant amount of lithium is contained in this component. As a fact, LIBs in the market are referenced according to the cathode composition, and the key decisive factors in the material selection are gravimetric energy (capability of quick charging), power density, structural stability, safety, and cost [87–89]. On the other hand, the anode can enhance the inserting and escaping capacity of the lithium ions, and this electrode can be made of either carbon and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), Li metal, or Li (Si) alloys. The battery electrolyte is a solution that allows Li ion transfers between electrodes, and it should provide high lithium-ion transport under any operating and external conditions, such as extreme weather. The electrolyte is usually a lithium salt, such as lithium hexafluorophosphate (LiPF_6) or lithium perchlorate (LiClO_4) dissolved in a mixture of ethylene carbonate and either dimethyl carbonate, diethyl carbonate, or ethyl methyl carbonate. This organic solvent is selected for its high electrochemical stability, meaning the battery is able to operate on a higher voltage range. However, the composition could change based on the electrode material [90].

The separating membrane is a micro-porous material that allows Li-ions to pass across the pores, and is an important component for ensuring the safe operation and service life of the battery. These separators should be mechanically robust, electrochemically stable, electrolyte wettable, flexible, and offer high lithium-ion conduction. Separators should be equipped with thermal shutdown to prevent safety issues caused by the elevating temperature during operation. This feature can promptly cut off the current and prevent the electrodes from contacting [87,91,92].

2.3. Lithium Demand and Economic Perspective

According to forecasts, global lithium demand will increase significantly, and it is expected to become scarce [30,93]. Investors’ reports affirm that the demand might treble by 2025 and outpace supply [94], and other sources forecast the global demand for Li will exceed 2 million metric tons by 2030 [6,95]. The accelerating electrification transition,

supported by the global commitment to decarbonization, will be a strong driver of Li consumption in the next decade.

The surge in lithium demand goes alongside the exponential growth in the sale of electric vehicles. The improved range, broader model availability, and increased performance are among the factors driving sales. In addition, EVs are being promoted by policymakers through various policies and incentives, such as rebates, tax credits, discounts, zero-interest loans, and charging station deployment [26,96]. In relation to carbon neutrality targets, there is an expectation for energy storage applications to keep pace with the strong growth in renewable energy deployment around the world.

Lithium has many end use applications aside from batteries, as previously mentioned. The global consumption of the metal is mainly in the lithium battery sector: 46% of the lithium produced is used for battery production. However, glass and ceramics manufacturing consume a significant amount as well—over 27%. Lubricants and greases account for 9%, and continuous casting and polymer production consume around 5% each. Additional industrial applications, such as sanitization, organic synthesis, construction, pharmaceuticals, alloys, and alkyd resins, account for about 9%. The estimated share of the global lithium market is shown in Figure 2 [18,26].

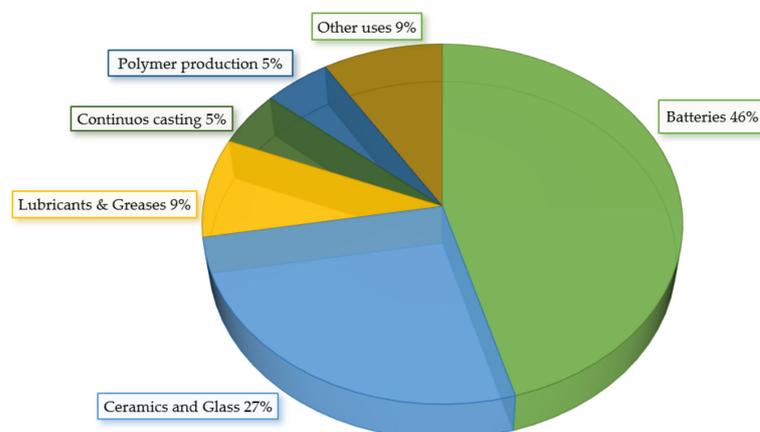


Figure 2. Global lithium end-use market shares [18,26].

The increasing demand for lithium is affecting the price of the metal. In addition, lithium deposits are concentrated in a small number of countries; therefore, there is only a limited supply of this element, a factor that also determines the price of the metal. As shown in Figure 3, in 2010, the lithium carbonate price was under 4000 USD/t, and at the end of 2015, the value rose to 6900 USD/t. This is an increase of 56% in just five years. By 2016, it amounted to 7200 USD/t [26], and in 2021 the average price was estimated at 17,000 USD/t [57]. The price of lithium in the world market will continue increasing as demand is expected to outstrip supply. Financial institutions affirm that supply could be stretched to meet the current demand; however, the response might not be enough to contain the lithium price [94].

The global demand for Li will be difficult to meet unless alternate resources and efficient techniques to recover this valuable metal are implemented. Investing in research and innovation is a critical enabler for the development of new technologies to recover lithium and secure a sustainable supply of the raw material. Funding and more engagement from electronics manufacturing companies and automakers (the biggest consumers of lithium) will increase the likelihood of novel supply coming to the market. Therefore, it is essential to look for more alternatives to cater to the demand for Li in various fields.

As noted earlier, precipitation is touted to be the most efficient, cost effective, and practical solution. It should be placed as the top consideration for Li recovery.

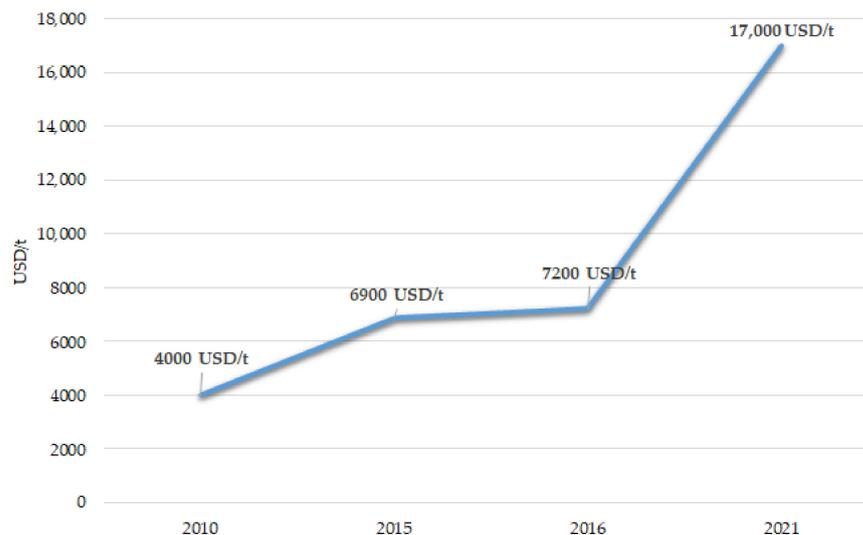


Figure 3. Lithium carbonate price (2010 to 2021) [26,57].

3. Lithium Recovery via Chemical Precipitation

Chemical precipitation is a method used in wastewater treatment to remove ionic components from aqueous wastes by adding counter-ions to reduce their solubility, thereby changing a dissolved material in water into solid particles. It is considered the most efficient technology for the removal of trace metals and rare earth elements from wastewater. The method is relatively simple and inexpensive to operate. The adjustment of pH is an essential step in the precipitation process. For instance, in some scenarios, basic conditions usually allow the dissolved metal to be converted into solid metal hydroxide, which is separated by sedimentation or filtration [97].

Lithium recovery via chemical precipitation has been the object of study in the past few decades. Different approaches have been developed, such as the carbonate precipitation method, phosphate precipitation method, and aluminate precipitation method.

3.1. Current Technology and Challenges

As previously mentioned, the traditional evaporation method requires large evaporation ponds, is time intensive, and is not suitable for all geographical locations, as it requires a dry climate and abundant sunlight. On the other hand, the efficiency of lithium recovery depends on the brine composition, as these aquifers contain high concentrations of other ions, and the co-precipitation of these impurities makes Li extraction more complicated. For example, lithium and magnesium are both alkali/alkaline earth metals and share similar ionic properties, as their ionic size is almost the same. Additionally, their radii are similar: 72 pm for Mg^{2+} and 76 pm for Li^+ . Therefore, mining Li from brines with a high Mg/Li ratio has been a decades-long technical challenge. A high Mg/Li ratio requires large amounts of precipitant, which results in a huge amount of solid waste generation and high costs. Additionally, the method has a low recovery rate, as lithium is lost due to co-precipitation [98,99].

Carbonate precipitation is the current technology used for lithium extraction from brines at an industrial scale. However, this conventional process is ineffective for most new brine discoveries, with a low concentration of lithium. To obtain a significant level of lithium recovery, the initial Li concentration should be greater than 20 g/L [12]. In addition, the solubility of the precipitate Li_2CO_3 is still considerably high ($K_{sp} = 8.15 \times 10^{-4}$); therefore, a large amount of Na_2CO_3 is used. In addition, a high temperature ($\sim 100^\circ C$) is required to precipitate Li as Li_2CO_3 , due to its lower solubility at higher temperatures. Such processes make the mining of Li from brines challenging when it is at a low concentration [100–102].

3.2. Current Advancements

In the past few decades, the chemical precipitation of lithium has been intensively studied from an economical and scientific perspective. Different materials have been used, such as carbonate, phosphate, and aluminate, in the precipitation method.

Several studies have been conducted using sodium phosphate salts, such as Di-sodium phosphate (Na_2HPO_4), tri-sodium phosphate (Na_3PO_4), sodium pyro-phosphate ($\text{Na}_4\text{P}_2\text{O}_7$), and sodium tri-polyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) [103–106]. The results obtained by Alsabbagh, Aljarrah [103] show that the four types of salts studied can be used as lithium-precipitating reagents, as the lithium recovery achieved was between 23% and 27%. However, the highest percentage of lithium recovery was achieved by using tri-sodium phosphate (TSP). The research obtained a 40% recovery rate using TSP in a Dead Sea evaporated end brine with an initial lithium concentration of 40 mg/L [103]. Alsabbagh, Aljarrah [103] studied the effects of operating conditions, and the results show that the amount of precipitating reagent had a significant effect on the percentage of Li extracted. In this phase, 1 to 10 g of TSP was used, and 7 g achieved the highest recovery. The stirring speed was adjusted from 150 to 1000 rpm and the ANOVA statistical analysis showed that the stirring speed had a substantial effect. The best percentage extracted was reached at 450 rpm. The time was studied from 30 to 180 min, and the results show that the Li extraction rate did not change significantly with time, and two hours is enough for the process. Finally, the study on the influence of the temperature showed that at 40 °C, the percentage of Li extracted was slightly better than that at other temperatures (25–70 °C). Accordingly, at optimum conditions, more than 40% of the lithium was extracted from Dead Sea evaporated end brine using TSP. In this work, the pH value was neither changed nor studied.

Mulwanda, Senanayake [107] recovered lithium from an alkaline leach solution using phosphoric acid (H_3PO_4). With the purpose of increasing the efficiency of lithium extraction as Li_3PO_4 , the study alternatively used H_3PO_4 instead of Na_3PO_4 to minimize the presence of sodium ions (Na^+) in the alkaline liquor. The Li-to-P molar ratio was varied from 3:1 to 3:2 to evaluate its effect on the lithium precipitation rate. The operating conditions were fixed to 90 °C, with a 2 h reaction time, initial pH of 12.5, and initial lithium concentration of 5.6 g/L. The highest precipitation efficiency (92%) was obtained at a Li:P ratio of 3:2; however, the XRD scan of the precipitate showed an additional phase in the solid, Li_2NaPO_4 (impurity). Therefore, the authors determined a molar ratio of Li:P = 3:1.6 as the most desirable, achieving around 83% recovery as Li_3PO_4 .

As a new resource of lithium, Shin, Jeong [108] used the waste Li solution generated from the cathode manufacturing process. The recovery of Li as Li_3PO_4 was achieved by using phosphoric acid with the Li/ PO_4 molar ratio of three. The effects of the initial Li concentration and the reaction time were studied in a synthetic solution at room temperature for three days. At various Li concentrations of 100, 250, 500, 1000, 2000, and 3000 mg/L, the results indicate that no precipitation was observed when the initial concentration was lower than 250 mg/L; once it was increased from 500 mg/L to 1000 and above, the precipitation reaction started increasing, reaching equilibrium within 12 h.

Shin, Jeong [108] concluded that the number of lithium and phosphorus ions in the solution can be a relevant factor to the precipitation rate of Li_3PO_4 ; therefore, at concentrations lower than 1000 mg/L, precipitation was not achieved due to a low number of Li-P nuclei. In contrast, at initial Li concentrations of 1000, 2000, and 3000 mg/L, the precipitation efficiencies achieved were 87%, 96%, and 97%, respectively, after three days of reaction. The study tested the phosphoric acid at the Li/ PO_4 molar ratio of 3 in a real Li waste solution with a concentration of 2174 mg/L. The experiment was conducted at pH values of 7.0, 9.2, 11.0, and 12.4, and the precipitation efficiency achieved went from 0.2 to 81%, which indicated that the higher the pH, the higher the precipitation efficiency of Li_3PO_4 . In the same study, tri-sodium phosphate was tested to evaluate the precipitation efficiency of each precipitating reagent. The experiment was conducted at a Li/ PO_4 molar ratio of 3, initial Li concentration of 2000 mg/L, and initial pH of 12.9. After 24 h of reaction,

the results revealed that H_3PO_4 had 92% precipitation efficiency, whereas the Na_3PO_4 recovered was 87%.

The precipitation of lithium with activated aluminum-based alloys was proposed by Li, Zhao [109]. Li was recovered as $\text{LiCl}\cdot\text{Al}(\text{OH})_3\cdot x\text{H}_2\text{O}$. At first, Al–Ca alloy and Al–Fe alloy, each with 70% aluminum contents, were assessed to determine the lithium precipitation performance. The experiment was conducted with an initial Li concentration of 1 g/L, at 70 °C, 4:1 Al/Li ratio, and with a three-hour reaction time. The results obtained show that the precipitation rate of lithium with Al–Ca alloy was 93.6%, whereas the Al–Fe alloy achieved only 23.8%. In the subsequent experiments, the effects of the molar ratio of Al to Li, the Ca content of the Al–Ca alloy, the initial Li concentration, the reaction temperature, and the reaction time were evaluated to determine the optimum conditions.

With an initial lithium concentration of 1 g/L, a 3 h reaction time, at 70 °C, and with a 30% Ca content in the Al–Ca alloy, the results show that the molar ratio of Al/Li had a significant effect on the lithium precipitation rate. At the Al-to-Li ratio of 2:1, the recovery achieved was only 72.1%. However, the precipitation rate was improved as the molar ratio was adjusted to higher values, and at an Al/Li of 3.5:1, the process achieved 93.8% recovery. However, as the molar ratio continued to increase, an insignificant improvement in the precipitation rate was obtained. The calcium content in the Al–Ca alloy also played an important part in the precipitation process. In this phase, the Ca content was varied from 10% to 40%, and the results showed a significant increase in the Li extraction rate, from 87.1% to 94.7%, as the Ca content was adjusted from 10% to 35%. This improvement was attributed to an Al–Ca alloy with a larger surface area as the Ca content was increased.

The initial lithium concentration did not show a major effect on the precipitation rate. The recovery achieved went from 71.3% to 95.3% when the lithium-ion concentration was adjusted from 0.4 to 0.8 g/L. Still, greater values did not exhibit better recovery rates. When the temperature was evaluated, it was found that at temperatures over 70 °C, the lithium precipitation rate significantly dropped, going from 93.6% to 66% once the temperature was raised from 70 to 90 °C.

This phenomenon was attributed to thermal motion at high temperatures, where part of the $\text{LiCl}\cdot\text{Al}(\text{OH})_3\cdot x\text{H}_2\text{O}$ decomposes and LiCl dissolves. Finally, with the previous parameters evaluated, the effect of the reaction time was studied, from 0.5 to 3 h under the conditions of a 3.5:1 Al/Li molar ratio, 35% Ca content, 8 g/L initial Li concentration, and 70 °C. The precipitation reaction was very fast, and after 1 h, 94.6% of the lithium was extracted from brine using the Al–Ca alloy.

As mentioned in the previous section, the extraction of lithium in brines with high Mg/Li mass ratio is one of the main challenges of the precipitation process. The study conducted by Liu, Zhong [99] tested aluminum-based materials in a salt-lake brine, to evaluate the influence of the Mg/Li mass ratio, among other parameters, on the Li precipitation rate. The Al-based materials showed good results, as the extraction rate achieved was 64.8% of Li and only 0.8% of Mg, in a solution containing 1 mol/L LiCl and 1 mol/L MgCl_2 .

The following experiments were conducted using a solution containing an initial Li concentration of 1 g/L and 20 g/L of Mg. The temperature is an important factor in the precipitation process, and in this case had a significant effect when it was increased from 20 to 90 °C. The Li precipitation rate reached 65.8% at 80 °C, whereas only 18.14% was acquired at 20 °C. Interestingly, the result shows that Mg is independent of the change in temperature, as its precipitation rates at various temperatures remained below 0.16%. The reaction time was evaluated, and the results show that from 60 to 180 min, the precipitation rate improved from 34.8% to 62.8%. However, when the reaction time was above 180 min, an insubstantial change was obtained. The concentration of Mg was fixed at 20 g/L to study the effect of lithium initial concentration on the extraction of Li. As the lithium concentration was adjusted from 0.2 to 1 g/L, an evident increase in the precipitation was observed, from 30% to 64.8%. However, it dropped to 52.3% when the Li concentration was 1.5 g/L. The authors determined that as a large number of precipitates are formed at a higher Li concentration, the surface of the Al-based materials gets coated, which

decreases the reaction performance. The incrementation of the initial concentration of Mg^{2+} was studied to determine its effect on the Li precipitation rate. The results reveal that an excess of Mg^{2+} in the solution had detrimental effects on the precipitation of Li. The Li precipitation rate dropped from 78.3% to 49.4% when the Mg initial concentration was increased from 15 to 40 g/L.

The production of high-purity lithium carbonate with the current technology requires re-dissolution and re-precipitation of the already precipitated Li_2CO_3 . This method consumes large amounts of freshwater and chemicals. Additionally, a high Li concentration is needed to obtain a high Li recovery rate. Zhao, Zhang [101] proposed a potential approach to recover lithium from a low-concentration Li solution and obtain industrial-grade Li_2CO_3 by a one-step precipitation method, with the use of ultrasound. Initially, a comparison of ultrasound and a stirring method at different initial lithium concentrations was conducted to assess the effects of both technologies on the Li recovery rate and purity grade of Li_2CO_3 . The results show that at an initial Li concentration of 10 g/L, the Li recovery rate by the ultrasound method outstripped that of the traditional technology, as more than 80% of the Li was extracted. In addition, the Li_2CO_3 produced exceeded industrial-grade purity. On the other hand, the traditional stirring method recovered over 80% of Li only when the initial Li concentration was raised to 20 g/L. Moreover, this technology did not achieve the desirable purity for industrial-grade Li_2CO_3 .

Ultrasonic radiation was used to increase the efficiency of the precipitation reaction. The reason involves the formation of cavitation bubbles that provide hot spots with very high temperature and pressure gradients, and these spots can enhance mixing and particle collisions and facilitate the chemical reaction. As part of the study of the ultrasound technology, the power was varied from 90 to 300 W, at 20 KHz, to improve the recovery rate of Li. The results show an increase of more than 10% when the power was incremented from 0 until 150 W. However, at values above 150 W, minor changes were obtained.

The influences of the amount of precipitant reagent (Na_2CO_3) on the lithium precipitation rate and the purity of Li_2CO_3 were evaluated. The dosage was changed from 1 to 1.4 Na/Li (molar ratio). In this phase, the Li recovery rate increased, but the purity of Li_2CO_3 declined. The authors deduced that the increase in carbonate ions in the solution will accelerate the chemical reaction and improve the extraction of lithium. However, the presence of more ions could increase the probability of being trapped in the Li_2CO_3 complex, which increases impurities in the final product and reduces its purity. It is important to highlight that the study investigated the difference between dosing solid Na_2CO_3 versus a highly concentrated Na_2CO_3 solution in the Li recovery. The solid precipitant achieved a higher lithium recovery rate than the saturated solution. Therefore, the solid Na_2CO_3 was used throughout the whole study.

The effect of the reaction temperature was evaluated, and the results showed that the increase in the temperature accelerated the rate of the chemical reaction. When it was raised from 25 to 80 °C, the Li recovery went from 64 to 82%. Moreover, the reaction reached equilibrium in only 5 min at high temperatures. The purity of the Li_2CO_3 also improved from 96% to 99%. Such an increase was attributed to the high temperature, as Na_2CO_3 remained in solution without affecting the precipitate composition, whereas at low temperatures, the Na_2CO_3 dissolved gradually, and some of the undissolved particles were wrapped in the Li_2CO_3 precipitate.

At optimum conditions of 10 g/L of Li, solid Na_2CO_3 , ultrasonic power of 150 W, and 35 min reaction time at 80 °C, the lithium recovery rate reached 82.62%, and the Li_2CO_3 was 99.01% pure. The recovery of residual lithium (2 g/L) in the filtrate was consequently extracted by the Na_3PO_4 precipitation method. Therefore, the overall recovery rate reached by the researchers was 97.4%.

3.2.1. Materials Used in the Recovery Process

In the past few decades, the chemical precipitation of lithium from aqueous sources has been intensively studied, and different materials and methods have been proposed—

in particular, carbonate precipitation, phosphate precipitation and aluminate precipitation. Table 1 shows the precipitant materials used for the extraction of lithium from various Li-containing solutions and the lithium recovery rate by precipitant at optimum operating conditions.

Table 1. Lithium recovery rate by precipitant at optimum operating conditions.

Reagents/Precipitant	Dosage	pH	T (°C)	Time (hours)	Efficiency (Li Recovery)	Reference
Sodium carbonate (Na ₂ CO ₃)	Stoichiometric amount of solid Na ₂ CO ₃	12	80	3	72.9%	[110]
Lime milk, NaOH, oxalic acid and carbonate	-	4.6	85	-	84%	[111]
Al–Ca alloy	Al/Li mole ratio of 3.5:1	-	70	3	94.6%	[109]
Aluminum powder and NaCl	-	6	80	3	78.3%	[99]
Tri-sodium phosphate (Na ₃ PO ₄ ·12H ₂ O)	1:1 theoretical amount	11–13	25	5	96.5%	[102]
Tri-sodium phosphate (Na ₃ PO ₄)	PO ₄ ³⁻ /Li ⁺ molar ratio of 1.3:3	-	65	2	65%	[106]
Sodium carbonate (Na ₂ CO ₃)	Na/Li molar ratio of 1	-	80	0.6	82.62%	[101]
Sodium carbonate (Na ₂ CO ₃)	CO ₃ ²⁻ /Li ⁺ molar ratio of 1.1:2	7–8	95	-	46.5%	[112]
Al/Na ₂ SO ₄ composite	Al/Li mole ratio of 3:1	-	70	3	89.2%	[113]
NaOH and Na ₂ CO ₃ solution	-	-	80	1.5	85%	[100]
Aluminum chloride (AlCl ₃ ·6H ₂ O)	30–40 g/L	6.6–7.2	25	3	90%	[93]
Al/Na ₂ SO ₄ composite	Al/Li mole ratio of 3:1	-	70	3	89.2%	[113]
Tri-sodium phosphate (Na ₃ PO ₄)	Li/Na ₃ PO ₄ mole ratio of 1	9.5	90	5	95.4%	[105]
Tri-sodium phosphate (Na ₃ PO ₄)	5 g/L	6.3	40	0.5	40%	[103]
Facet engineered Li ₃ PO ₄ crystal and sodium phosphate dodecahydrate (Na ₃ PO ₄ ·12H ₂ O)	40 g/L(S/L ratio) seed + 3:1 theoretical Li ⁺ /PO ₄ ³⁻ molar ratio of Na ₃ PO ₄ ·12H ₂ O	10–12	30	0.5	51.62%	[114]
Tri-sodium phosphate dodecahydrate (Na ₃ PO ₄ ·12H ₂ O)	Li/P mole ratio of 3:1	10–10.3	30	2	88.49%	[115]
Tri-sodium phosphate (Na ₃ PO ₄)	1.2:1 theoretical amount	8	70	1.5	88.44%	[104]
Activated Al–Ca and Al–Fe alloys	30–40 g/L	-	70	1	94.6%	[15]
Phosphoric acid H ₃ PO ₄	Li/P mole ratio of 3:1.6	12.5	90	2	83%	[107]
Phosphoric acid H ₃ PO ₄	Li ⁺ /PO ₄ ³⁻ mole ratio of 3	12.4–13.5	25	24	81%	[108]

3.2.2. Operating Conditions and Performance

The lithium recovery rate and the operation conditions can differ considerably among precipitant materials. Additionally, the nature of the Li-bearing solution appears to be a

determining factor that influences the operating conditions, as the selection of the optimum parameters for the chemical precipitation will benefit the extraction of Li rather than other ions.

Influence of pH on Lithium Precipitation

pH is a key parameter in the chemical precipitation process, and finding its optimum value is crucial to efficiently extract lithium. Li, Li [104] examined the influence of pH on the lithium precipitation rate by the phosphate precipitation method. The authors concluded that the Li extraction rate increases as the pH value reaches the basic range. When the reaction pH is above 8, the lithium extraction rate stabilizes, at nearly 80%. In acidic conditions, soluble Li compounds are formed, as the many H^+ molecules in the solution react with PO_4^{3-} to produce HPO_4^- and $H_2PO_4^-$; subsequently, Li^+ reacts with HPO_4^- and $H_2PO_4^-$ to produce Li_2HPO_4 and LiH_2PO_4 , which are highly soluble in water and therefore affect the precipitation of lithium.

High concentrations of other ions have a significant effect on the pH adjustment. To effectively precipitate Li and avoid the co-precipitation of impurities, the adjustment of pH is an essential step in the Li extraction. The recovery of Li from leach liquors could be quite challenging, as these solutions contain various dissolved species. Xiao and Zeng [102] recovered lithium from a Li-containing leach solution using Na_3PO_4 . During the step of pH adjustment, the researchers noticed a substantial reduction in the concentration of ferric ions (Fe^{3+}) instead of lithium, when the pH was varied from 0 to 5.5. The rationale behind the change involves the formation of $FePO_4$, as phosphate preferentially precipitates ferric ions rather than Li ions at pH values from 0 to 5.5. From this study, the authors concluded that the extraction of lithium from a solution containing Li^+ and Fe^{3+} using phosphate materials should be kept in the pH range of 5.5 to 14.0. The optimum pH window to recover lithium as Li_3PO_4 was on the scale of 11.0–13.0. At pH values higher than 13.5, the study found that Li was being precipitated as lithium hydroxide (LiOH) rather than lithium phosphate. This finding further validated the optimum pH window of 11.0 to 13.0. Lastly, the verification experiment achieved a 96.5% lithium recovery rate at a pH of 11.

Shin, Jeong [108] recovered lithium from a lithium waste solution using phosphoric acid. The effect of the pH on the Li precipitation rate was evaluated using pH levels of 7.0, 9.2, and 12.4. The results show a significant improvement in the lithium precipitation rate as the pH became more basic. The precipitation efficiency went from 0.2 to 81% as the pH of the solution increased from 6.4 to 12.4.

Increasing the pH might not be a critical step when using aluminum-based materials. Liu, Zhong's [99] study is a case in point. They achieved a 78.3% lithium recovery rate by adding aluminum-based materials, and the pH value (5.5) of the brine remained unchanged throughout the precipitation process. The authors highlighted that a change in pH in the brine could lead to negative effects within the salt-lake ecosystem.

Influence of Temperature on Lithium Precipitation

According to the collision theory of reactivity, chemical reactions occur when reactant particles "effectively collide". Moreover, an effective molecular collision requires a minimum amount of kinetic energy in the molecule. A high temperature increases the average kinetic energy of the reactant molecules and causes molecules to move faster, increasing the rate of intermolecular collisions. These collisions promote more molecules to interact in the reaction and increase the reaction rate. Thus, in theory, the precipitation rate of lithium should increase with the increase in the temperature.

For example, Shin, Joo [105] used Na_3PO_4 to study the effect of the temperature on the Li precipitation rate, at 30, 60, and 90 °C. The results showed that at 90 °C, the precipitation rate obtained was over 90% in only 5 min of reaction time, regardless of the initial Li concentration (1.7, 4.0 and, 7 g/L). At 30 °C, the lithium extracted was only 70% over the same period of time, and high recovery was only achieved at the highest Li concentration.

The maximum precipitation rate of Li, Li [104] was reached at 70 °C, using Na₃PO₄ as the precipitant, in a Li solution containing 262.43 mg/L of lithium. When the temperature was increased from 50 to 70 °C, the extraction increased from about 77% to 86.57%. The authors observed that the higher the temperature, the better the Na₃PO₄ precipitation of lithium. However, once the temperature was raised from 70 to 90 °C, the extraction rate plateaued.

Li, Zhao [109] extracted lithium as LiCl·Al(OH)₃·xH₂O from a salt-lake brine using aluminum-based alloys. In this study, the increase in the temperature (50 to 90 °C) did not have a positive effect on the lithium recovery rate. First, there was no significant difference in the Li extraction efficiency when the temperature was raised from 50 to 70 °C. As the temperature was increased from 70 to 90 °C, a significant decline in the Li precipitation rate was observed, dropping from 93.6 to 66%. The authors stated that at more than 70 °C, LiCl·Al(OH)₃·xH₂O disintegrates and LiCl dissolves in water, decreasing the extraction rate of Li.

About 90% of Li was extracted from Dead Sea brine as lithium aluminate, using aluminum chloride (AlCl₃·6H₂O). The highest yields were achieved at room temperature, and as the temperature was increased, the lithium recovery declined [93,116]. Theoretically, a high temperature increases the rate of a reaction; however, temperature does not exhibit the same behavior in all precipitation methods. High lithium recovery can be achieved at room temperature and prolonged reaction times when the initial Li concentration is high.

The solubility product of the precipitate plays an important part in the selection of the reaction temperature. For example, the solubility product of Li₂CO₃ is relatively high, 8.15×10^{-4} (pK_{sp} = 2.2), in comparison with Li₃PO₄, 2.37×10^{-11} (pK_{sp} = 10.63) [104]. Therefore, the carbonate precipitation method is usually conducted in the range of 80 to 100 °C, as the solubility of Li₂CO₃ decreases as the temperature rises [110,112].

Influence of Reaction Time on Lithium Precipitation

The reaction time may perhaps be linked to the initial Li concentration of the solution and the reaction temperature: high Li concentrations and high temperatures shorten the time required to achieve efficient lithium extraction. Shin, Joo [105] studied the precipitation efficiency of lithium over time at different temperatures and initial lithium concentrations. In only five minutes, more than 90% of the lithium was extracted at 90 °C, despite the initial Li concentration. At 30 °C, only 70% was extracted in the first five minutes; however, the precipitation efficiency of lithium increased gradually, given more time, and at higher Li concentrations. The authors indicated that to obtain the critical size in the crystallization of Li into Li₃PO₄, a longer period of time is needed. Therefore, the extraction rate of lithium as Li₃PO₄ is slow at low temperatures, and the higher the temperature, the faster the rate.

Xiao and Zeng [102] used Na₃PO₄ to extract lithium from a synthetic LiCl solution; the precipitation of Li reached 96.5% after 5 h of reaction time at 25 °C. Shin, Jeong [108] used phosphoric acid to recover Li from a LiOH solution. The experiment achieved around 92% precipitation efficiency after 24 h of reaction time at room temperature, with an initial Li concentration of 2000 mg/L. Evidently, a low reaction temperature requires a longer period of time to extract lithium as Li₃PO₄, and a high lithium concentration is key to obtaining a significant extraction rate.

3.3. Challenges and Outlook

Although much progress has been made in lithium recovery via chemical precipitation, there are still some challenges to overcome. Many studies have been conducted to separate lithium from magnesium in salt-lake brines; however, a high Mg/Li ratio requires large amounts of precipitant, which results in huge amount of solid waste generation and high costs [98]. The study of the aluminate precipitation method showed high lithium recovery. However, increasing the magnesium concentration to a Mg/Li mass ratio of 20:1 was detrimental to the precipitation process, and the lithium precipitation efficiency decreased [113].

To improve the precipitation separation of lithium from magnesium, the effects of various parameters on the precipitation process must be entirely and systematically studied.

The efficiency of lithium recovery depends on the Li-bearing composition. High concentrations of dissolved ions result in the co-precipitation of these impurities, making the Li extraction process more complicated. To efficiently harvest lithium from waste solutions, the characteristics of impurity removal and the interactions between the present ions must be understood. Once the removal of impurities is achieved, Li can be recovered in a one-step precipitation process with a high recovery rate and high purity of the final Li product [117].

The phosphate precipitation method has shown promising results in recovering lithium from aqueous sources. However, the direct recovery of lithium from solutions with low concentrations of lithium faces serious challenges, such as low induction period and low efficiency. Additionally, the formation of a Li_3PO_4 precipitate requires large supersaturation and a high nucleation energy barrier [114]. To achieve a high recovery rate, the reaction temperature should be raised to 70 °C or higher, and the initial lithium concentration should be higher than 2 g/L [105,114,118]. Thus, a high recovery rate is still conditional on a high initial lithium concentration.

Even though the proposed chemical precipitation technologies are technically feasible, the majority of the reported materials are still at the bench scale. To prove the concept and evaluate the feasibility of the proposed methods, pilot-scale tests would be an important step.

Lanthanum compounds have received lots of attention in various applications because of their flexibility and multifunctionality. There is indeed significant evidence of La^{3+} ions being extensively used to remove toxic pollutants from wastewater [119–121]. Lanthanum reagents have shown several advantages over traditional precipitation methods, such as high performance with and without pH adjustment. Although it is called a rare earth element (RE), La is relatively abundant, which means it offers a potentially cost-effective option. RE technology for wastewater treatment does not have negative effects on the ecosystem. Moreover, the La precipitation method has favorable characteristics for closed-loop technology, as it can form insoluble complexes with carbonate (CO_3^{2-}), hydroxide (OH^-), and fluoride (F^-) [122], favoring its recovery for reuse. In summary, the RE technology exhibits promising features for precipitating Li from wastewater with closed-loop technology, which aligns with the circular economy principles.

4. Conclusions

Current extraction methods are water- and energy-intensive. The conventional process for extracting lithium from brines requires a dry climate, abundant sunlight, and large evaporation ponds that are harmful to the environment. The inherent slowness of the process, and the demands for both land and freshwater made by the method, raise questions regarding the sustainability of the process. Lithium-brine developers need new technology to quickly and efficiently achieve the intended production levels.

The accelerating electrification transition, supported by the global commitment to decarbonization, is a strong driver of Li consumption. In addition, there is an expectation for energy storage applications to keep pace with the strong growth in renewable energy deployment around the world. The growing trend is projected to continue, to the point that Li availability may become scarce.

The increasing demand for lithium is affecting the price of the metal. In fact, the price of lithium on the world market has significantly increased since 2010, and this is not expected to be temporary.

The global demand for Lithium will be difficult to meet unless alternate resources and efficient techniques to recover this valuable metal are implemented.

Chemical precipitation is a mature technology, and is considered the most efficient method for the removal of trace metals and rare earth elements from wastewater. In the past few decades, the chemical precipitation of lithium has been intensively studied, and it

has shown great potential due to the high lithium recovery rates (>98%) and high purity of the final product (more than 99%). At the optimum operating conditions, lithium can be precipitated in quite a short time, and the method can selectively precipitate lithium and avoid co-precipitation of impurities. Different methods and materials used to recover lithium from aqueous solutions were critically reviewed above.

Mining Li from brines with high Mg/Li ratios is still challenging, as these elements share similar ionic properties. Aluminate precipitation can effectively precipitate lithium in brines of this type; however, the method involves high alkali consumption and a high cost of production.

Further research should be conducted on harvesting lithium from new brines with lower grades of Li (<100 mg/L). The vast majority of studies have focused on the precipitation of lithium from solutions with above 1 g/L of Li.

Investing in research and innovation is a critical enabler for the development of new technologies to recover lithium and secure a sustainable supply of the raw material. Funding and more engagement from the industrial sector will increase the likelihood of novel supplies coming into market.

In summary, the development of a sustainable process to harvest lithium from Li waste solutions, such as produced water, may result in a new revenue stream for companies. At the same time, it may contribute to the circular economy by converting hazardous waste into a raw material. Moreover, by recovering lithium from wastewater, Li production can be bolstered to meet the growing demands and power the energy economy.

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